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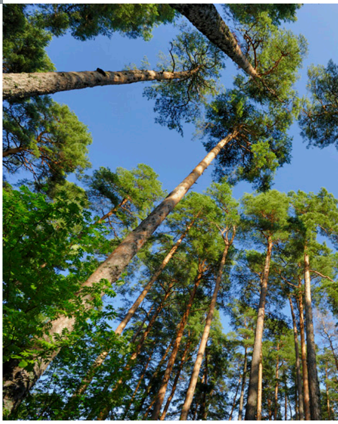

NWBC 2018

Proceedings of the 8th Nordic Wood Biorefinery Conference

Eemeli Hytönen | Jessica Vepsäläinen (eds.)

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VTT Technical Research Centre of Finland Ltd

Jessica Vepsäläinen (ed.)

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The conference organizers would like to thank warmly all the sponsors for their valuable contributions.

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Preface

It is our great pleasure to welcome you to the 8th Nordic Wood Biorefinery Conference. The Conference takes place in Helsinki, in Marina Congress Center located by the sea in idyllic Katajanokka next to Uspenski Cathedral and the Helsinki SkyWheel, from the 22nd to the 25th of October.

The 8th edition of the Conference, and this book of proceedings, continue the tradition of NWBC on building the foundation of a sustainable bio-economy. This requires that the many aspects of the foundation are systematically considered, including for example societal issues, design and consumer needs, technological performance and economics of production. Furthermore, findings both from industrial experiences from all linked sectors in implementation and R&D projects and academic research needs to be communicated to close the loop. The organizers hope that the selected scientific contributions, industrial viewpoints and the conference format are able to contribute to building yet another layer on this foundation.

The organisers of the NWBC 2018 wish to thank all people involved in the process of making the conference; Programme advisory committee members and session chairs for their contribution in planning and executing the conference agenda, and all speakers, poster presenters and their coauthors for their valuable contributions to the contents of the conference.

Enjoy the conference!

With best wishes,

On behalf of the whole Organizing Committee

Eemeli Hytönen

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Welcome to Helsinki

Sitting on the edge of the Baltic, the modern, cosmopolitan city of Helsinki was the World Design Capital for 2012. The beauty of the surrounding nature blends seamlessly with high-tech achievements and contemporary trends. Walking tours of the city center show layers of history, while modern architecture and cutting-edge style stake the city's claim to the future.

Finland is a republic and is an independent country since 1917. It became a member of the European Union in 1995 and part of the European Monetary Union in 2002 and the only Nordic country using the Euro as currency. Finland was the third country in the world and the first one in Europe allowing women to vote. This happened as early as 1906. The electronics, machinery, forestry, high-tech and design industries are Finland's most important revenue sources.

Finnish language is a non-Indo-European language belonging to the Uralic family, along with Estonian and Hungarian. However, language is not a problem. As most Finns take it for granted that you do not speak their language, they are glad to make use of their English or other European languages they master. Finland is in fact a bilingual country, the second official language being Swedish.

Climate and weather

Helsinki's climate combines characteristics of both a maritime and a continental climate. The proximity of the Arctic Ocean and the North Atlantic creates cold weather, while the Gulf Stream brings in warmer air.

Average temperatures in Helsinki

- Entire year: +5.9°C
- Warmest month: July +17,8°C
- Coldest month: February -4,7°C

Helsinki Tourist Information (www.myhelsinki.fi) offers free information about the city, sights, events and services including a wide range of brochures and maps all year round.

Scientific Advisory Committee

- Dr. Peter Axegård | RISE Bioeconomy, Sweden, **Honorary Member**
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- Dr. Alex Berg | University of Concepción, Chile
- Prof. James Clark | University of York, UK
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- MSc. Chem Eng. Per Tomani | RISE Bioeconomy, Sweden
- Prof. Adriaan van Heiningen | The University of Maine, USA
- Dr. Niklas von Weymarn | Metsä Fibre, Finland

Keynote speakers

James Clark
Professor (Department of Chemistry)
Director of the Green Chemistry Centre
University of York

Woody biomass as a sustainable feedstock for biobased chemicals

Bernard de Galembert
Innovation and Bioeconomy Director
CEPI - Confederation of European Paper Industries

IT´S TIME TO de-fossilise our economy

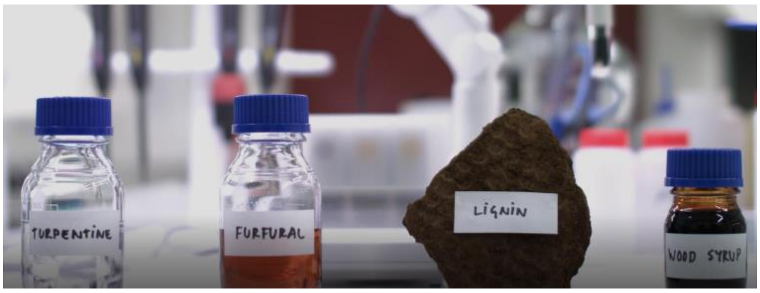
Berry Wiersum
Chief Executive Officer
Sappi Europe

FORESTS: dealing with desire and greed in a transforming environment

Tour and social events

Visit to St1 Cellunolix® plant in Kajaani

St1 produces advanced ethanol for traffic use and other renewable products Kajaani Cellunolix® demonstration biorefinery from sawdust. The plant is located at the paper mill site in Renforsin Ranta, Kajaani in Northern Finland. The production capacity of the plant is 10 million liters of advanced ethanol in a year. Production was started in the beginning of 2017. All produced ethanol is used as renewable traffic biofuel component. Kajaani Cellunolix® plant is the first in the world utilizing saw mill residues of softwood in ethanol production in commercial scale. Feedstock is sourced from saw mills located around the Kajaani plant. Lignin, wood vinasse, wood turpentine, furfural, carbon dioxide and biogas are produced in the Cellunolix® biorefinery.



The brown field location of the plant is optimal because Pölkky Kajaaniwood saw mill and Kainuun Voima power plant are located in the same area in Renforsin Ranta. Together St1, Pölkky and Kainuun Voima form an ecosystem where process residues from Pölkky's saw milling process are utilized in St1's ethanol production while Kainuun Voima is providing utilities to St1. Today St1 delivers side products to Kainuun Voima to be used in renewable heat and power production. St1 aims to develop together with partners these products to valuable renewable building blocks and products in various Industries.

St1 is planning to invest five times larger Cellunolix® biorefineries in Nordic countries in near future and further on in all softwood producing countries in the world. Feasibility studies and environmental impact assessments for three sites - two in Finland and one in Norway are already processed

Welcome Reception at Bioruukki Pilot Center

Unique innovation and demonstration platform for bio- and circular economy businesses

We can help you solve your innovation challenges. With all the required expertise, modelling and piloting capability under one roof, VTT delivers optimal solutions, from initial development to end product.

Bioruukki supports business opportunities in:

- Low carbon energy solutions
- Efficient biomass refining
- New biomass-based products
- Recycling and waste utilisation
- Sustainable chemicals

In the first stage gasification and pyrolysis research activities will be started in Bioruukki. Expanding in to other research areas will be realised in the coming years.

Conference Dinner

The conference dinner will be in Wednesday evening. We warmly invite all to participate this evening event of our conference. The dinner will take place at the meeting venue in Restaurant Marine

Scientific Programme

Monday 22.10.2018

8:00 – 16:00 Side event: Visit to ST1 cellunolix® in Kajaani

Tuesday 23.10.2018

8.00 – 16.00 **Registration**

8.30 – 8.45 **Opening of the conference**

Keynote
FORESTS: dealing with desire and greed in a transforming environment
Berend John Wiersum (Sappi Europe, Belgium)

9.15 – 10.05 **Panel discussion: NWBC 2018 Sponsors**

Session chair:
Jussi Manninen (VTT)
Panelists:
Patrick Pitkänen (St1)
Mikael Hannus (Stora Enso)
Niklas von Weymarn (Metsä Spring)
N.N. (Valmet)

10.05 – 10.30 **Coffee & poster viewing**

10.30 – 11.30 **Policies**

Global megatrends – impacts on the forest sector in Finland
Matleena Kniivilä (LUKE, Finland)

Wealth from bio economy - national economy perspective on integrated bio- and low carbon technologies
Antti Arasto (VTT, Finland)

Modelling impacts of policy schemes for increased forest-based biofuel production in the Nordic countries
Eirik Ogner Jåstad (Norwegian University of Life Sciences, Norway)

11.30 – 12.30 **Lunch and Poster viewing**

12.30 – 14.10 **Concepts 1: Industrial developments**

Zambezi Biorefinery: “Pure” glucose and lignin from 2nd generation feedstocks
Ed de Jong (Avantium, The Netherlands)

Ultra-low cost ionic liquids for waste wood biorefining
Agnieszka Brandt-Talbot (Imperial College & Chrysalix Technologies Ltd., United Kingdom)

Butanol production from volatile lignocellulosic feedstocks. Development of an optimized bioprocess
Florian Gattermayr (Kompetenzzentrum Holz GmbH Linz, Austria)

Crude Tall Oil-based Renewable Diesel as Sustainable Biofuel Component
Ville Vauhkonen (UPM, Finland)

	Biorefining at Borregaard: Recent developments *Oskar Bengtsson (Borregaard, Norway)*
	Revisiting Biorefinery Strategies: The Case of Large-Scale Production of Drop-In Biofuels *Frédéric Clerc (EnVertis Consulting Inc., Canada)*
14.10 – 14.40	**Coffee & poster viewing**
14.40 – 17:00	**Concepts 2: New concepts and applications from wood based raw materials**
	Replace fossil gas in industrial burners with renewable biogas *Thomas Bräck (Meva Energy, Sweden)*
	Turning bio-sludge into bio-carbon through zero-energy hydrothermal carbonization *Peter Axegård (C-Green, Sweden9*
	Designing from Scratch – Challenges of Dialogue between Material Research and End Products when Application Areas are in Architecture *Heidi Turunen (Aalto University, Finland)*
	From wood to food: addressing the protein gap in animal feed and Human food with lignocellulosic biomass *Amelie Drouault (Arbiom, France)*
	Water post-hydrolysis of hardwood kraft pulp to produce viscose-grade pulp and xylan *Marc Borrega (VTT, Finland)*
	The Bioeconomy Research Programme 2018–2020 *Fredrik Aldaeus (RISE, Sweden)*
	Evaluation of Alternative Routes for production of Bio-oil from Forest Residues and Kraft Lignin *Marie Anheden (RISE Bioeconomy, Sweden)*
18.00 – 21.00	Welcome Reception at Bioruukki Pilot Center

Wednesday 24.10.2018

8.00 – 18.00 **Registration**

8.30 – 10.00 **Keynote**
It´s time to de-fossilise our economy
Bernard de Galembert (CEPI, Belgium)

Panel discussion: NWBC 2018 Keynote speakers

Session chair:
John Kettle (LUKE)
Panelists:
Berry Wiersum (Sappi Europe)
Bernard de Galembert (CEPI)
James Clark (University of York)

10.00 – 10.30 **Coffee & poster viewing**

10.30 – 12.10 **Side streams: Processing of bark and wood to value-added products**

Purification scheme for the production of phenolic compounds from subcritical water extracts of chestnut wood
Pierre-Yves Pontalier (Fibre Excellence Saint Gaudens SAS, France)

Polyphenols from softwood bark in adhesive applications
Sami Alakurtti (VTT, Finland)

A novel process for biomass extraction: The basis for a pine bark biorefinery
Alex Berg (Universidad de Concepción, Chile)

Bark-Based Biorefinery for Production of Biocomposites
Marzouk Benali (Natural Resources Canada, CanmetENERGY, Canada)

Bio4Products: Unlocking the potential of biomass for a new range of bio-based products
Hans Heeres (BTG, The Netherlands)

12.10 – 13.10 **Lunch and Poster viewing**

13.10 – 15.30 **Lignin 1: Processing & tailoring properties**

LigniOx lignins – High performance concrete plasticizers and versatile dispersants
Anna Katariina Kalliola (VTT, Finland)

Aqueous solvent fractionation of kraft lignin - technoeconomical perspective
Juha Leppävuori (Neste, Finland)

Enzymatic Modification of Lignin from a Hydrothermal Biorefinery Concept and Use Thereof in Polymer Compounds
Xihua Hu (TUHH, Germany)

Laccase pretreatment to decrease lignin-induced fouling in the membrane filtration of birch hot-water extracts
Tiina Virtanen (LUT, Finland)

Cyclic organic carbonates as reagents for the functionalization of lignins and hemicelluloses
Ralph Lehnen (Thünen Institute of Wood Research, Germany)

15.30 – 15.50 **Coffee & poster viewing**

15.50 – 17.50 **Lignin 2: Applications**

Designing kraft lignin based dispersants for clay suspensions
Mohan Kalyan Konduri (FPInnovations, Canada)

Lignin as novel renewable binder in pigment-based paper coating formulations
Gibson S. Nyanhongo (BOKU, Austria)

DES-lignin as a biobased hydrophilicity promoter in polyethersulphone (PES) membranes
Ikenna Anugwom (LUT, Finland)

Recent achievements in the valorization of technical lignins
Mikhail Balakshin (Aalto University, Finland & BOKU, Austria)

Melt spun lignin-based carbon fiber from softwood kraft lignin: Effect of lignin pretreatment and fiber conversion conditions
Sverker Danielsson (RISE Bioeconomy, Sweden)

Synthesis of Bio Adhesive from Waste Biomass from Pulp and Paper Industry for Wood based Industry
Vipin Chawla (IPIRTI, MOEF&CC, India)

19.00 – 22.00 **Conference Dinner**

Thursday 25.10.2018

8.00 – 16.00	**Registration**
8.30 – 9.00	**Keynote** Woody biomass as a sustainable feedstock for biobased chemicals *James Clark (University of York, United Kingdom)*
9.00 – 9.30	**Coffee & poster viewing**
9.30 – 11.10	**Processing 1: Piloting & equipment design**
	Pilot scale pretreatment of lignocellulosic biomass: design considerations vs operational challenges *Raimo Van der Linden BPF, The Netherlands)*
	Production of nanofibrillated cellulose reinforced nanopaper using pilot scale Experimental Paper Machine (XPM) *Zoheb Karim (MoRe Research, Sweden)*
	Increase accessibility for enzymatic hydrolysis of Norway spruce by organosolv pre-treatment in a novel reactor *Mihaela Tanase-Opedal (RISE PFI, Norway)*
	Degradation of cellulose by hydrogen chloride gas under elevated pressure in a custom-built reactor *Eero Kontturi (Aalto University, Finland)*
	Cost-efficient sugar-based cellulase production *Simo Ellilä (VTT, Finland)*
11.10 – 12.10	**Lunch and Poster viewing**
12.10 – 13.30	**Processing 2: Fundamentals**
	Impregnation of wood chips for acidic processes and the influence of wood chips length *Jessica Gard Timmerfors (Umeå University, Sweden)*
	Lignin carbohydrate complexes studies on sulfite dissolving pulps *Raghu Deshpande (MoRe Research, Sweden)*
	Solubility and Compatibility of Various Lignins in Solvents and Polymers: Experimental and Computer-Based Evaluation *Marzouk Benali, Natural Resources Canada, CanmetENERGY, Canada)*
	Digging in the structure and functionality of lignocellulosic raw material – from academic knowledge towards industrial applications *Jerk Rönnols (RISE Bioeconomy, Sweden)*

13.30 – 14.00 **Coffee & poster viewing**

14.00 – 15.20 **Processing 3: Separation, purification and recovery**

Recovery of high-added value functional monomeric lignin derivatives from lignin oil: a comparison of separation technologies
Kelly Servaes (VITO, Belgium)

Hydroxy carboxylic acids from spent alkaline pulping liquors
Jari Heinonen (LUTechnology, Finland)

A-Recovery+ - the next generation of chemical recovery cycle
Lauri Pehu-Lehtonen (Andritz Oy, Finland)

Possibilities of membrane filtration processes in recycling of Deep Eutectic Solvents (DES)
Mari Kallioinen (LUT, Finland)

15.20 – 15.30 **Closing the conference and announcing the next NWBC**

ORAL

PRESENTATIONS

TUESDAY 23.10.2018

Forests, dealing with desire and greed in a transforming environment

B.J. (Berry) Wiersum

Sappi Europe, Belgium

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We've had a hot summer and like many farmers, we lost a large part of our harvest. We are seed potato farmers in the north of Holland and the drought, which lasted from May to the end of July, stunted the growth of the potatoes. Of course, the market price can make up for the poor harvest, as it did the last time we had one of these years which was in 1976. 1976 you say? Well, then there's no cause for alarm; after all, this sort of freak summer only happens once every 40 years….Except that we're getting freaky weather conditions more frequently nowadays. Whatever your thoughts on Climate change, European law makers are taking it seriously and are taking measures to force us to change; it's perhaps the only thing they can agree on. And so is China – just look what they're doing to waste paper imports. Here in Europe ETS certificate prices have risen to €18 from a low of €4.5 in May 2017 and Carbon Tracker predicts they will go to €25 by the end of the year. Lots of industries are heading for the trees, either as a source of energy or raw material, not to forget recreation. The EU Commission is designing forestry plans and certifiers are struggling to keep up with a changing reality. Paper packaging producers have transmogrified from hate figure to saviour of the world in less than 10 years, but the way we convert trees to paper is going to have to change. Roadmaps, high level thinking groups, politicians, bankers, suppliers, customers and, of course, earnest consultants abound in their efforts to influence what we do as an industry and make money out of us. I will offer a few humble thoughts on the environment and the big questions we have to answer to keep the forestry industry green, growing and great.

Policies

Global megatrends – impacts on the forest sector in Finland

Matleena Kniivilä, Antti Mutanen and Jari Viitanen

Natural Resources Institute Finland (Luke)

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Megatrends reshape the world we live in. Climate change, population growth, especially a significant increase in the middle class, urbanization, and changes in consumption habits affect world's forests and their utilization profoundly. Changes in global economy and rising standards of living in emerging economies have already increased the demand for wood fiber and other wood-based products significantly. In the struggle against climate change, wood fibers and wood-based biofuels provide promising options to replace products based on oil and other fossil fuels. In addition to wood as a raw material, forests also provide other ecosystem services: they act as carbon sinks mitigating the climate change, they provide biodiversity and non-wood forest products, such as berries and mushrooms, and recreation possibilities valuable for humans and their well-being. Growing and partly contradicting demands for the different products and services offered by the forests increase the risk of conflicts related to the utilization of forests in the future.

Raw material shortages induced by the growing demand for wood fiber can be alleviated by increasing the area of planted forests especially in the southern hemisphere. It is expected that in the future, the proportion of wood originating from plantation forests will grow significantly. However, increasing demand for fiber can also be seen in northern forests. In Finland, investments and investment plans in the forest sector have soared during the last years. The main driver has been the growth in demand for forest products in Asia and in China, especially. Due to lack of domestic forest resources, Chinese companies have also begun showing growing interest in the Finnish forests and forest industry, and Chinese money is playing a significant role in many current investment plans. Increasing demand for wood and greater harvesting volumes has caused vibrant as well as critical discussion on the reconciliation of different uses of forests in a sustainable way in Finland.

Wealth from bio economy - national economy perspective on integrated bio- and low carbon technologies

Antti Arasto, Tiina Koljonen and Antti Lehtilä

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It is clear that integrated targets of European Commissions 2030 low carbon policy create an increasing need for more detailed EU and national level tools for integrated assessments and impact evaluation. This work evaluates pathways to bio economy and low carbon economy in Finland relation to the European climate policies. The focus is on most promising concepts and impact of technology deployment on national economy level.

What is the realistic magnitude of impact, both from greenhouse gas impact and from national economy perspective of implementation of forest and agriculture based bio economy? This question has been investigated through creating storylines representing different implementation pathways and integrated bio economy scenarios. This work takes into account existing and projected future biomass resources, energy system transition, future bio economy products and integrated concept in detail to cost optimize the system change and use of constrained resources. Most promising future concepts, capable for significant scale of production in Finland have been identified and potential value chains to products promoting both targets have been assessed.

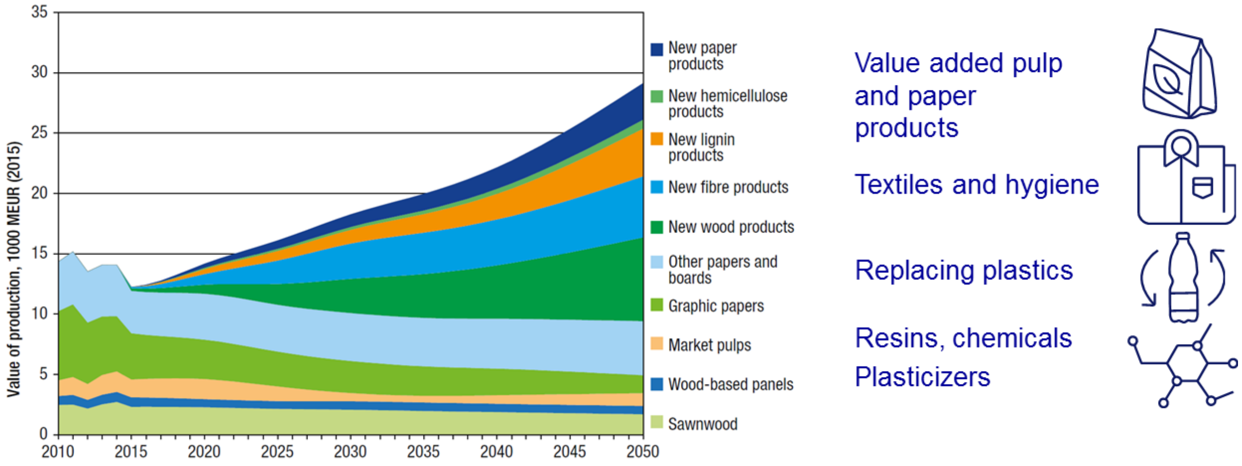

Figure 1. New forest sector products can double the value added of forest sector

Concretizing the roadmaps outlined for moving to a low carbon economy by 2050 into detailed policies is a challenging task. Using ETSAP-TIMES as the central modeling tool, we have analyzed the implications of low carbon policies within Europe, with a special focus on the Finnish energy system. The main objective of the work was to identify cost-effective pathways combining implementation of low carbon energy policy and maximizing value created by bio economy concepts and value networks while moving towards low carbon society by 2050. The scenario results indicate that Finland has good opportunities for achieving its low carbon targets by 2050 due to its large natural resources and significant opportunities in new type of bio economy concepts already being in industrial implementation.

Modelling impacts of policy schemes for increased forest-based biofuel production in the Nordic countries

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The Nordic countries have ambitious plans to reduce the use of fossil fuels. One possible solution is to blend-in biofuel into the liquid fuel mix. A large share of this biofuel can be produced from forest biomass, since biomass from the forest is an easy available resource in the Nordic countries. However, technologies for producing biofuel from forest-based biomass are in an early stage of technological development. This leads to a significant uncertainty for investors. The investor's uncertainties may be reduced by introducing different types of support schemes. The aim of this study is to describe how the government can implement different subsidy schemes and analyse the effects of those on the production of forest-based biofuels in the Nordic countries. For doing this, we use the new partial equilibrium forest sector model, Nordic Forest Sector Model (NFSM). In the scenario analyses, we use up-to-date datasets for both the forest sector and the different biofuel technologies that potentially can be used in the Nordic countries. We have used an nth plant estimate for the various biofuel technologies and applied different types of subsidies, including investment support, feed-in premiums, quota obligations, increase in fossil fuel price and support for using harvest residuals. We estimate the total subsidy costs under the different support schemes. A feed-in premium gives the lowest subsidy cost for production under 6 billion litre forest-based biofuel, while for production levels over 6 billion litre, quota obligation is the cheapest option according to the model results. The lowest total subsidy cost is in the range 0.9-1.2 €/l for realistic amounts of biofuel production. In all scenarios, the biomass prices increase up to 26 % from the base scenario.

Introduction

The European Union have set a target to reach 10% renewable energy in the transportation sector by 2020 and 32 % within 2030[1,2]. In order to increasing the renewable share, the different countries may introduce different kinds of subsidy, such as feed-in tariffs, feed-in premiums, quota obligations, tax exemptions, tenders and investment support. All of them are at present in use within the European Union[3]. The subsidies are not harmonized across EU/EEA allowing the member states to choose their own subsidy schemes and level of subsidy. All of the above mention subsidy schemes are hence, suitable for increasing biofuel production in the Nordic countries.

For stimulating biofuel producers, have Norway, Finland, and Denmark introduced quota obligations. In Norway 10% of the fuel traded has to be biofuel, of which 3.5% (with double counting) has to be advanced biofuel. Norway plan to increase the use of biofuel to 20% within 2020[4]. Finland has set the quota obligation at 15% and plan to increase to 20% in 2020[5]. Denmark has set the quota obligation at 5.75% and plan to increase to 10% within 2020[6]. Sweden has set an aim to reduce total carbon emission at 2.6% for gasoline and 19.3% for diesel compared with the fossil alternative. The goal is to increase the reduction to 70% by 2030[7]. The Swedish carbon reduction is implemented as a tax reduction subsidy.

In this study, we focus on finding what level of biofuel subsidy will make biofuel investments in the Nordic countries profitable for the investors. We answer which type of subsidies that is most beneficial to the forest sector and give highest production volume of biofuel at lowest cost for the society.

Method

The Nordic forest sector model (NFSM) is a spatial, partial equilibrium model, covering forestry, forest industry, and bioenergy in Norway, Sweden, Finland, and Denmark. NFSM maximizes social welfare, i.e. consumer plus producer surplus, for each simulation period. Roundwood supply, industrial production, consumption of final products and trade between regions are estimated simultaneous. For further explanation of the model and data, see Mustapha[8].

The model is solved as a Mixed Integer Linear Programming (MILP) problem, with the CPLEX solver using General Algebraic Modelling System (GAMS)[9].

Different conversion routes with different level of economic maturation, efficiency, and other technical parameters[10] may produce biofuel. In this study, we assume a biomass carbon efficiency of 58%, i.e. 2 MWh (1 m^3) biomass is needed for producing 116 l biofuel. The efficiency is assumed to be the same for all the different raw materials: spruce, pine, and non-conifers pulpwood, residuals from sawmills, harvest residuals, and a mix of them. The model assumes that new investments are in fixed size production units. The exogenous production costs for the different production unit sizes are shown in Table 1. All costs are estimated as yearly costs. Table 2 shows the main exogenous product prices in NFSM and the total fossil fuel consumption in the Nordic countries.

Table 1. Labour [h/1000 l], fixed and investment costs [€/l/year] and production level [million l /year] for the different plant sizes [input feedstock]. Source: Serrano and Sandquist[11].

	150 MW	**300 MW**	**450 MW**	**600 MW**
Labour input [h/1000 l]	0.57	0.44	0.38	0.42
Fix costs [€/l]	0.56	0.49	0.45	0.42
Investment cost [€/l]	0.40	0.34	0.31	0.29
Production [mill. l]	79	157	236	315

Table 2. Main prices related to biofuel production in NFSM and consumption of fossil fuel for the Nordic countries.

	Norway	**Sweden**	**Finland**	**Denmark**	**Source**
Power [€/MWh]	39.9	41.3	42.9	54.4	12
Natural gas [€/MWh]	36.1	36.1	36.1	36.1	11
Labour [€/h]	39	20	18	27	13
Fossil gasoline [€/l]	0.43	0.43	0.43	0.43	14
Fossil diesel [€/l]	0.44	0.44	0.44	0.44	
VAT [%]	25	25	24	25	15
Special fuel taxes gasoline [€/l]	0.66	0.64	0.65	0.62	
Special fuel taxes diesel [€/l]	0.53	0.42	0.50	0.46	
Consumption diesel [mill. l]	3 831	6 197	3 236	3 048	16-19
Consumption gasoline [mill. l]	1 089	3 400	1 834	1 673	

We have analysed investments support (invest), with subsidy level varying from 0-100% of the total investment cost for each factory sizes given in Table 1. Regarding feed-in premiums (feed-in), we have analysed 0-2 €/l produced. Quota obligation, in total (quota) and for each country (quota 2), are estimated for 0-100 % of the total liquid fuel consumption. We have further estimated the effects of a fossil fuel price increase (fossil inc) in the range 0-500 % (0.44-2.2 €/l). Finally, support of using harvest residuals as raw material for biofuel production (raw) is also included in the analyses, at levels 0-90 €/MWh input.

Results and discussion

Five of the subsidy scheme mention above, gave production of biofuel within the range given. Feed-in premiums induce production at 0.88 €/l, quota obligations both total and the Nordic countries, increase in the fossil price production starts at 0.88 €/l and support of using harvest residuals at 67 €/MWh.

Investment support and tax exemptions for special fuel taxes gave no production for reasonable size of the subsidies. However, we increased the subsidy and find that investment support results in production at 0.75 €/l, which is 0.46 €/l higher than the assumed investment costs. For tax exemptions, production starts at a support at 146 % of the level in table 2. This show that investment support and tax exemptions are not suitable alone to get cost competitive biofuel production, but they may reduce the risk of investing in a biofuel plant. For this reason, i.e. reduced risk, biofuel production may happen with lower subsidy levels than show in this study; this is however outside what the NFSM can handle.

The total direct cost of the different subsidy schemes is shown in Figure 1a, while the unit cost is shown in Figure 1b. The total cost is parabolic increasing with increasing amount of biofuel produced. We observe the highest unit costs for support of harvest residuals. The four other subsidy scheme have almost equal total support up to about 25 % biofuel share for transportation. For larger volumes, quota obligations are less expensive than feed-in premiums and increasing fossil fuel prices. Quota obligations has slightly higher unit cost for small volumes (<5%), since the biofuel demand is lower than the most cost effective production volumes.

The quota obligations has lower levels of total support for higher production volumes (>25 %) than feed-in premiums and increasing fossil fuel price. This since quota obligations has to support the producers with the difference between producer cost (Figure 1d) and fossil prices. This is done by increasing the sales price of fossil fuel. Quota obligations linearly increase the production cost, while the feed-in premium and increasing fossil fuel price do not have linearly increasing cost, because of the producers increasing raw material costs.

All scenarios have declining surplus with increasing production of biofuel (Figure 1c) since biofuel production increases the raw material prices. Except for raw material support (harvest residuals), the effect is almost the same for all subsidy schemes. The reason for the rapid decrease for the former is that the use of harvest residuals has only minor effect on the rest of the forest sector since they seldom are used for non-energy purpose. Quota obligations for each of the Nordic countries shows a steeper decline than the other subsidies, owing to the need for allocation more biofuel production in Norway and Denmark having a slightly higher production cost.

The production cost of biofuel is always increasing with increasing biofuel production (Figure 1d), due to increased chips prices. Production costs are highest for national quota obligations in each countries due to higher labour costs and less available biomass in Norway and Denmark than in Sweden and Finland. Lowest unit costs are observed for harvest residues, due to the low demand of harvest residues in rest of the forest sector.

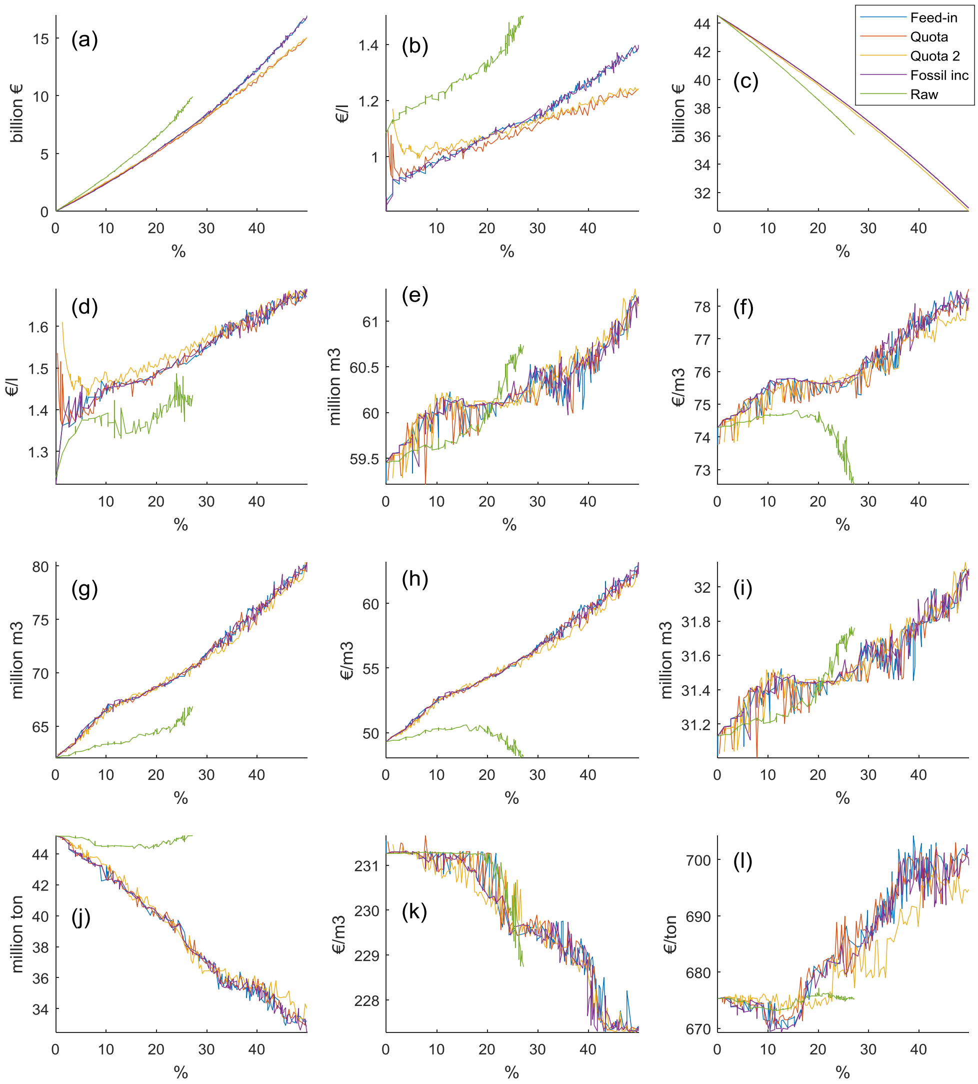

Figure 1. Modelled total (a) and unit (b) subsidy amount needed for biofuel production, total welfare quantified by model minus cost of the subsidy (c) the unit production cost (d), sawlog harvest (e), sawlog price (f), pulpwood harvest (g), pulpwood price (h), sawnwood production (i), sawnwood price (j), pulp and paper production (k), and pulp and paper price (l), for the different support schemes, plotted against the liquid biofuel share in the Nordic liquid fuel.

Modelled harvest and price increase for both sawlogs and pulpwood (Figure 1e-h), but the increase is largest for pulpwood (Figure 1g-h) since the increased demand for biomass in biofuel production. All subsidy scheme have the same trend, due to a similar level of biomass demanded for biofuel production, except for raw materials support where prices and harvests are on the reference level up to a 27 % share of biofuel. From that point, harvest increases rapidly simultaneous as the price decreases rapidly, due to all easy available harvest residuals being harvested. Form 27 % biofuel share the forest owners start to harvest more roundwood in order to sell more harvest residuals to the biofuel producers. The “unnecessarily” harvest is dumped on the market. This show that harvest residuals support above 90 €/MWh gives non-intendent effects on the roundwood market.

At the same time as the sawlogs harvest increase (Figure 1e), the sawnwood production (Figure 1i) and the market price (Figure 1j) increases. The sawnwood price decreases with increased production until 47 % when the sawnwood price increases due to increased export and increased production at small sawmills. The pulp and paper production reduce with biofuel production (Figure 1k), due to increasing pulpwood price, while pulp and paper prices increase slightly (Figure 1l). Also for production and prices, subsidy for harvest residuals deviates from the rest of the cases, due to less raw material competition.

Feed-in premiums and increased fossil fuel prices will have similar impact on the optimal biofuel production level. Feed-in premiums lower the production costs, while increase in fossil fuel price increases the alternative fuel price. For feed-in premiums, the government has to pay the producers for each produced unit of biofuel directly. For increased fossil fuel prices, the government has only to increase taxes on fossil fuel in order to increase the fossil fuel prices; this is (almost) the same as the consumers of fossil fuel has to pay for the production of biofuel. When increasing retail prices we may get some market effects, which will lead to lower demand of liquid fuel if the fuel prices increases, this effect is not handled in the model.

Harvest residuals are traditional rarely used for other application than district heating; we find that harvest residuals can be used to some extend for biofuel production. However, raw materials support scheme has to be in a relatively narrow interval (67-90 €/MWh) if not the artificially high demand of harvest residuals would drive the roundwood market leading to a large reduction in the prices for roundwood. On the other hand, biofuel production from harvest residuals can to some extend happen without interfering with the traditional forest sector. Subsidising harvest residuals make most sense if the government want to increase the use of harvest residuals, but not if the goal is to produce forest-based biofuel in an efficient way.

When deciding on which type of subsidy scheme that is best, it is important that the subsidy is not favouring a specific technology or raw material; this may set constraint on the research and development. For this reason, to subsidise use of harvest residuals will increase the usage of harvest residuals, but may also lead to less research and development for other raw materials that may become cheaper in the long term. Both feed-in premiums and increasing the fossil price are independent from technology and raw materials, which will stimulating the best production option and further research on biofuels. They are easy to implement since feed-in premiums is already in use in the power sector and fossil fuel tax already exist. But, if the goal is to increase the renewable share for transportation, increasing the fossil fuel price may be more beneficial than feed-in premiums. This since higher fossil fuel prices will not only stimulate investments in forest-based biofuel but also increase the use of electrical cars and food-based biofuel. If introducing a feed-in premium it will be possible to divide between forest-based biofuel and food-based biofuel. It will stimulate the production of forest-based biofuel and not food-based biofuel. This will be almost impossible to do with an increase in fossil fuel prices. No matter which type of subsidy is used for increasing the implementation on biofuels, a long time horizon and predictability of the subsidy is important.

Conclusion

According to this model study, Nordic biofuel production needs a support of 5-6.5 billion € to reach a share of 20 % of the Nordic liquid fuel consumption. This amounts to a support of 1.1-1.3 €/l produced. For a production share in range 15-25 %, quota obligations, feed-in premium, and increased fossil fuel taxes will have almost the same level of impact and economic efficiency. Out of them, quota obligations or feed-in premium will be most profitable.

For low levels of biofuel production, feed-in premium will have lowest cost, while for higher production volume quota obligations yields lowest cost.

Quota obligations, feed-in premium, and increasing fossil fuel will interact with the forest sector and give higher roundwood prices. While support of harvest residuals will almost not interfere with the traditional forest sector.

Acknowledgements

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Concepts 1:

Industrial developments

Zambezi Biorefinery: “Pure” glucose and lignin from 2nd generation feedstocks

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Many chemical building blocks can be produced from biomass, nowadays mainly from 1st generation based carbohydrates[1] but in the longer term brand-owners want to have the option to choose between 1st and 2nd generation feedstocks. The use of non-edible lignocellulosic feedstocks is an equally attractive source to produce chemical intermediates and an important part of the solution addressing these global issues (Paris targets). Avantium’s strategic objective is to deliver with it’s 2nd generation Zambezi technology the best in class 2G “pure” glucose technology for (bio-)chemical & bioenergy applications for a sustainable future; in parallel delivering value generation from the implementation of this technology. With the production of 2nd generation glucose also a large amounts of lignin will be available and all products streams should be marketed at their highest value[2]. In this presentation particular attention will be given to the Zambezi technology for the production “pure” 2nd generation glucose and the lignin streams that are produced during this process. Valorization of these concentrated acid type lignins is not trivial and most available research on lignin conversion is performed on lignins originating in alkali or organosolv processes [3]. Avantium has achieved a range of technological improvements on the concentrated mineral acid based process to make the process techno-economic competitive. A consortium consisting of AkzoNobel, RWE, Chemport Europe and Staatsbosbeheer has been established to bring this technology to commercial scale. As a first step a demonstration plant will be built in Delfzijl, the Netherlands to be operational in 2018.

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Ultra-low cost ionic liquids for waste wood biorefining

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With high raw material and processing costs compared to the petrochemical industry, the bio-based industries have been struggling to win over markets. The use of currently unwanted or underused waste wood represents a promising opportunity to reduce the cost of bio-based processes and products, however, it is inherently difficult to utilise such complex waste streams.

Ionic liquids (ILs) have proven to be highly tunable 'designer solvents' capable of a wide range of exciting chemistries. Industrial application at large scale is hampered by high solvent cost, however, this cost is a tunable feature of the solvent itself – provided the ion selection is handled with a careful eye aimed at limiting synthetic complexity. A number of ultra-low cost ionic liquids (UCILs) have been successfully used in the pretreatment of lignocellulosic biomass, yielding cellulose that can be hydrolysed and fermented to chemicals and fuels, and a separate, clean lignin stream. Lowering biomass feedstock cost will further increase opportunities for bulk processing of lignocellulose with ionic liquids – including applications such as biofuels.

The lignocellulose fractionations using UCILs has now been optimised for pretreatment of metal-treated construction wood. We demonstrate that UCIL pretreatment effectively fractionates metal treated construction wood, resulting in digestible cellulose, a separate lignin stream and various metals dissolved in the IL solution, ready for electrochemical redeposition. Preliminary economic modelling shows that the profit margin of the UCIL pretreatment process can be very attractive as a result of the reduced feedstock cost, with >98% of the metals extracted. This enables the use of metal treated wood waste for the cost-effective production of bio-derived chemicals and fuels.

Introduction

Fractionation of wood biomass with the BioFlex process

Governments and industry around the globe have pledged to decarbonise their economy; many have outlined clear goals to move towards a fully renewable economy, including bio-based chemical and fuel sectors. Recently, ionic liquid (IL)-based pretreatment aimed at fractionating lignocellulose biomass has shown high promise in improving process performance and techno-economic competitiveness of cellulosic sugar production compared to other conventional pretreatment methods. The process innovation and strengths stem from the use of low-cost protic ILs (~\$1.25 per kg; similar to acetone) that is able to fractionate recalcitrant lignocellulosic biomass into a cellulose pulp and an odour-free, low ash content lignin (Figure 1). The ILs are chemically and thermally stable, and offer near-quantitative solvent recovery rate due to their non-volatility. The lignin can be burned for generating bio-heat and power, or used for material applications such as carbon fibres, resins and fillers. Hemicellulose derived compounds such as acetic acid and furfural can be isolated by simple distillation from the non-volatile solvent. A number of feedstocks have been successfully fractionated with UCILs, including softwood, hardwood, and grasses, and optimum pretreatment times of around 15 min at 20% loading identified[1].

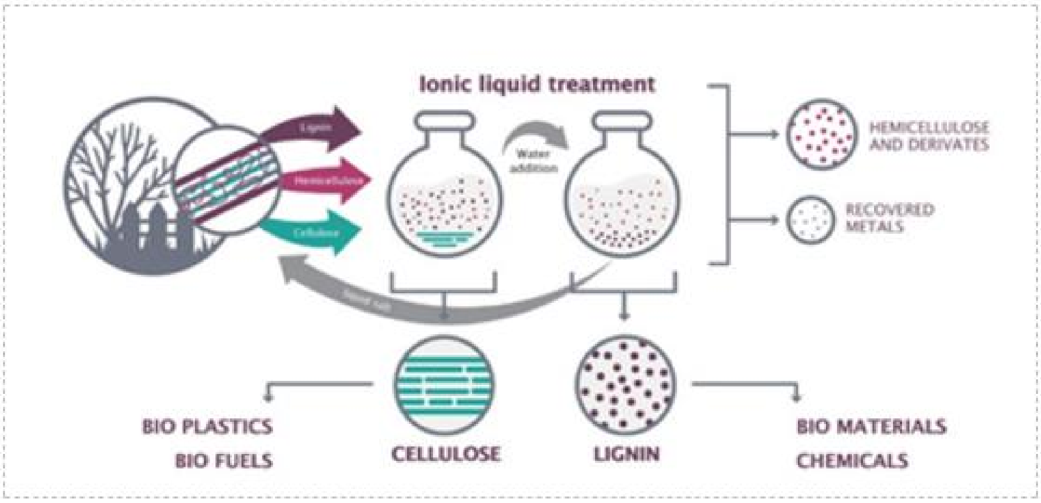

Figure 1. The BioFlex process

Waste wood as a feedstock for biorefining

A big challenge for the bio-based industry has been its feedstock source, cost, supply, availability and sustainability. A solution to this problem is to turn to wood containing waste materials as feedstocks. Waste wood comes from many different sources including timber processing and manufacturing, pallets and wooden packaging, construction, demolition, and municipal wood waste.

While wood waste numbers are generally poorly reported, it is estimated that around 70 million tonnes are generated in the EU annually, of which *ca.* 50% is recycled. Local, regional and national governments and corporations are actively setting targets to reduce waste wood incineration or landfilling, and increase recycling rates instead.

Wood used in construction is typically treated with a copper containing preservative (“pressure treated timber”), while other toxic heavy metals such as lead and chromium are often present in legacy demolition waste wood. This results in a recycling problem for these waste streams. While lower metal content wood may be used in particleboard manufacture, deriving value from waste wood with high heavy metal content is not possible at present. Options for disposal are summarised in Figure 2. All of them require the wood waste owner to pay a disposal fee. A significant amount of collected municipal wood waste ends up as a very fine, heavy metal polluted powder that is not suitable for incineration.

It may be possible to use such feedstock for biorefining, however, in addition to high sugar release, the hydrolysate needs to be free of fermentation inhibitors, which includes heavy metals. The amount of copper and other heavy metal ions contained in treated timber results in the inhibition of sugar fermentation, hence they need to be removed.

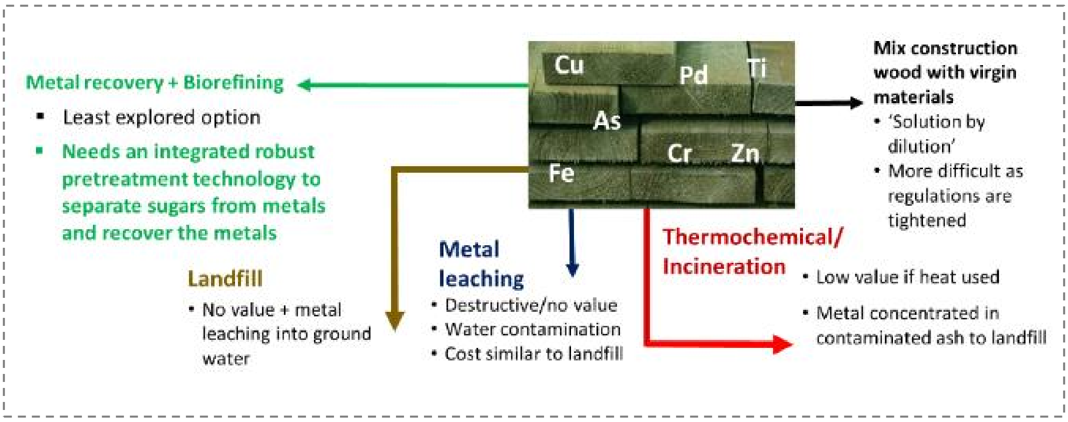
Cu
Pd
Ti
As
Cr
Zn
Fe
Metal recovery + Biorefining
Least explored option
Needs an integrated robust pretreatment technology to separate sugars from metals and recover the metals
Mix construction wood with virgin materials
'Solution by dilution'
More difficult as regulations are tightened
Landfill
No value + metal leaching into ground water
Metal leaching
Destructive/no value
Water contamination
Cost similar to landfill
Thermochemical/ Incineration
Low value if heat used
Metal concentrated in contaminated ash to landfill

Figure 2. End of life destinations for heavy metal containing waste wood

The BioFlex process and metal polluted waste wood

In this presentation, we highlight our latest, patented technology development (BioFlex) in conditioning heavy metal polluted waste wood into a sugar source for fermentation[2]. Previously we have demonstrated successfully the fractionation of herbaceous biomass (*Miscanthus*, sugarcane bagasse) and hardwood (willow) and softwood (pine). BioFlex ILs are produced from sulphuric or hydrochloric acid and simples amines, and produce ionic liquid in quantitative yield, which results in their extremely low cost. The structures of the ions relevant for this work are shown in Figure 3.

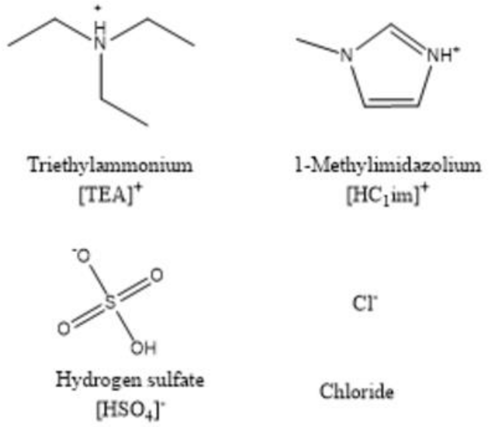
Triethylammonium
[TEA]+
1-Methylimidazolium
[HC1im]+
Hydrogen sulfate
[HSO4]-
Cl-
Chloride

Figure 3. Structures of UCIL ions used for waste wood fractionation

Experimental

BioFlex fractionation

Ionic liquid/water mixtures were prepared according to Gschwend *et al*, 2016, as was the wood waste fractionation[3]. 10±0.05 g of ionic liquid/water master-mix was added into a glass pressure tube and the exact weight recorded. Copper azole treated softwood (1.0 g oven-dried basis) with particle sizes of 180-850 µm was added, the tube sealed and the contents mixed until all of the biomass was in contact with ionic liquid solution. The vial was placed in a preheated convection oven at 170°C for 30 min. After the incubation, the mixture was transferred into a 50 mL centrifuge tube together with 40 mL of ethanol. The solids and liquids were separated by centrifugation followed by decantation. The washing step was repeated 2-3 more times. The remaining solid was transferred to a cellulose thimble and washed by Soxhlet extraction with refluxing ethanol for 22 h. The pulp was left to dry in the thimble on the bench overnight. The ethanol used for the Soxhlet extraction was combined with the previous washes and evaporated under reduced pressure at 40°C, leaving a dried ionic liquid/lignin mixture. To the dried ionic liquid/lignin mixture, 30 mL of water was added in order to precipitate the lignin. The suspension was centrifuged and separated by decantation. This washing step was repeated 3 times. The oven-dried yield was determined for both pulp and lignin.

Copper solubility

Solubility of copper in BioFlex ionic liquids was tested by dissolving copper oxide in the ionic liquid solution until no further dissolution was observed overnight. The excess solid was removed by filtration and the obtained solutions subjected to ICP-OES.

Quantification of metal content by ICP-OES

Inductively coupled plasma optical emission spectrophotometry (ICP-OES, Perkin Elmer Optima 2000DB) was used to analyse wood and the ionic liquid solutions for metal content. A mixed metal standard for ICP analysis (TraceCERT grade, Sigma Aldrich) was diluted to the required concentrations with 5% nitric acid. The water content of the ionic liquid liquors prior to analysis was determined by Karl-Fischer titration. The ionic liquid solutions were diluted to below 10 ppm of copper and a maximum of 1 wt% ionic liquid with 5% nitric acid before being analysed. For solid samples, a known amount of ~100 mg of ground wood was digested in 1 mL 69% nitric acid in a closed PTFE vessel (MARSXpress vessel and microwave with power/time control by CEM). The following sequence was used: 300 W at 83% power for 5 min, 600 W at 66% power for 5 min and 1200 W at 58% power for 6 min. The obtained solution was cooled in a freezer for an hour before diluting to 10 mL with 5% nitric acid and filtration through a 0.4 µm PTFE syringe filter, followed by analysis. The wood's measured copper content was used to calculate the percentage of copper extracted into the ionic liquid solution.

Compositional analysis

The carbohydrate, lignin and ash content of copper treated timber was determined following the LAP procedures "Preparation of samples for compositional analysis" (NREL/TP-510-42620) and`Determination of Structural Carbohydrates and Lignin in Biomass" (NREL/TP-510-42618). The extractives in untreated copper treated timber were removed and quantified according to LAP "Determination of extractives in biomass" (NREL/TP-510-42619). The oven-dry weight (ODW) of lignocellulosic biomass was determined according to the procedure described in the LAP "Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples" (NREL/TP-510-42621).

Enzymatic saccharification

Enzymatic saccharification was performed according to LAP "Enzymatic saccharification of lignocellulosic biomass" (NREL/TP-510-42629). The cellulose mixture used was Novozymes enzyme mixture NS-22201 (50 µL of enzyme solution was used per 100 mg of sample). Glucose yields were calculated based on the glucose content of the untreated biomass.

Electrochemical metal redeposition

Cyclic voltammetry and chronoamperometry were used. In both cases, liquor from biomass pre-treatment was saturated with copper(II) ions by dissolution of CuO and filtering off undissolved solid. The liquors tested contained 20 wt% water. Cyclic voltammetry was carried out in a three-electrode cell at room temperature. Platinum foil was used as working and counter electrode, both with an active area of 5.1 cm^2. An Ag/AgCl reference electrode was placed externally to the cell and connected to the main compartment through a Luggin capillary whose tip was placed as close to the working electrode surface as possible. Three consecutive CV scans with a scan rate of 10mV/s were performed from 0.6 to -0.7 V, starting at 0.3 V in negative direction.

Process modelling

The gross profit was estimated using the following assumptions:

- Material capacity of the plant30,000 t.p.a.
- Operation24h x 7d
- Biomass loading30%
- IL recycling rate99.5%
- IL price£0.76/kg

Results and Discussion

Copper solubility in hydrogen sulfate ionic liquids

Copper is the most common metal used in timber preservatives today. Therefore copper solubility test were carried out in two protic BioFlex ionic liquids (1-methylimidazolium hydrogen sulfate, $[HC_1im][HSO_4]$, and the lower cost triethylammonium hydrogen sulfate $[TEA][HSO_4]$, in order to establish solubility limits. Solubility limits for copper(II) in ionic liquids at 20 wt% water are shown in Table 2. It is demonstrated that the ionic liquids have a high solubility for copper ions, and that imidazolium cations tend to have a higher solubility. Excess base further increased the copper solubility, suggesting that the acid:base ratio in BioFlex ionic liquids may be tuned to optimise metal extraction behaviour.

Table 1. Copper solubility in ionic liquids

Ionic Liquid	Copper(II)solubility/ppm
$[HC_1im][HSO_4]$	4,752 ± 715
$[TEA][HSO_4]$	2,043 ± 433
$[HC_1im][HSO_4]$ 5%excess base	10,845 ±2,050
$[TEA][HSO_4]$ 5%excess base	13,712 ±4,068

Metal extraction from waste wood

We tested the metal extraction for chromated copper arsenate (CCA) treated timber (Table 3) and processed wood (Table 4). Processed wood waste is chipped waste wood of various origins and had some metal parts, mainly iron, mechanically removed. We found very high extraction capabilities for arsenic, zinc, lead, chromium and copper ions, heavy metals commonly found in timber and a concern in waste wood disposal/recycling. It can be seen that 1-methylimidazolium chloride, $[HC_1im]Cl$, was particularly effective in extracting metal ions from treated (waste) timber.

Table 2. Metal extraction from CCA treated wood with $[HC_4im][HSO_4]$ pretreatment at150°C for 1 h

	Arsenic(V)	**Chromium(VI)**	**Copper(II)**
Metal content/ppm	4268 (605)	4664 (745)	2784 (365)
Metal extracted	99% (0.06%)	99% (0.14%)	98% (0.46%)

Table 3. Metal content and extraction from processed mixed wood waste using different types of ILs

	Zinc (II)	**Lead (II)**	**Iron (II/III)**	**Chromium (VI)**	**Copper (II)**
Metal content/ppm	114 (0.3)	367 (18.7)	331 (31.7)	55 (2.1)	82 (5.0)
Metal extracted with [HC_1im][HSO_4]	70% (6.2%)	39% (4.4%)	52% (14.8%)	77% (2.6)	48% (2.7%)
Metal extracted with [HC_1im]Cl	89% (0.4%)	96% (1.9%)	56% (9.3%)	93% (0.5%)	97% (0.3%)

BioFlex fractionation and enzymatic saccharification yields

We carried out BioFlex fractionation on copper azole treated softwood, followed by enzymatic saccharification of the cellulose pulp. Table 5 demonstrates that the ionic liquid solutions were able to extract the metal ions as well as separate lignin and cellulose. The decontaminated cellulose can be hydrolysed to glucose. The best performing ionic liquid solution contained 1-methylimidazolium chloride, [HC_1im]Cl. For comparison, the non BioFlex ionic liquid 1-ethyl-3-methylimidazolium triflate, [EMIM][OTf], extracted a substantial proportion of copper ions, but did not result in lignin cellulose separation. The integrated detoxification and pretreatment is a unique feature of the BioFlex process.

Table 4. Fractionation results for copper azole treated softwood and BioFlex ionic liquids (with 20 wt% water)

Ionic liquid	**Copper extraction /%**	**Saccharification yield /%**	**Cellulose pulp yield /%**	**Lignin yield/%**
[TEA][HSO_4]	87±1	55.2±2.6	56.7±0.3	8.7±0.2
[HC_1im][HSO_4]	82±1	15.7±2.6	58.9±0.5	7.0±1.7
[HC_1im]Cl	98±2	75.7±2.5	43.1±0.8	14.3±0.7
[EMIM][OTf]	68±1	9.7±0.3	92.7±0.4	BDL
Untreated	-	9.9±0.2	100	-

Metal redeposition

We have demonstrated that copper can be redeposited from the ionic liquid solutions (Figure 3). The deposition of copper out of an ionic liquid liquor was shown for [HC_1im][HSO_4] as well as for the less expensive triethylammonium hydrogen sulfate ([TEA][HSO_4]). In order to establish the effect of solubilised biomass components (lignin and hemicellulose derived fragments) present in the liquor on the deposition behaviour of copper, a cyclic voltammogram of copper (II) saturated fresh ionic liquid was compared to that obtained for the copper (II) saturated recycled ionic liquid. Integration of current time data [HC_1im][HSO_4] confirmed that the copper deposition was not measurably affected by biomass degradation products, as charge efficiencies in both cases were *ca.* 94% under the tested conditions.

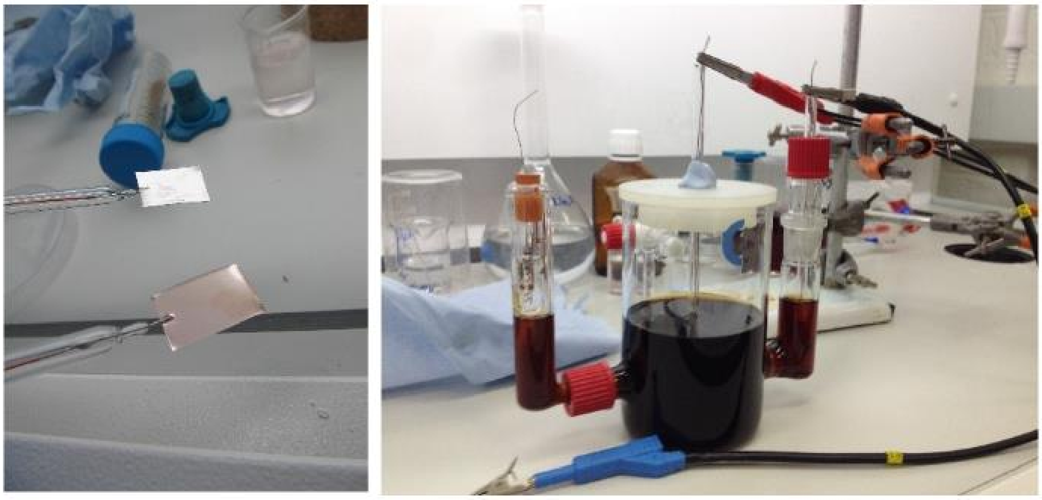

Figure 4. Electrochemical recovery of copper from a BioFlex ionic liquid solution after fractionation.

Techno-economic model

We have modelled the BioFlex process based on the assumption that recycled ionic liquid is used for pulp washing and diluted ionic liquid for lignin precipitation, with a 99.5 % recycling rate, which has been demonstrated by us on the lab scale, as shown in Brandt-Talbot et al, 2017[4]. We assumed that there was no income from heavy metal recovery, however, it avoids disposal costs associated with metal containing ash. We show that an attractive gross profit can be obtained when using heavy metal polluted waste wood as a feedstock, even at small commercial scale. The use of virgin material would make operation on such a scale challenging.

Table 5. Financial estimate of the operating cost for a BioFlex plant

Income	**Waste wood**	**Virgin wood**
Gate fee	£25	-
Lignin (40% yield)	£120	£120
Pulp (45% yield)	£300	£300
Costs		
Feedstock	-	£60
Solvent	£14	£14
Water	£1	£1
Energy	£50	£50
Labour costs	£5	£5
Transport		
◗ Cellulose*	£15	£15
◗ Lignin*	£15	£15
Machine maintenance	£4.30	£4.30
Gross profit	£119.99	£18.17

Conclusions

The BioFlex process is a lignocellulose fractionation process that can treat many different lignocellulosic input materials in a one-size-fits-all system. This now includes low value metal polluted waste wood.

We have demonstrated high metal extraction can be achieved with ultra-low cost BioFlex ILs. The ionic liquid solution based on 1-methylimidazolium chloride was shown to be particularly effectively in removing heavy metals from waste wood while affording a cellulose pulp that results in high glucose yields after enzymatic saccharification. It has further been shown that copper can be deposited from BioFlex ionic liquids. The presence of biomass degradation products from pretreatment did not alter the deposition behaviour.

Ionic liquid based pretreatment therefore represents a promising platform for the decontamination of metal contaminated waste wood while concomitantly producing intermediate fractions that can be used for biorefining. Our techno-economic estimate shows that the BioFlex process with metal polluted waste wood is economically attractive at a small commercial scale. The next focus is finding suitable applications for the BioFlex process outputs.

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Butanol production from volatile lignocellulosic feedstocks. Development of an optimized bioprocess

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In our research project Combined Agro-Forest Biorefinery (CAFB) we aim to utilize a multifeedstock biorefinery process to efficiently convert industrially based lignocellulosic waste streams, such as black liquors or hydrolysates, into high value-added chemicals such as butanol. However, the use of these feed-stocks poses a challenge due to their volatile composition and quality. For ex-ample varied concentrations of carbon sources like organic acids and sugars are known to significantly affect the overall stability and productivity of the fer-mentation process.

In the presented study we successfully established a fermentation setup in-cluding methods and analytics to gain detailed information of our process. We will use the extracted information to carefully plan our next step: continuous solventogenic phase fermentation with C. saccharoperbutylacetonicum. The knowledge generated during this project will be a stepping stone for a mul-tifeedstock butanol based biorefinery concept suitable for utilization of volatile lignocellulosic waste streams.

Introduction

A typical Aceton-Butanol-Ethanol (ABE) fermentation with clostridia has – with a certain overlap – two characteristic phases: the acidogenesis and the solvento-genesis. During acidogenesis organic acids are built. They act both as inductor (due to the lowered pH) and as co-substrate for the following solventogenesis. Thus they will be again taken up and rebuilt to solvents[1-4]. But these organic acids do not necessarily have to come from acidogenic phase fermentation. Based on the carboxylate platform, acids can be derived from various (pre)processes within a biorefinery. This greatly enhances feedstock flexibility. However, solely feeding acids is not possible. Glucose has always have to be present in the medium, as it serves both as source of ATP and electrons for the conversion of butyric acid to butanol and as carbon source for biomass growth[5].

To gain knowledge about uptake rates and robustness of our fermentations, we carried out several batch fermentations where we fed pulses of either acetic acid or butyric acid during the solventogenic phase and closely observed the response of the culture.

Experimental

Culture and media

C. saccharoperbutylacetonicum was used as organism in this study. The strain was stored as 100 µL aliquots of a dense spore suspension in cryovials at -80 °C. The suspension of one vial was transferred aseptically to a Hungate tube containing 10 mL modified CG media (10 g L-1 glucose), heat-shocked in boiling water for 1 min and cultured at 30 °C for 24 h. Two more pre-culture steps were carried out before the fermenters could be inoculated. This had the purpose of providing both, a vital culture as well as a sufficiently large volume for fermenter inoculation.

A modified Clostridial Growth Medium (CGM) medium was used for all exper-iments. It contained the following compounds where values given in parenthe-ses were used in pre-cultures only: 20 (10) g L^{-1} glucose, 2.5 (5) g L^{-1} yeast extract, 2 g L^{-1} $(NH_4)_2SO_4$, 0.1 (0.75) g L^{-1} KH_2PO_4, 0.1 (0.75) g L^{-1} K_2HPO_4, 0.712 g L^{-1} $MgSO_4 \cdot 7\ H_2O$, 0.015 g L^{-1} $FeSO_4 \cdot 7\ H_2O$, 0.01 g L^{-1} $MnSO_4 \cdot H_2O$, 0.01 g L^{-1} NaCl, 1.5 (2.25) g L^{-1} asparagin · H_2O and 0.75 g L^{-1} L-cystein hydrochlorid monohydrate. All components, except glucose and L-cysteine, were dissolved in deionized water before being autoclaved for 15 min at 121 °C. Still warm, the medium was cooled down under vacuum for at least 2 h to make it anoxic. Glu-cose was autoclaved separately as a 100 g L-1 solution and made anoxic, follow-ing the same principle as described above. Glucose and L-cystein hydrochlorid monohydrate (via a sterile filter) were aseptically transferred to the rest of the medium shortly before it was being used.

Fermentations

Fermentations were carried out on a parallel bioreactor system (Eppendorf DASGIP). The system was improved with mass flow controllers (Bronkhorst) which allowed us to purge our culture at a defined flow and independent from any back pressure. Every fermenter was constantly purged with 5 L h-1 of sterile N2 to maintain anaerobic conditions as well as to have a high enough off-gas stream for GC measurement.

The starting pH was set to 7.1 and after an initial sample was taken, the ves-sels were inoculated with 10 % of the total working volume of 1.6 L. The fermen-tation was controlled at 30 °C and constantly stirred at 100 rpm. Samples were frequently collected from the reactor for HPLC analysis, determination of the cell dry weight (CDW) and measurement of the optical density (OD).

A pulse experiment consisted of at least one addition of either butyric or acetic acid diluted in a total volume of 50 mL per batch. Subsequent shots also con-tained glucose at a molar ratio of 1.5 (glucose/acid) based on experiments by Tashiro et al[7]. This was to compensate for already low glucose concentrations at this time of fermentation. A pulse was slowly dispensed to the reactor via a sterile 0.2 µm syringe filter while at the same time pH was not allowed to drop below 4.3 by manually dosing 3 M NaOH. This was done to prevent a so called “acid crash”, where a threshold of 57 mmol L-1 of undissociated butyric acid should not be exceeded as reported by Maddox et al[6]. In an experiment we always ran two fermentations in parallel, where one reactor was pulsed with butyric acid and the other one with acetic acid. For comparability both the butyric and the acetic acid shots had the same concentration based on mol carbon per liter.

Analytical Methods

CDW was determined in triplicate by sterile filtration on every second sample. For that purpose 5 mL of cell suspension (kept on ice) were dispensed on a prior weighed filter, vacuum filtrated and washed twice with 5 mL deionized water. The filters were dried at 80 °C for 4 h, cooled in a desiccator and then again weighed. OD was measured of every sample at 600 nm with an UV-VIS Spectrophotometer (Thermo Scientific). At times were no CDW was directly deter-mined, it was calculated via interpolation using OD values and the CDW values gained from the previous sample and the next sample.

Substrates (glucose, xylose and organic acids) and products (acetone, buta-nol and ethanol) were quantified by HPLC (Shimadzu). Off-gas (CO_2, H2 and N2) was measured online via a Micro GC Gas Analyzer (Inficon) every 10 min. The detailed HPLC and GC settings are shown in Table 1.

Table 1. HPLC and GC method settings

	HPLC settings	GC settings
Column(s)	Bio-Rad HPX-87H	Rt-Molsieve 5A 0.25 mm (10m), Rt-Q-Bond 0.25 mm (12m)
Temperature	40 °C	80 °C / 60 – 240 °C
Eluent / Carrier gas	5 mM H_2SO_4	Argon
Flow / Column pressure	0.6 mL min^{-1}	30 psi
Detectors	DAD @ 210 nm & 269 nm; RID	TCD

Results and discussion

Several batch fermentations have been conducted. Due to the reduced content in complex media components like yeast extract, the mass balance for carbon could always be closed by more than 92 %. Taking into account the complex media, all the combined methods and measurement inaccuracies, this was found to be acceptable.

It was observed that the fed butyric acid was taken up relatively fast with a maximal specific uptake rate of 0.26 gacid gcells-1 h-1 and mainly rebuilt to butanol as can be seen in Figure 1. The highest specific production rate of butanol was with 0.28 gbutanol gcells-1 h-1 shortly after the first butyric acid pulse where the culture was still growing. Although the experiments are not quite comparable due to different media and culture conditions, this is in the range of other published data[4,7].

In a parallel experiment the fed acetic acid was taken up at a maximum spe-cific rate of 0.27 gacid gcells-1 h-1 (Figure 2) but had a greater impact on the generation of acetone and CO_2 than on butanol. So the maximum specific production rate of butanol was only 0.09 gbutanol gcells-1 h-1. Time of feeding was crucial as when growth seized and glucose was almost depleted no more acids were tak-en up. In another experiment a butyric acid concentration of 2.4 g L-1 in the fer-mentation broth resulted in a complete collapse within 2 h, although the total concentration of undissociated acids was below 30 mmol L-1. This could have had several reasons including low cell density of only 1.1 g L-1 as well as simply the cell inhibiting characteristic of undissociated butyric acid.

Our pulse experiments are crucial for the scientific understanding of the pro-cess and for designing feeding strategies for the follow up experiments on con-tinuous fermentation.

Conclusions

We demonstrated the successful uptake and conversion to solvents of added butyric and acetic acid. Presented experiments enable us to go one step further and ultimately help us in establishing long term stable continuous solventogenic phase fermentation with C. saccharoperbutylacetonicum on volatile lignocellulo-sic waste streams.

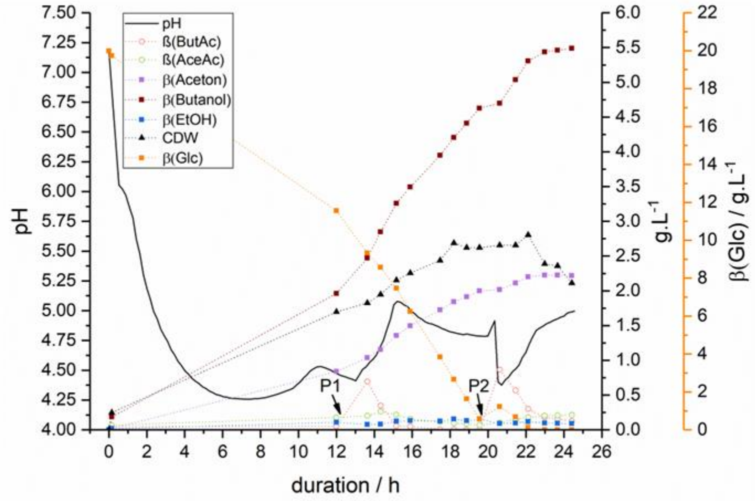

Figure 1. Fermentation kinetics and pH course of a butyric acid pulse experi-ment (pulses marked with P1 and P2). Dotted lines were inserted for better read-ing and are not representing the true course between measuring points.

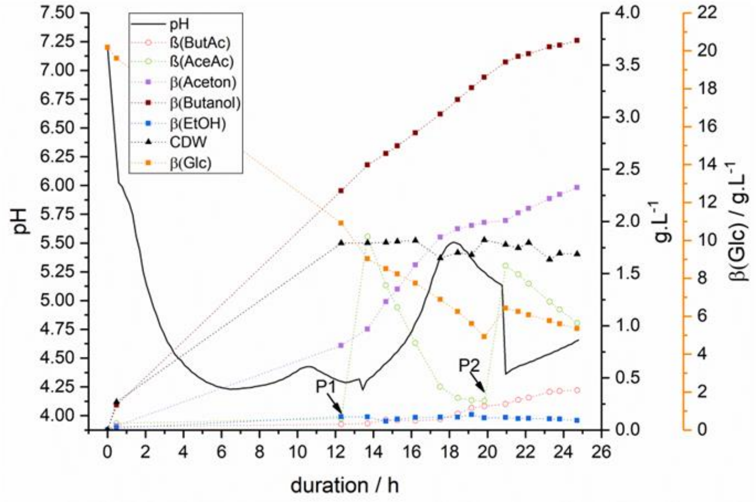

Figure 2. Fermentation kinetics and pH course of an acetic acid pulse experi-ment (pulses marked with P1 and P2). Dotted lines were inserted for better read-ing and are not representing the true course between measuring points.

Acknowledgements

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Crude tall oil-based renewable diesel as sustainable biofuel component

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The need for high quality renewable fuels is increasing globally. This is due to the legislations and the need to have fuel that reduces significantly CO_2 emissions over the whole lifecycle. The Finnish pulp and paper company, UPM, has built a first of a kind biorefinery producing wood-based biofuels to Lappeenranta, Finland. The biorefinery has been operational and delivering renewable diesel fuel to customers since the beginning of 2015. The fuel can be used as such or as a biocomponent in various different diesel fuel types, such as EN590 diesel and Mk1 diesel fuel commonly used in Sweden. The UPM BioVerno wood-based renewable diesel reduces greenhouse gas (GHG) emissions by up to 80% compared to traditional diesel fuel. In the field and engine tests, the renewable diesel, UPM BioVerno, has proved to be a high quality fuels and blending component that performs well in all diesel engines, reducing most of the regulated emissions (e.g. PM, NOx, CO, HC).

UPM BioVerno, a high quality drop-in renewable diesel fuel has been studied as a blending component in EN590 and MK1 diesel fuels in several studies by different engineering companies, universities and research facilities in Europe. The functionality and emission characteristics of the pure UPM BioVerno renewable diesel have also been tested with both engine and fleet tests.

The field and engine test have shown that UPM BioVerno wood-based diesel is a high quality renewable diesel component that does not have an effect to the functionality of diesel engines. Thus, UPM BioVerno diesel significantly reduces harmful particulate emissions as well as carbon monoxide, hydrocarbons and nitrogen oxides emissions polluting the air. The relevance of using renewable diesel in older cars that do not have exhaust after treatment equipment is even greater. In addition, the tests have shown that the fuel economy of the engine stays the same or is improved lowering the overall fuel consumption. These results show that the use of UPM BioVerno in a fuel blend lowers the tail pipe emissions without compromising the engines functionality or the fuel consumption.

Biorefining at Borregaard: Recent developments

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Borregaard operates what is possibly the world's most advanced biorefinery. By using natural, sustainable raw materials, Borregaard produces advanced and environmentally friendly biochemicals and biomaterials that replace oil-based products. The cellulose fibrils from the Exilva plant represent a recent addition to a product portfolio which already includes lignin performance chemicals, specialty cellulose, wood based vanillin and cellulosic ethanol (advanced biofuel), all produced from Norway spruce. An update on this as well as other recent developments within lignin, cellulose and ethanol will be given. The presentation will also touch upon projects from the innovation pipeline, including Excello sugars from the BALI™ process.

Revisiting biorefinery strategies: The case of large-scale production of drop-in biofuels

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To date, the production of drop-in[1] hydrocarbon fuels at the large scale[2] from 2nd generation (2G) biomass has not been an attractive pathway for forest product companies to invest in due to a gamut of reasons including high capital intensity of the thermochemical platform, commodity markets with tight margins, exposure to oil price volatility, dependency on policies, technology challenges related to scale and use of woody biomass feedstock, as well as low overall yields.

However, lignocellulosic biomass remains a potentially-attractive feedstock for biofuel producers due to (1) its sustainability, i.e. no direct competition with food supply chain; limited impact on land-use change; and positive environmental profile (>60-70% GHG reduction targets); and (2) its availability in large quantities and in particular cases, at a relatively low cost.

Policy-driven mandates targeting minimum blending rates of 2G biofuels are driving the development of a new generation of biofuel projects, in particular in the US and in the EU. In the US, the Renewable Fuels Standard 2 (RFS2) at the federal level and the Low Carbon Fuel Standard (LCFS) in California are offering large premiums, up to 3x times the fuel value, for each liter of 2G biofuel sold – targeting 60 Billon liters of 2G biofuels to be produced by 2022. In Europe, the Renewable Energy Directive 2 (RED2) has been recently promulgated, supported by a specific mandate for 2G biofuels targeting 3.5% of fuel production by 2030, i.e. approximately 15 billion liters. RED2 also plans to limit the production of 1st generation biofuels, and to phase-out feedstocks having high impact on Indirect Land Use Change such as palm oil and some soybean oil, creating a strong driver for feedstock alternatives such as woody biomass.

In implementing first-of-kind 2G biofuels production facilities at the large-scale, and replicating them around the world in jurisdictions offering favourable policies and/or feedstock opportunities, different business models can be considered. Traditionally, forestry companies evaluating the potential of investing in drop-in biofuels production would consider themselves competing against large oil and gas companies.

For 2G biofuels production to become reality at the large scale, this presentation explores how the gap between the forestry industry and the oil and gas industry can be overcome (Figure 1), building on synergies while addressing the complexity of early-stage design issues characterized by a high number of product-process options and high uncertainty on data, technology advancement, policy, etc.

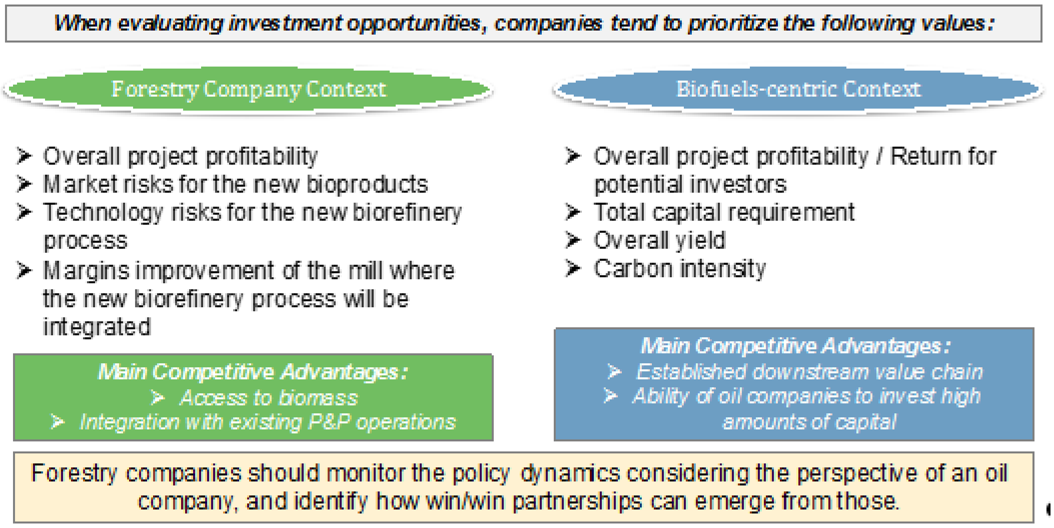
When evaluating investment opportunities, companies tend to prioritize the following values:
Forestry Company Context
Overall project profitability
Market risks for the new bioproducts
Technology risks for the new biorefinery process
Margins improvement of the mill where the new biorefinery process will be integrated
Main Competitive Advantages:
Access to biomass
Integration with existing P&P operations
Biofuels-centric Context
Overall project profitability / Return for potential investors
Total capital requirement
Overall yield
Carbon intensity
Main Competitive Advantages:
Established downstream value chain
Ability of oil companies to invest high amounts of capital
Forestry companies should monitor the policy dynamics considering the perspective of an oil company, and identify how win/win partnerships can emerge from those.

Figure 1. Basis for Partnerships between Forestry and Petroleum Companies

Approach to Identify Promising Biorefinery Strategies

Companies investing in successful biorefinery strategies are setting long term goals while defining near-term activities to transform over the longer-term. A phased-approach (Figure 2) is required in order to mitigate technology and market risks while implementing a robust biorefinery strategy and maximizing margins over the long term. Near-term phases typically focus on creating competitive advantage through synergies with the core business and minimizing risk, while longer-term phases seek to "climb the value ladder" through full scale production, secondary conversion processes to value-added bioproducts, including downstream market partnership strategies.

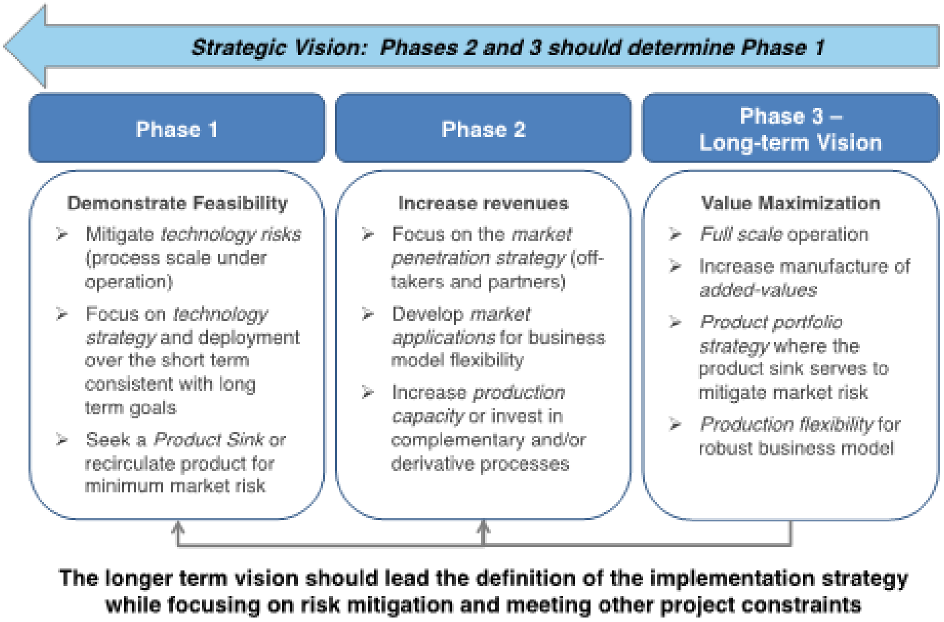
Strategic Vision: Phases 2 and 3 should determine Phase 1
Phase 1
Phase 2
Phase 3 – Long-term Vision
Demonstrate Feasibility
Mitigate technology risks (process scale under operation)
Focus on technology strategy and deployment over the short term consistent with long term goals
Seek a Product Sink or recirculate product for minimum market risk
Increase revenues
Focus on the market penetration strategy (off-takers and partners)
Develop market applications for business model flexibility
Increase production capacity or invest in complementary and/or derivative processes
Value Maximization
Full scale operation
Increase manufacture of added-values
Product portfolio strategy where the product sink serves to mitigate market risk
Production flexibility for robust business model
The longer term vision should lead the definition of the implementation strategy while focusing on risk mitigation and meeting other project constraints

Figure 2. A Phased Approach for Implementing the Biorefinery

In order to identify and assess potential technology strategies for producing drop-in biofuels from forest residues at large scale, a systematic 3-part methodology (Figure 3) has been employed for this assessment:

- *Part 1*: A set of possible technology *solutions* is identified based on a review of the technology landscape including surveys with leading players, which is refined and triaged into a set of technology *strategies* considering the phased implementation approach to mitigate risk and maximize margins.
- *Part 2*: The early-stage assessment of each retained technology strategy is completed considering (a) early-stage techno-economics, (b) policy scenarios considering different types of incentives, and (c) market considerations.
- *Part 3*: "Preferred" technology strategies are identified through a multi-criteria decision-making (MCDM) panel involving the gamut of project stakeholders. MCDM is a panel-based methodology that (1) results in systematic knowledge transfer of the project to the stakeholder group, and awareness of the key decision-making issues related to biorefinery decision-making, (2) requires panel members to interpret decision-making criteria that emphasize critical issues such as longer-term sustainability and risk of transformation strategies, and (3) builds alignment between project stakeholders regarding the preferred strategies, including the strengths and weaknesses of each strategy.

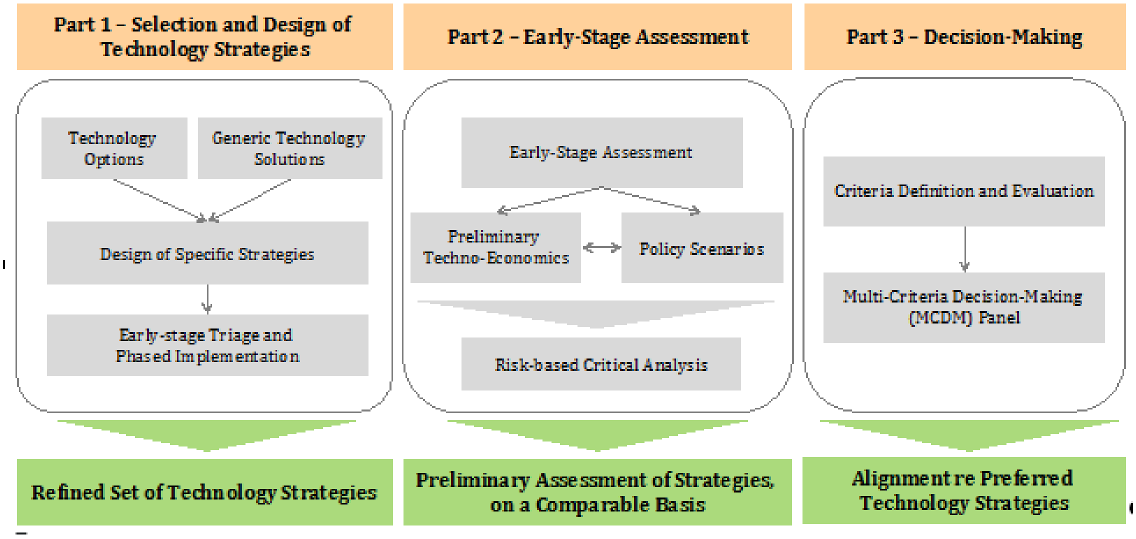
Part 1 – Selection and Design of Technology Strategies
Part 2 – Early-Stage Assessment
Part 3 – Decision-Making
Technology Options
Generic Technology Solutions
Design of Specific Strategies
Early-stage Triage and Phased Implementation
Early-Stage Assessment
Preliminary Techno-Economics
Policy Scenarios
Risk-based Critical Analysis
Criteria Definition and Evaluation
Multi-Criteria Decision-Making (MCDM) Panel
Refined Set of Technology Strategies
Preliminary Assessment of Strategies, on a Comparable Basis
Alignment re Preferred Technology Strategies

Figure 3. Overall Methodology to Identify Preferred Technology Strategies for the production of large-scale drop-in 2G biofuels.

Results of Case Study applied to Large-Scale Production of Drop-In Biofuels

The previously described methodology was adapted and applied in the context of a forestry company and a petroleum company collaboration, seeking preferred technologies for the production of large-scale production of heavy transportation drop-in hydrocarbon fuels from forest residues.

The main technology routes were mapped (Figure 4) and characterized (Table 1).

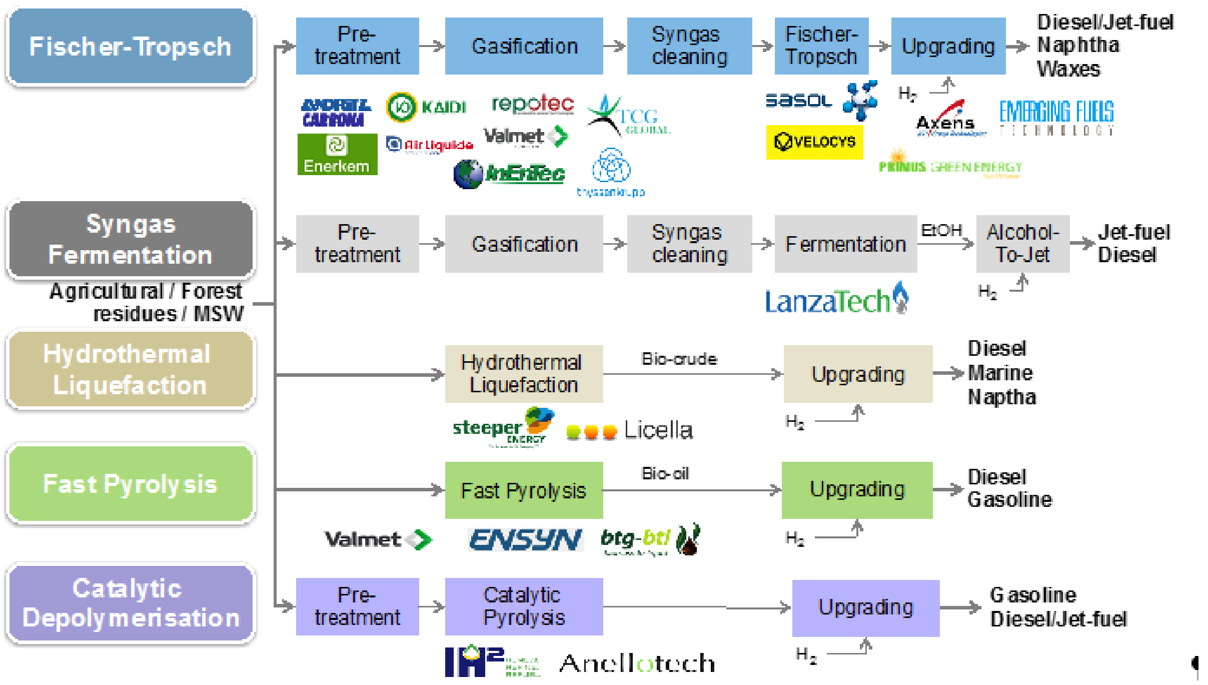
Fischer-Tropsch
Pre-treatment
Gasification
Syngas cleaning
Fischer-Tropsch
Upgrading
Diesel/Jet-fuel
Naphtha
Waxes
H₂
Andritz Carbona
KAIDI
repotec
TCG Global
Enerkem
Air Liquide
Valmet
InEnTec
thyssenkrupp
sasol
Velocys
Axens
Emerging Fuels Technology
Primus Green Energy
Syngas Fermentation
Agricultural / Forest residues / MSW
Pre-treatment
Gasification
Syngas cleaning
Fermentation
EtOH
Alcohol-To-Jet
Jet-fuel
Diesel
H₂
LanzaTech
Hydrothermal Liquefaction
Hydrothermal Liquefaction
Bio-crude
Upgrading
Diesel
Marine
Naptha
H₂
steeper energy
Licella
Fast Pyrolysis
Fast Pyrolysis
Bio-oil
Upgrading
Diesel
Gasoline
H₂
Valmet
ENSYN
btg-btl
Catalytic Depolymerisation
Pre-treatment
Catalytic Pyrolysis
Upgrading
Gasoline
Diesel/Jet-fuel
H₂
IH²
Anellotech

Figure 4. Main thermochemical routes for the production of heavy transportation drop-in hydrocarbon fuels from forest residues.

Table 1. General characterization of the main thermochemical routes to drop-in 2G hydrocarbon drop-in biofuels

	Gasification + Fischer-Tropsch	**Gas. + Fermentation + A-T-J**	**Hydrothermal Liquefaction + Upgrading**	**Fast Pyrolysis + Upgrading**	**Catalytic Depolymerization**
Main Products (1)	Diesel/Jet-fuel Naphtha	Diesel Jet-fuel	Diesel Marine Lights/Naphtha	Diesel/Jet-fuel Gasoline	Diesel/Jet-fuel Gasoline
Typical Yield (2)	~15-20% (3)	~20-25%	~30-40%	~20-25%	~22-28%
Largest Operating Plant	150 t/d of wood to methane plant (GoBiGas) 4 t/d of wood to drop-in fuels (TRI/ Velocys)	60 ML/y of ethanol from steel mill gases in China (Lanzatech)	30 t/d of feedstock plant (Licella)	~200 t/d of feedstock plant (Valmet/Fortum; Ensyn Côte Nord) – FP only, no upgrading	5 t/d of feedstock plant (IH2)
Main Future Plants in Development (Public)	• Red Rock Biofuels: 500 t/d of wood residues (TCG Global/Velocys) • Fulcrum Bioenergy: 500 t/d of MSW (TRI/Emerging Fuels) • Bayou Fuels: 1,000 t/d of wood residues (TRI/Velocys)	Aemetis: 45 ML/y of ethanol from wood/fruits residues (InEnTec/LanzaTech)	Canfor: 80 ML/y of bio-crude from pulp mill residues (Licella)	400 t/d (Ensyn: Brazil; US) 120 t/d (BTG: Europe)	For now, limited to JDA announcement with Biozin in Sweden
CAPEX (4)	US$ 1.1-1.4 Billion	US$ 1-1.2 Billion	US$ 0.9-1.1 Billion	US$ 0.9-1.1 Billion	US$ 0.7-0.9 Billion
Demonstrated Feedstock Flexibility (1)	• Wood • Forest residues • Agricultural crops • Agricultural wastes • MSW • Pyrolysis oil	• Wood • Forest residues • Agricultural crops • Agricultural wastes • MSW	• Wood • Forest residues • Agricultural crops • Agricultural wastes • MSW	• Wood • Forest residues • Agricultural crops • Agricultural wastes	• Wood • Forest residues • Agricultural crops • Agricultural wastes • MSW
Major Technology Bottleneck(s) for Scale-up	• Biomass feeding to gasifier • Impact of biomass inorganics and impurities on gasification operations and syngas clean-up efficiency	• Biomass feeding to gasifier • Impact of biomass inorganics and impurities on gasification • Fermentation reactors	• High-pressure reactors size • Charring and heat management • Catalysts requirements for the upgrading of bio-crude	• Biomass high rate/ large scale feeding into FP reactor • Energy transfer	• Process efficiency, in particular in the 1st reactor feeding pressurized hydrogen and catalysts
Main Technology Advantage(s)	• Relatively mature set of technologies • Scalability of gasification and fisher-tropsch reactors	• Product flexibility • Gas fermentation is more robust to syngas contaminants and variability	• Potential for disruptive high yield • Large volume of marine fuel obtained, in addition to diesel	• Well known technology, demonstrated on forest residues at the demo scale • Bio-oil co-refining opportunity	• Integrated and simplified process • Auto-sufficient supply/generation of H_2

(1) Does not include co-products such as char; non condensable gases, etc. The Fischer-Tropsch route has some production flexibility to targeted higher value products such as waxes.
(2) Overall mass yield on a dry basis from forest residues to fuels, for comparison purposes based on leading technologies in each route.
(3) Addition of H_2 (e.g. through SMR or water electrolysis) can improve the yield by more than 50%, i.e. to about 30% overall.
(4) Order-of-magnitude estimates for a 2,000 t/d plant, for comparison purposes based on leading technologies in each route.
(5) Feedstocks that technology providers claim they have run trials on for a significant period of time

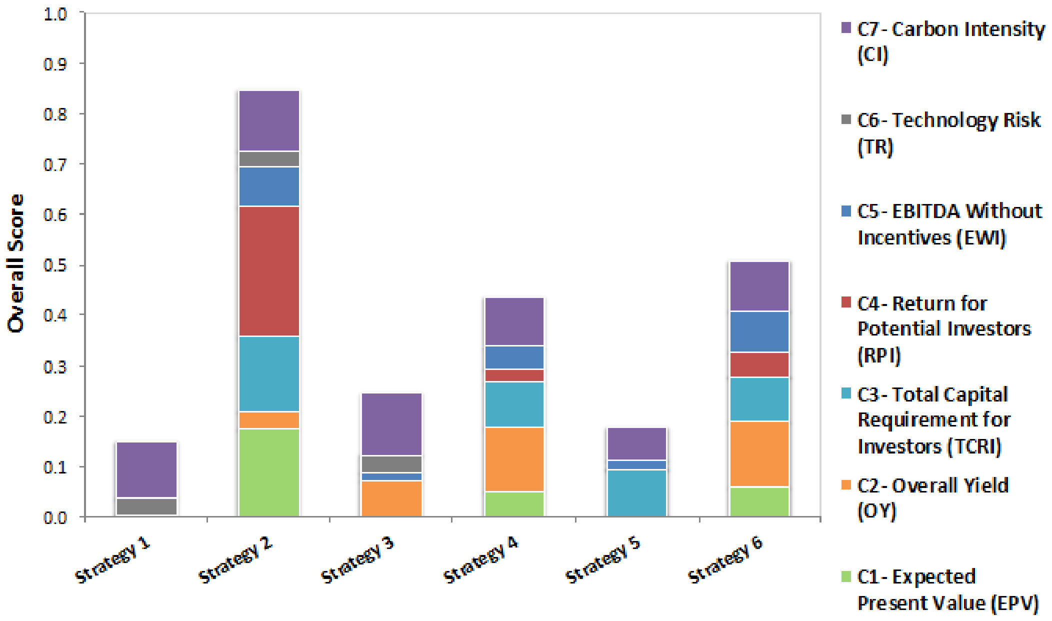

Figure 5. Preferred Biorefinery Strategies Resulting from the MCDM Panel Trade-Off

6 strategies were retained and assessed in greater detail considering techno-economics, policy scenarios, and technical/market risks. The results were employed in a MCDM panel involving decision-makers from the forestry company and the petroleum company in order to align on the most preferred technology strategies. A set of 7 evaluation criteria was used spanning different risk categories such as: economic risk, financing risk, long-term competitiveness risk, technology risk and environmental benefits. The criteria were evaluated and interpreted in the context of the results and were individually weighed by panel members. “Preferred” strategy rankings resulted from the panel trade-off (Figure 5) mainly driven by the project profitability metric including capital and operating costs and policies.

Conclusion

Heuristics for the Development of 2G drop-in biofuels Projects

Key lessons learnt from this project led to the identification of 5 important project heuristics when considering the implementation of 2G drop-in biofuel projects:

Investment risk: large-scale conversion processes for 2G drop-in biofuels will remain capital-intensive, i.e. >1 billion US$, in particular in the context of pioneer plants. The level of risk for the investors must be acceptable, in particular:

The technology must be demonstrated at a representative scale using representative feedstock(s), and corresponding mass/energy balances to prove yields/performance.

Key technology risks are related to the experience with biomass handling/feeding, level of demonstration of each process unit, and level of integration of all process units into a single line.

Policy: the existence of biofuel mandates (which guarantee a minimum demand for biofuels in specific jurisdiction as well as potential price premiums) is a pre-requisite to attract investors.

Subsidies on capital cost are an essential pre-requisite to mitigate financial risk for first-of-kind facilities.

Economics: return on investment, considering the high level of policy incentives, should be expected to be reasonably low (e.g. 10-15% IRR). However, it is important that the process/technology can be replicable for wide-scale deployment. The overall process yield to products eligible for incentives/credits, is a particularly important factor for process economics in large-capacity processes.

Stakeholders: investments in 2G biofuels are more likely to be driven by petroleum companies due to the synergies with their core business, their ability to mobilize large amounts of capital, refinery operating experience (high pressure vessels, use of hydrogen and catalysts, etc.), as well as their established supply chains to access markets.

Sustainability: carbon intensity - in CO2eq/MJ of fuel - is recognized as an easily-understandable indicator of GHG reduction potential, favoured under all policy scenarios, and therefore weighs in the attractiveness of a given technology and its potential to be replicated in different jurisdictions.

Concepts 2:

New concepts and applications from wood based raw materials

Replace fossil gas in industrial burners with renewable biogas

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Energy Technology Center at the Swedish research institutes, RISE, has conducted research studies on replacing fossil industrial burner gas for the tissue industry with renewable syngas from Meva Energy, a Swedish company active within gasification of solid biomass. The background is a wish from the tissue industry to become fossil free by removing one of the main remaining emission source, process heat that use fossil gas.

Drying, firing, heating etc. requires process heat. In many processes, such as for instance drying of tissue paper, the process heat also needs to be in contact with the product, resulting in that fossil gases (e.g. LPG, LNG) has been the only existing cost-efficient solution that could meet the requirements.

RISE reports show that Meva syngas can create a stable flame, sufficient heating value to generate the required combustion temperature, no odor or visual imperfections on the product, and concludes that it is possible to replace the fossil gas with renewable syngas from Meva.

Designing from scratch – challenges of dialogue between material research and end products when application areas are in architecture

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New materials and material combinations can be designed to support products related to living environments due to the increased knowledge of material science and chemistry, and our ability to process renewable resources. However, material knowledge and scientific research, which have been generated in laboratories, might sometimes be removed from the practical needs on the product level. The objective of this study was to understand what needs to be observed when developing new material for architecture. Research material has been examined using the down-to-up and top-down approaches. The top-down approach can be described as a market-pull process, whilst the down-to-up approach focuses more on the inherent aspects of materials and can be called a material-driven process. Within these two approaches, different aspects during the material lifecycle have been tentatively reviewed, especially on the level of ranging from the produced material through to maintenance of the end product. The research material was four case studies made during a multidisciplinary research project. The studied case materials were early stage designed cellulosic samples.

Introduction

Both working and interacting with materials have been generally practiced in the artistic works related to architecture. During present times, manufacturing chains have been lengthened, and several experts from various fields of materials development are committed to processes. Because of this, in scientific research projects, the gap between the actual product and the material to be developed might be wide, for many reasons. From the material point of view, the reason might be that the signifying properties might not be clear at the early stage, the targets are too far away or that the idea is obscure.

When developing new materials for a specific area, it might be useful to understand which aspects are valuable from the point of view of a person who has the possibility to make decisions. Persons who work with material development, like chemists or material scientists, might be too removed to understand which aspects an architect emphasises when considering suitable materials during the design phase. In general, during the design process, architects have an opportunity to influence the material selection of the buildings and interiors, albeit with some limits. Architects mostly have the possibility to influence the materials which are in close contact to the user or experiencer and which affect the spatiality or are visible. Those aspects can be very practical, related to the use of the building or to the experimental aspects considered when generating atmospheres for the user.

Aspects which affect decisions and what kind of information is needed when designers or architects curate materials during the design phase have all been researched lately. There have been studies about which aspects have been thought to be significant during product designers' material selection process[1]. In architecture, these aspects have also been considered through many aspects, like the experience-centred approach[2]. The objective of this study was to realise the wide thinking process that architects use when evaluating suitable materials during the design process, and the main approach was to bring the information back as feedback to the different phases of the material's lifecycle. As a result, the practical implication of this research is gained through generating knowledge of what kind of aspects need to be emphasised when developing materials for the construction industry from the point of view of an architect.

The Research Material

The objective of this study was considered from two approaches. The first examination was from material to product – the down-to-up approach – and the second examination was from product to material – the top-down approach. The top-down approach has a background in market-pull thinking whilst the down-to-up approach is based more in the inherent aspects of materials and can be described as a material-driven process. Within these two approaches, different stages during a material's lifecycle have been tentatively reviewed, ranging from the level of the produced material up to the maintenance of the end product, or ranging in the opposite direction.

Research approaches have been studied with the help of designed case studies where cellulose was the main material (Figure 1). The case studies were done during the Design Driven Value Chains in the World of Cellulose (DWoC) research project. The project was explorative, visualising the potentials of the cellulosic materials for interior decoration or the construction industry. Due to this explorative nature, the aim was not to make products from the developed materials nor to design commercial material for future products. The material design cases were cases at the Department of Architecture, Aalto University, or they were co-operative research with the VTT Technical Research Centre of Finland Ltd. The down-to-up approach (from the raw material to the products) has been studied using cases of foamed cellulose and casted wood. The top-down approach – in which there are markets for a certain product, but not yet suitable material to fulfil design demands – has been studied using cases of cellulose nanofibril coating when used as paint and for laminated structures. The design cases were:

Foamed cellulose (down to up): Cellulose foam is pressed to create stiff and dimensionally stable material. The material can be three-dimensionally patterned, shaped by using a water jet cutter or printed on top of the material. Application areas can be plain boards, structures for the construction industry or interiors.

Casted wood (down to up): Casted material is created by combining dry wood flour and wet nanocellulose. The material can be uniformly dyed using pigments. The main method for processing this material is casting, which enables three-dimensional shapes to be cast, but also flat boards are feasible. Application areas can be three-dimensional shapes in interiors, such as acoustic elements or furniture.

Cellulose nanofibril coating as paint (top down): In this case wooden materials, such as solid wood or plywood, were coated with dyed cellulose nanofibril layers. The coating creates a uniform colourful layer on the top of the material, whilst enabling humidity to pass through the layer. In this study, the material was dyed using food colorants. Application areas can be found among coating applications.

Laminated structures (top down): Laminated cellulose material consists of paper which has been laminated using nanocellulose to create an all-cellulose base material for advanced structures. The material can be machined by milling or cutter, and shaped using moulds. Printing or painting on the material is possible because the surface is made out of paper. Application areas can be furniture and flat or moulded surfaces in interiors.

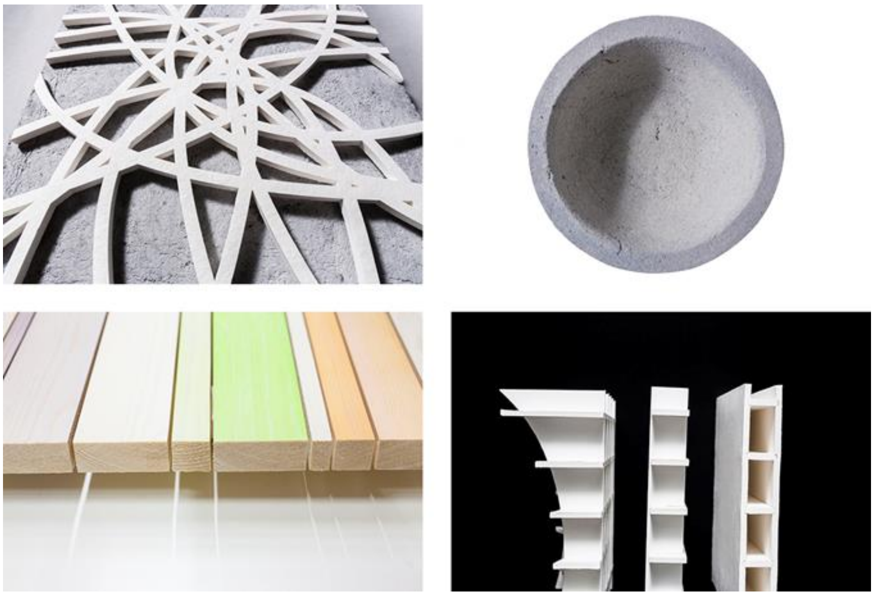

Figure 1. Top left: Foamed cellulose (research team: Heidi Turunen, Aalto ARTS, Jani Lehmonen, VTT). Top right: Casted wood (research team: Heidi Turunen, Aalto ARTS). Lower left: CNF coating as paint (research team: Heidi Turunen, Aalto ARTS, Vesa Kunnari and Jaakko Pere, VTT). Lower right: Laminated structures (research team: Heidi Turunen, Aalto ARTS, Vesa Kunnari, Ali Harlin, Timo Kaljunen and Jaakko Pere VTT). Photos: Eeva Suorlahti.

Results: Considerable Issues When Developing New Material

In general, both approaches showed that the means by which an architect can benefit from material research is very practical, such as clarifying the necessary technical characteristics at the point of use and clarifying the aspects related to legislation. Other similar clarifying factors were water tolerance and the ease of cleaning, repairing or replacing the material during periods of use and maintenance. In addition to these, the customisation abilities of the material and the visual possibilities were important connective properties. A similar concern in both cases was whether the material would change in an unwanted direction if the material is modified, taking into account the purpose of the building and the spatial experience. Also common to these two approaches was that both tried to understand how material properties affect the experience of the material. The neutrality of the material, as well as possible patina appearances, came up in both approaches. One more common point in the down-to-up and top-down approaches was discovering what could be learned from closely related materials, products or methods from the point of view of culture and an environment. In both, the down-to-up and top-down approaches it also became a necessity to find out which properties or traditions could help a material to adapt to a culture. The aim of the down-to-up approach was also to understand the traditions involved in the material itself. Similar in both the down-to-up and top-down approaches were questions regarding if the material is affordable to produce during different phases of the material's life cycle and also material identity from the point of view of considering the business aspects.

There were also differences in these two approaches. The starting point of the down-to-up approach was understood more widely, due to low prevalence of non-limiting aspects, while the premises of the top-down approach were more defined. With the down-to-up approach there was a demand to define limitative aspects for the material, such as external dimensions and intrinsic shapes, and also to concentrate on design aspects like detailing, joints and combining the side-by-side or joint materials. With the top-down approach, the limitative aspects have been mostly defined at the design brief for the end product, where the general idea of the use and demands related to the design, details and shapes have been disclosed. With this approach, the observations focus on how the material will cope with preset needs for the product imago for human use. With the down-to-up approach the concern was also about the imago of the material, but on a general level, especially regarding how it is related to human use and other materials. The down-to-top approach was more concentrated on the disturbing elements which occur during material development, while the top-down approach was concentrated on the already-existing elements which can be disturbed. Compared to the down-to-top approach, the top-down approach examined the ease of use and maintenance in more accurate way. While the top-down approach concentrates on how the material will create pleasant atmosphere and how it can interact with surroundings, the down-to-up approach concentrates on how the developed material adapts to culture and environments on a more general level. As a result, the focus of the down-to-up approach appeared to be knowledge generation and getting familiar with the properties of the new materials, whilst in the top-down approach the idea was to determine if the material is suitable for its intended use. If it is close enough to being suitable, the approach then considers how it can be made even more applicable.

Conclusion

This preliminary study aims to clarify, with the help of four case studies, how material development could benefit from understanding the mindset of architects when making decisions during the design process. Research material has been observed through the full journey of its material life cycle, from produced material through to maintenance of the end product, or running in the opposite direction. The down-to-up approach describes the journey from the produced material towards maintenance of the end product and the top-down approach studies the journey from end product towards the produced material. Architecturally related cases have been selected from the research project DWoC. In the future, this research aims to benefit the co-working of multidisciplinary research among materials where the end products are related to architecture. This research will be continued.

Acknowledgements

I would like to thank all the persons on the research teams that implemented the research cases, Professor Pekka Heikkinen for the initial idea for the studied subject and Tekes, the Finnish Funding Agency on for Innovation (now named Business Finland), for funding part of this research.

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From wood to food: addressing the protein gap in animal feed and human food with lignocellulosic biomass

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Arbiom's bioprocessing and fermentation technology enables an economically viable production pathway from wood to food – unlocking an untapped and abundant carbohydrate source from wood, an otherwise non-edible plant, therefore decoupling the production of food from conventional foodstuffs, and representing a disruptive innovation that can expand global nutritional production, requiring less resources to meet the nutritional needs of animals (e.g. salmon, ruminants, companion animals) and humans.

Arbiom's technology utilizes woody biomass to create distinct 5- and 6-carbon sugar-rich streams for the production of torula yeast, or other fermentation applications. Further, Arbiom has developed a novel strain that has high overall nutrient bioavailability and increased levels of key essential amino acids. The amino acid profile of the enhanced torula yeast makes it a favorable substitute for conventional high-protein sources, such as fish meal or soy protein concentrates based on digestible indispensable amino acid score. The result is a natural, economical, traceable and sustainable solution to meet global protein production challenges.

The bioconversion process technology was developed with the goal of an optimal recovery of the value inherent within non-food, readily available biomass feedstock, such as wood. Presently, in North America and Europe, wood stocks are increasing faster than demand for wood, representing an abundant and sustainable source of carbon. Additionally, the global forest products & paper industry has core competencies in sourcing and processing a long-term, renewable biomass supply, with mature supply chains and sizeable asset base, presenting an opportunity to apply technology to unlock new value creation opportunities, such as the production of feed and food.

Arbiom is committed to meeting the sharp increase in global protein requirements with technology that transforms the most sustainable and readily available carbon source in the world – wood – into production of a natural, economical, traceable, and sustainable supply of protein with enhanced amino acid content for animal feed. Arbiom is collaborating with large and small companies, research institutes and other organizations to produce, test and develop its protein ingredient, and other products. Arbiom's team of 30+ employees work in Europe (Paris, France) and the United States (HQ: Durham, NC, Pilot: Norton, VA).

Water post-hydrolysis of hardwood kraft pulp to produce viscose-grade pulp and xylan

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In the last decade, the global demand of dissolving pulps has doubled, reaching nearly 8 million tons in 2017. This increase in pulp demand, mainly for the manufacture of viscose textile fibers, is related to an increasing world population as well as to an increasing purchasing power in Asian markets, and thus is expected to continue increasing in the future[1]. This situation, coupled with a simultaneous decrease in the demand of paper-grade pulps, has driven the conversion of many kraft mills into pre-hydrolysis kraft (PHK) mills. The PHK process utilizes a water hydrolytic stage (i.e. pre-hydrolysis) prior to kraft pulping to remove the hemicelluloses from wood and thus reach high levels of cellulose purity in the final pulp.

Here, we suggest the application of water post-hydrolysis of unbleached kraft pulp to extract the hemicelluloses and produce a high-purity pulp that could be used in the manufacture of viscose fibers. The post-hydrolysis process is performed in a flow-through system to minimize the degradation of the cellulose fraction in the pulp and the extracted hemicelluloses in the aqueous hydrolysate. Compared to traditional PHK pulping of birch wood, water post-hydrolysis of unbleached birch kraft pulp produces a cellulose fraction with lower viscosity but up to 20% higher cellulose yield (i.e. 5-7% higher pulp yield)[2]. Water post-hydrolysis of eucalyptus kraft pulp, with lower xylan content than birch pulp, results in cellulosic fibers with higher viscosity at a given pulp purity[3]. Under selected operational conditions, the chemical and macromolecular properties of post-hydrolysed pulps may be suitable for the production of viscose fibers. However, the higher temperatures (about 240 ^{0}C) used in pulp post-hydrolysis, compared to wood pre-hydrolysis, appear to promote the aggregation of cellulose fibrils and decrease the accessibility of -OH groups[2], which may affect the reactivity of cellulose. Further studies are yet needed to assess the performance of post-hydrolysed pulps during the actual viscose conversion process.

In a flow through system, water post-hydrolysis of hardwood kraft pulp allows the recovery of xylan-based products, but their yield and molar mass depends on the flow rate used[3]. At high flow rates, the xylan extracted from the pulp can be recovered nearly quantitatively from the aqueous hydrolysate. The xylan yield from birch kraft pulp is about 10% on wood, which is similar to that obtained in pre-hydrolysis of birch wood, but the purity and molar mass of the xylan fraction is higher in the post-hydrolysis process[2]. The higher purity of the xylan fraction can be expected to facilitate the recovery of the sugars by membrane filtration, while the relatively high molar mass of the xylan (~5-10 kDa) widens the range of product application.

Finally, a techno-economic analysis of the water post-hydrolysis process indicates that the investment and operational costs are higher than in PHK mills, mainly due to the utilization of a flow-through system with membrane separation units for the partial concentration of the hydrolysate and the recirculation of the process water. Nonetheless, the higher revenues obtained by the considerably higher pulp yields result in higher profits than PHK pulping. Moreover, the profits may be even higher if the xylan fraction in the aqueous side-stream is recovered for its conversion to value-added products.

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The Bioeconomy Research Programme 2018–2020

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The Bioeconomy Research Programme 2018–2020 is an international, industrial and innovative initiative. More than 37 companies from 12 countries have gathered in in a joint effort to accelerate the industrial transformation to the new bioeconomy.

This multi-client programme – coordinated by RISE – offers a unique business network, a meeting place for discussion and plenty of headspace for challenging ideas. The research topics are based on industrial needs, global trends and market drivers and will continuously be reviewed, refined and ranked throughout the programme. The projects within the programme are designed to achieve client benefit and to create value in new technologies, and the outcome of the conducted research is shared between the participating parties.

The main effects of the research results are intended to

- Minimize cost and environmental impact through efficient use of energy and biomass resources
- Maximize volume and quality through production efficiency and runnability
- Meet societal needs with products made from forest biomass
- Enable circular economy through key technologies and business models

The programme covers several areas related to wood biorefining, such as pulping, lignin, nanocellulose, bioplastics and biofuels. For instance, to understand which applications lignins from various sources are best suited for, the research programme will include studies on separation techniques, tailoring of properties, and material development. The target products are carbonised lignin applications such as carbon fibres, energy storage and emission control, where lignin represents an affordable and sustainable alternative to current fossil-based components. Non-carbonised lignin applications, for example, adhesives, coatings and sealants will also be studied and techno-economically evaluated.

Another example is the expanding nanocellulose field with the accelerating development of new applications. Yet, some applications have not been realized largely due to uncertainties regarding the best starting material, pre-treatment procedures, dewatering mechanisms and the processing of nanocellulose into various materials. These uncertainties will be addressed and elucidated using characterization as a key ingredient, further accelerating nanocellulose applications.

The challenges within the biorefinery areas that will be addressed will be discussed during this oral presentation.

Acknowledgements

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Evaluation of alternative routes for production of bio-oil from forest residues and kraft lignin

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The present work has investigated emerging technologies for bio-oils with a lower oxygen content than what is currently achieved through near commercial fast pyrolysis. In addition, alternative routes for production of hydrogen with a lower climate impact than the leading technology for hydrogen production today, which commonly is based on steam reforming of natural gas, have been evaluated

The results show that there are emerging technologies for bio-oil production under development that has the potential to produce bio-oil with a lower oxygen content than through fast pyrolysis. In this study, hydropyrolysis and hydrothermal liquefaction (HTL) have been identified as promising emerging technologies. The production cost for transportation fuel components from fast pyrolysis is in the range of 100 EUR/MWh (or 0.9 EUR/l), while the emerging technologies have a production cost in the range of 65 EUR/MWh (or 0.6 EUR/l). These productions costs compete with the price on the European spot market in 2016.

Introduction

The increased demands on renewable transportation fuels requires a transformation of the petroleum industry to an industry that produces and delivers sustainable fuels with a substantial lower climate impact. Today about 90% of the biofuels used in Sweden are imported. However, residues and waste from the Swedish forest industry are very interesting raw materials due to the large availability in Sweden. This type of raw material can be processed in existing refinery processes or in stand-alone plants after transformation to bio-oil.

A challenge with bio-oils is the high content of oxygen compared to fossil crude oil that has an oxygen content close to zero. Use of refinery hydrodeoxygenation processes where hydrogen gas is used to reduce the oxygen content or entirely remove all oxygen in the bio-oil at the same time cracking to molecular structures suitable for transportation fuels is required. The hydrogen has a big impact on the economy and the CO_2 footprint of the transportation fuel and is dependent on the source and the process for production of hydrogen. The conventional fossil feedstock has a limited demand for hydrogen and the hydrogen production capacity in present refineries is normally too low to supply the hydrogen for bio-oil upgrading and large investments are necessary to increase the hydrogen production. The oxygen content in the bio-oil and the production path for hydrogen are the most important parameters for economic and environmental sustainability in addition to the yield from raw material to transportation fuel[1,2]. A potential future route for renewable transportation fuels is to produce bio-oil with low oxygen content from forest raw material through i.e. fast pyrolysis or the emerging technologies hydropyrolysis and hydrothermal liquefaction (HTL), which is then upgraded to a transportation fuel at an existing refinery.

Experimental

The value chains investigated are focusing on production of transportation fuel components in the diesel and gasoline range starting from forest residues or kraft lignin that both are classified as raw materials for advanced biofuels. These feedstocks are upgraded to an intermediate, pumpable bio-oil product in a depolymerisation process integrated with a kraft pulp mill. The intermediate product is in a next step considered to be transported to an oil refinery for further upgrading to transportation fuel components using processes commonly used in the oil industry. The target is to produce 100 000 ton/year of transportation fuel components.

The selected technologies for forest residues were hydropyrolysis (**HydroPyr-FR**) (data mainly based on published literature from the IH2 process by GTI and CRI) and hydrothermal liquefaction (**HTL-FR**) (data based on research and evaluations from PNNL, Pacific North West National Laboratories).

For kraft lignin, two different approaches to hydrothermal liquefaction, HTL, were selected; hydrothermal liquefaction of membrane separated kraft lignin (**HTL-MSL**) (based on data from SunCarbon, HTL process at milder process conditions) and base catalysed depolymerization of kraft lignin from the LignoBoost process (**HTL-LBL**) (based on Chalmers research and published data, HTL at more severe process conditions).

These technologies were compared to fast pyrolysis of forest residues (**Pyr-FR**), which is considered as more mature technology with several near commercial plants in operation.

The input data used in the calculations have been gathered from available open literature, databases, through contacts with technology developers and technology suppliers and based on discussions with technical experts from Preem[2]. For the emerging technologies the processes and that performance data will change over time as the processes are further developed.

Results and Discussion

Figure 1 to Figure 3 below illustrate the cost for the total value chain in EUR/MWh transport fuel components.

The estimated production cost for suppliers of ethanol and HVO today in Sweden is 1,15 and 1,10 SEK/kWh or 127 and 122 EUR/MWh transportation fuel[3]. The production cost estimates in this study are in the same range or lower (see comparison with the blue area in Figure 1), indicating a potential for profitability for investments in local production capacity on the Swedish market. The average yearly European spot market price (FOB, ARA) on ethanol and biodiesel has been about 5.30 SEK/l and 6.80 SEK/l, i.e. 99.80 EUR/MWh and 82.10 EUR/MWh during 2016, see the green area in Figure 1. Compared to this, the emerging technologies still have some profit margin to the spot market price except for the HTL-LBL case, while the production cost for the pyrolysis case is in the upper range of the European spot price, leaving a low margin for profit. In Figure 1, one can also clearly see that the OPEX costs are dominating the production cost for all cases. The CAPEX makes up about 10-30% of the production cost. From Figure 2 it is evident that the transportation costs for these value chains are relatively low, and that the major costs are related to raw material and production of the bio-oil intermediate. The impact from the final bio-oil upgrading step is low.

The case showing the largest transportation fuel production cost is the hydrothermal liquefaction of kraft lignin. The main cause of the relative high cost is the addition of phenol in the depolymerization step, which stands for 43% of the total cost. However, it also has a relatively high cost for preparation of feed through separation of lignin with the LignoBoost process, compared to the other process concepts. It is to be noted that different levels of data quality have been received for the different value chains. Since the technical maturity level of membrane separation of lignin is lower than for HTL-LBL, one could speculate if the other lignin value chain has other chemical cost not included in this assessment that will contribute to the total cost as well.

The three value chains hydropyrolysis and hydrothermal liquefaction of forest residues and hydrothermal liquefaction of membrane separated lignin seem to result in production costs in the same range, 50-70 EUR/MWh transportation fuel. The pyrolysis ends up with a cost of almost 100 EUR/MWh; the largest contribution to the cost is forest residue (~35%) and intermediate conversion and upgrading (~30%).

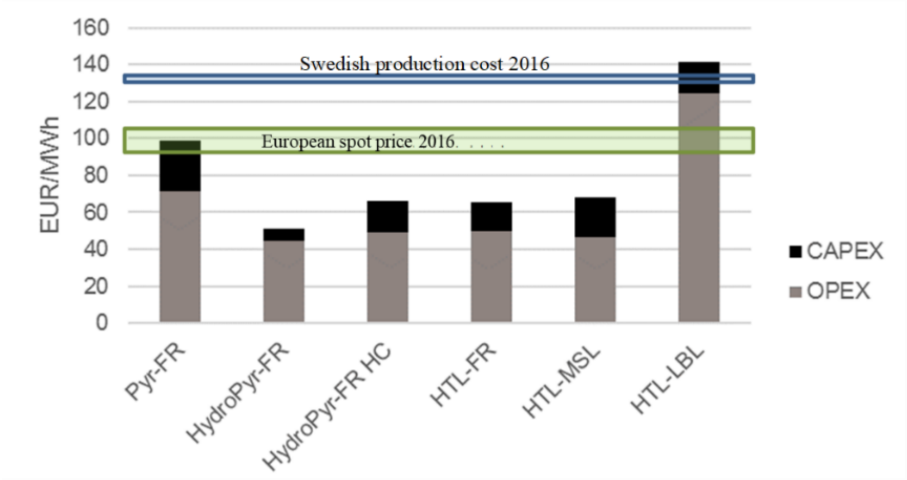

Figure 1**.** Total value chain production cost, including contribution of OPEX and CAPEX in EUR/MWh transportation fuel. The blue area indicates the current (2016) reported biofuel production cost for ethanol and HVO for Swedish suppliers, while the green area represents the yearly average spot prise (ARA, FOB) on the European market in 2016 [3].

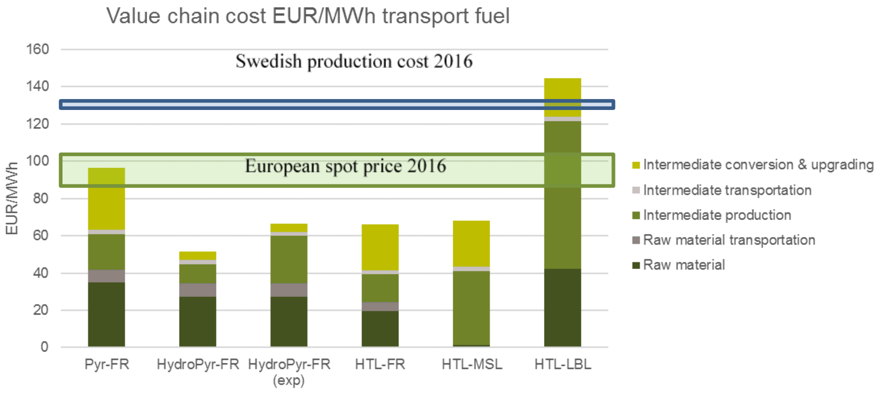

Figure 2. Total value chain production cost in EUR/MWh transport fuel.

From Figure 3 it is possible to see that the lost power production in the pulp mill in the two lignin cases make up a quite significant part of the production cost in a similar way as the cost of forest residues in the other value chains. One can also see the clear positive contribution from the refinery integration of the excess heat from the HDO an upgrading steps for all cases except for the hydropyrolysis case.

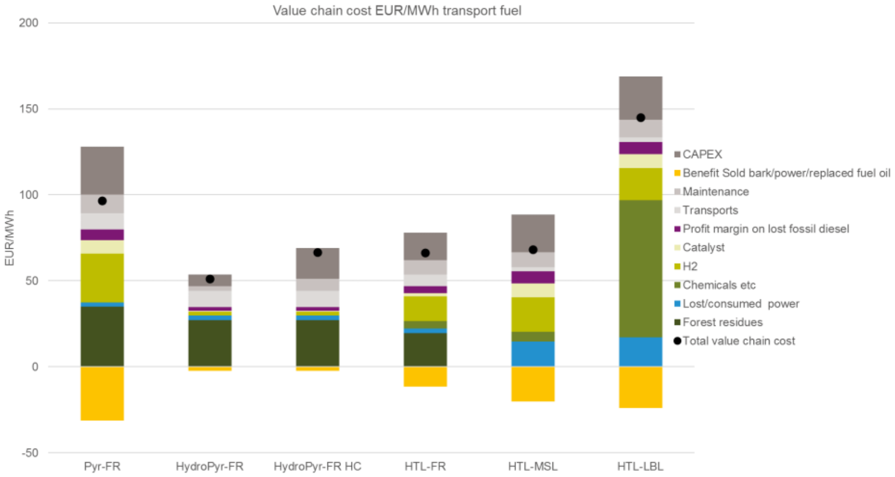

Figure 3. Total value chain production cost in EUR/MWh transportation fuel divided by cost and income items. The black dot indicates the net production cost.

It is also possible to distinguish the cost related to loss of profit margin for the necessary reduction in fossil diesel production due to that the bio-diesel fraction requires capacity in the common cracking and SynSat equipment. However, the contribution of the fossil diesel capacity reduction is in not dominating over other costs.

Looking at just the OPEX part of the costs in Figure 1 indicate that it is quite likely that the investigated emerging technologies will remain in operation once they are built since there is a good margin from the OPEX to the spot price, except for the HTL-LBL case.

Conclusions

It is concluded that there is an economic potential for establishing integrated value chains utilising forest residues or kraft lignin as raw material for production of transportation fuel components in the diesel and gasoline range. The main costs of producing transportation fuel components from the biomass are related to the raw material cost and the cost of producing the depolymerised lignin-oil.

There is not a single emerging technology that is obviously more favourable than the other technology in converting forest residues into transportation fuels, however the emerging technologies based on hydrothermal liquefaction (HTL) and hydropyrolysis show lower production cost compared to pyrolysis. The transportation fuel component production cost is about 100 EUR/MWh (about 0.9 EUR/l) for fast pyrolysis, while the emerging technologies have a production cost in the range of 65 EUR/MWh (about 0.6 EUR/l). The margin to the Swedish bio-fuel production cost of 122-127 EUR/MWh transportation fuel and the European spot market price of 82-100 EUR/MWh transportation fuel is acceptable for the emerging technologies, but critical for fast pyrolysis. On the other hand, HTL and hydropyrolysis have a lower technical maturity than pyrolysis and the estimates for these technologies are accordingly more uncertain in many aspects.

There is also an economic potential in using lignin as feedstock for transportation fuel production that seems to be in the same order of magnitude as for the emerging technologies for forest residues. The transportation fuel component production cost can also here be in the range of 65 EUR/ MWh. However, the technical maturity is also here considered as low, which results in a large uncertainty range.

Acknowledgements

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ORAL

PRESENTATIONS

WEDNESDAY 24.10.2018

It’s time to de-fossilise our economy

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Society realises that crucial environmental challenges are spreading. From rather abstract and remote, these challenges materialise now next door. Climate change is at the origin of droughts, storms, fires and other disasters. We eat and breathe plastics.

At the same time, unique commitments to address such challenges have been made globally: COP 21 in Paris has identified 2°C as the maximum temperature increase that our planet can afford by 2100. In the UN, the Sustainable Development Goals have been adopted in 2015 with the ambition to bring our economies back into the “safe and just space for humanity”, in other words delivering social inclusiveness while reducing the environmental footprint.

The circular bioeconomy has the potential to provide solutions to both these challenges and goals. And within the circular bioeconomy, the forest sector has a pivotal role to play.

We often hear that we must “decarbonise” the economy. Inspired by Poyry, we rather think that we must “de-fossilize” the economy. Because there is good, green, biogenic carbon that comes from the photosythesis and can nicely substitue “black” fossil carbon.

When exploring its future, the European pulp and paper industry has set to itself two ambitions: reduce its CO_2 emissions by 80% by 2050 and create 50% more value at the same time. And this by doing the best out of good carbon.

While requiring significant investments (around 45 billion Eur on top of “business as usual”), we believe that these ambitions are feasible.

Three avenues need to be considered:

- How can we modify our manufacturing processes to imrpove their efficiency, reduce the energy consumption and the related emissions? The CEPI Two Team Project has shown that there were possibilities for disruptive innovations here.
- How can we still be leading in pulp and paper production, while delivering to society and consumer what they expect, taking stock of the behaviour and consumption pattern changes ? Innovations in lightweight paper making, functionalised paper, smart packaging, etc show that the industry can adapt.
- How can we make best use of all the components of wood ? Innovative bio-based products are the way forward. Lignin that was burned for energy is now seen as a fantastic material. Nanocellulose seems to be a new Holy Grail. Pulp delivers hi-tech textile fibre. etc.

Delivering on these ambitions will require the right and enabling conditions to be in place, including at policy level.

Side streams:

Processing of bark and wood to value-added products

Purification scheme for the production of phenolic compounds from subcritical water extracts of chestnut wood

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Subcritical water extraction has been studied to extract hemicelluloses from hardwood chips as a pretreatment step before pulp processing like Kraft cooking[1,2]. This provides a solution to give a new breathe to this industry that is facing the problem of competitiveness and the decrease in paper consumption. Introducing the biorefinery concept in their current process will lead to the valorization of the non-cellulosic sugars and lignins that are usually removed from wood to be recycled as an energetic by-product in the paper mill process.

Furthermore, some hardwood species, such as chestnut and oak, are characterized by a high content in valuable phenolic compounds like tannins. The production of tannins from chestnut wood could be performed using soft subcritical conditions for applications in oenological, tanning or cosmetic fields[3].

This work focuses on the purification of different fractions of phenolic compounds, in chestnut wood aqueous extracts, using a two steps purification scheme involving membrane filtration and resin chromatography.

A preliminary study on the subcritical water extraction of phenolic compounds from chestnut wood, using an experimental design, has led to optimal experimental conditions: low temperature (120°C), short time (30 min to 60 min), low liquid/solid ratio (L/S=6) and autogeneous pressure[4]. The aqueous extracts were fully characterized by spectrophotometric and chromatographic methods, with a focus on phenolic compounds. These molecules were found in two forms, monomeric (ellagic and gallic acids) and oligomeric (gallotannins and ellagitannins). The purification scheme was developed to first separate tannins from phenolic acids by membrane filtration and then to separate gallic acid from ellagic acid by chromatography. Ultrafiltration performances, flux and rejection rate, were evaluated with membrane molecular weight cut off of 10, 30 and 50 kDa at different transmembrane pressures and shear rates. The permeate contained the acids that were separated by adsorption (XaD 8 and 16) or anion exchange on resins (Amberlite IRA 900 and 958). The retentate contained ellagitannins and gallotannins that were also purified by pulse chromatography with macroporous cationic resins.

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Polyphenols from softwood bark in adhesive applications

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Polyphenolic tannin extracts have been widely studied to replace phenol in phenol-formaldehyde (PF) resins. Majority of previous studies have concentrated to certain southern tree species such as wattle, mimosa, quebracho and Radiata pine. Here we show, that tannin extracts from Nordic tree species Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) can be used in PF resins to replace at least 30% of phenol in PF resins and still display comparable shear strength values to commercial reference. In addition to wood species and processing history, the effect of extraction parameters and chemical additives on tannin recovery was evaluated. The tannin extraction was scaled-up to multi-kilo scale and extracts were used to partly replace phenol in PF resins.

The highest yield of tannin was obtained from spruce bark from sawmill. In addition, spruce tannin extracts contained more polyphenols than pine tannin extracts. Direct UV-280 spectroscopic method results, which measures total aromatic content, correlated well with more tannin specific spectroscopic results. High extraction temperature and addition of Na_2CO_3 were the most important factors to increase tannin yields. In tannin PF resins, resins with 30% phenol replaced with tannin performed better compared resins with 50% tannin. In addition, shear strengths were better with longer curing time and with pine tannin.

Introduction

Roughly 3 million tons of softwood bark is produced as a low-value side-stream in the Finnish forest industry each year. Currently, most of the bark is burnt for energy. However, valuable polyphenolic tannin compounds could be produced in significant amounts from the bark. Polyphenols could partly replace fossil-based phenols in the global adhesive and resin market, and thus generate more value for bark and new business opportunities.

The tannins in softwood bark are condensed tannins, which are oligomers of flavonoids with complex polyphenolic structure consisting of flavonal subunits linked together by carbon-carbon bonds (Figure 1). Traditionally, condensed tannins are used in leather tanning. Condensed tannins have also high reactivity towards aldehydes, such as formaldehyde, which makes them potential replacements for phenol in the preparation of adhesives and resins. Tannins have also been proposed to be interesting raw materials in food and pharmaceutical industry[1,2,3].

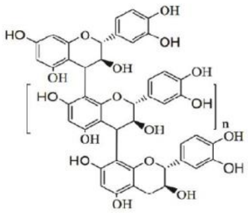

Figure 1. Schematic structure of condensed tannin (right)[1].

Experimental

Starting bark material

Norway spruce (picea abies) pulp mill bark was supplied by Sappi, Belgium and sawmill bark by Metsä Group, Finland. Scots pine (pinus sylvestris) pulp mill bark was from Stora-Enso, Finland and saw mill bark from Metsä Group, Finland. Bark samples contained 10-30 w-% of wood. Bark samples were grinded as received to small particles. Moisture content of bark samples and air dried bark samples was analysed.

Hot water extraction to obtain tannin extracts

Effect of bark origin to tannin yield was studied by extracting bark samples from different sources at 10% consistency with hot water in 50 g bark scale (total volume 500 g) in 1 L rotating autoclaves. The extract and solid residue were separated after the extraction by filtration. The extracts were analyzed by direct UV analysis at 280 nm for the total aromatic material. Folin-Ciocalteu (FC) method was used for the total phenolic content according to[4] and Acid-Butanol method (AB) was used for the condensed tannins according to[5].

Norway spruce pulp mill bark was used to study the effect of extraction chemicals to tannin yield. Experimental design program Modde Design of Experiments software was used to identify the most optimal extraction conditions. The original design was sketched out with Modde software but all subsequent data analyses were conducted in R (Version 3.3.2 (2016-10-31)) and RStudio(Version 1.0.153). Based on testing and model validation, second order model with linear, two-way interaction and pure quadratic effects was we selected as final model. Variables (factors) (Table 1) in the extractions were chosen based on previous experience and on literature. The extraction matrix contained total of 405 different combinations. However, by using Modde software, it was possible to reduce the amount of experiments from 405 to 150 without losing information. Extractions were performed in similar way as described above, with or without chemical additives.

Table 1. Design variables (factors) and responses used in extraction experiments.

Design variables (factors)	**Responses**
Extraction temperatures 70 °C, 90 °C, 110 °C	Extract yield w-%
Na_2CO_3: 0, 0.5 or 1 %	UV280
$NaHSO_3$: 0, 0.5 or 1 %	Acid Butanol
Urea: 0, 0.5 or 1 %	Folin Ciocalteu
Time (batch processing) 10, 30, 50, 70 and 90 min	

Scale-up

Grinded Scots pine and Norway spruce barks from sawmills were hot water extracted at 90 °C for 2h (dry solid content in extraction about 5%) in a 1800 L steel reactor. Residual bark cake was separated from aqueous tannin extract using decanter centrifuge. Small bark particles were removed by filtration using bagfilter with 100 µm filter. Next, dilute solution was concentrated by evaporation at 0.2 bar at 50 °C. Finally concentrated tannin solution was dried with spray dryer to obtain tannin extracts as brown powder.

Tannin wood adhesive resins

Consumption of formaldehyde (hydroxymethylation). Formaldehyde consumption and reactivity of tannin extracts was measured prior resin synthesis. Water (115.8 mL) and sodium hydroxide (25 mmol/ g tannin) were mixed and heated to 70 °C while stirring. Tannin (10 g) was added and stirring continued for two hours to ensure full dissolving. Formaldehyde (80 mmol) was added and the temperature was increased to 80 °C. Samples for residual free formaldehyde analysis by GC were collected hourly.

Resin cooking. Generalized example [formaldehyde addition (mmol) / tannin (g) was calculated from hydroxymethylation experiments and 30 w-% or 50 w-% of phenol was replaced by tannin. Amount of NaOH varied from 2 w-% to 5 w-%. Dry solid content in cooking was 40%]. Water (28.6 mL) and 50 w-% sodium hydroxide solution (1.6 mL) were heated to 70 °C and tannin (10.0 g) was added and the mixture was stirred for an hour. Formaldehyde solution (3.1 mL, 37 w-%) was added over a period of 30 minutes. Temperature was increased to 80 °C and stirred for an hour before adding the 90 w-% phenol solution (10.4 mL) and 50 w-% sodium hydroxide solution (2.2 mL). This was followed by the addition of 37 w-% formaldehyde solution (11.9 mL) over a period of 30 minutes. The cooking of the resin was initialized by raising the temperature to 90 °C. During the cooking pH was followed and resin synthesis was stopped by rapidly cooling resin in ice bath, when target viscosity of 3-3,5 Poise (p) was reached. Residual formaldehyde and phenol were analysed by GC.

Shear strength measurements

Shear strength of wood resins were measured by ABES (Automated Bonding Evaluation System), with the following parameters: front heat block 150 °C, rear heat block 150 °C, pressing time 60 - 480 s, contact area of wood/ glue line 4mm x 20mm. Mahogany Ltd. supplied the birch wood plies. Design of Experiments software Minitab 18 was used to analyse effect of different cooking and curing parameters to shear strength. A full factorial design of 2^4 led to 16 observations and hierarchical model was used in analysis.

Results and discussion

Tannin extraction and composition of tannin extracts

The direct UV 280 nm measurement was used for the evaluation of overall yield of aromatic material from barks of different origin. Sawmill bark gave higher tannin yields both for spruce and pine samples, when compared to pulp mill barks. Spruce pulp mill bark extract contained only 0.4 g/L (fresh sample) and 0.9 g/L (dried sample) of aromatics, where as saw mill samples 5.6 g/L (fresh sample) and 2.4 g/L (dried sample) aromatics. Pine pulp mill bark extracts contained 1.1 g/L (fresh sample) and 1.2 g/L (dried sample) of aromatics and saw mill bark 2.5 g/L (fresh sample) and 3.3 g/L (dried sample) of aromatics after two hour extraction at 90 °C. Interestingly, yields from dried samples were higher; however this might be due insufficient mixing of fresh bark and water during extraction.

Effect of extraction chemicals to tannin yields was analyzed by Desing of Experimets software Modde. Based on the results achieved via experimental design, we can conclude that temperature, Na_2CO_3 and extraction time are the most important factors defining the yield improvement of the extraction process. However, it seems that time is not a critical factor, which creates economic value by suggesting that the process can have lower throughput times. Regarding the other design variables ($NaHSO_3$ and urea), the use of these chemicals improve the yield but it seems that the improvement is marginal or can be compensated with other factors. The results also indicate that there is a good agreement between the UV280 method and the more labour intensive acid butanol and Folin-Ciocalteu methods (Figure 2). The carbohydrate content (as polysaccharides) in extracts varied between 15 and 30 %, depending on the extraction conditions. Better understanding of the effect of extraction conditions on the dissolved carbohydrates would require similar analyses as described above for tannin.

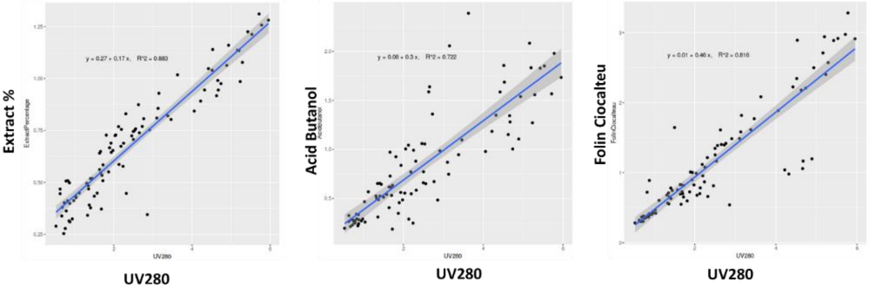

Figure 2. Correlation of UV280 response to tannin extract yield (%), to acid butanol and to Folin Ciocalteu measurements.

Based on preliminary extractions, saw mill pine and spruce barks were selected for scale up experiments. Hot water extractions were performed without chemical additions to avoid accumulation of salts to the tannin extracts. Solubilized yields for fresh spruce tannin extract was 13.7% and for pine 7.8%. Recovered isolated tannin extract yield was 10.9% (8.2 kg, dry solids 95.9%) from spruce bark and 4.9% (4.0 kg, dry solids 95.1%) from pine bark. Spruce tannin extract contained about 45% polyphenols, 35% carbohydrates and 5% ash. Pine tannin extract contained about 30% polyphenols, 40% carbohydrates and 5% ash. Weight average molecular weight for spruce tannin extract was 3.4 kDa and for pine 1.9 kDa.

Formaldehyde consumption

Formaldehyde reactivity and consumption correlated well with the measured amount of polyphenols in the tannin extracts. Pine tannin extract consumed 2.4 mmol (polyphenol content 30%), spruce 3.8 mmol (polyphenol content 45%) and commercial references (polyphenol content 75% and 79%) 6.8 mmol and 6.9 mmol per one gram tannin dry matter, respectively (Figure 3).

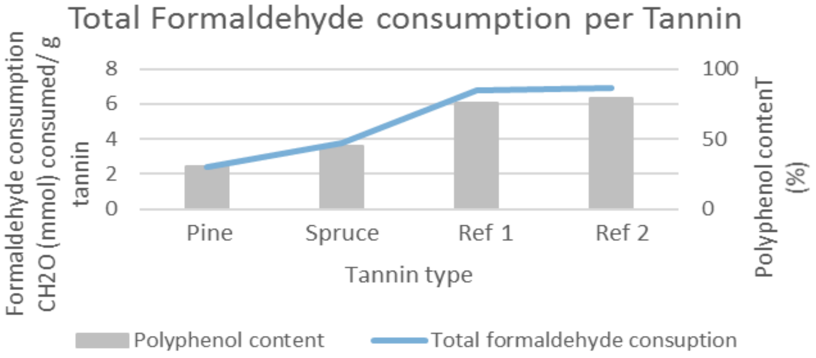

Figure 3. The amount of formaldehyde consumed per tannin corresponds to the polyphenol content.

Resin cooking

More than 20 different tannin containing PF resins were synthetized with spruce and pine tannin extracts from scale up extraction. In addition to tannin type, phenol replacement levels of 30% and 50% and different amount of alkali were studied. It is generally accepted that the alkaline content in the resin influences the reaction rates of the substitution (hydroxymethylation, first step) and the condensation (second step). The higher the alkali content, the faster the substitution takes place and the slower the condensation step[6,7]. This phenomena was also clearly observed in our experiments, since higher the pH, the longer it took to reach the desired viscosity level. Visualization of typical cooking is presented in Figure 4, including five process steps.

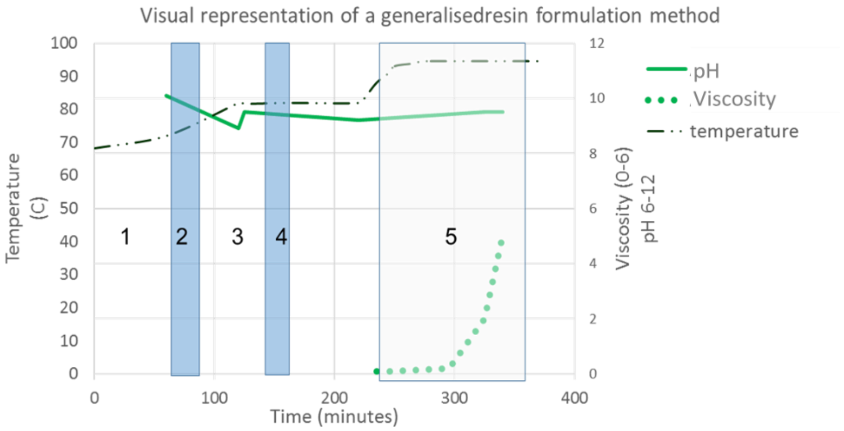

Figure 4. Visual representation of resin cooking. Cooking temperature on vertical axis and cooking time on horizontal axis. Process steps: (1) dissolution of tannin in alkali, (2) formaldehyde addition related to tannin, (3) phenol addition and more NaOH, (4) formaldehyde addition related to phenol and (5) cooking.

Chemical properties and shear strength of resins

Tannin PF resins. The resins were analysed on free-formaldehyde (FF) and free-phenol (FP) content by GC. Target limits for proper resins were set to <0,5 w-% of FF and <5 w-% for FP in resins. Almost all of the resins comply with the previously stated boundaries, except one resin with least alkali added. All resin formulations were cooked at 40% of dry solids content, which was monitored also by measuring dry solid content of resin after cooking (dry solids of resins were 39.4 - 42.1 w-%).

The wood ply samples were measured six to eight times each and outliers were determined and ruled out using Dixon's (Q) test to take account wood irregularities in some of the plies. Desing of Experimets software Minitab 18 was utilized to interpret the results how reaction parameters affected to ABES (Automated Bonding Evaluation System) shear strength results. Typically tannin PF resins displayed 5 - 5.5 N/mm^2 shear strength values. Amount of phenol was replaced (30% or 50%) by tannin effected the most, followed by tannin type (spruce or pine) and curing time (300 s or 480 s). Amount of alkali in cooking had no clear effect (Figure 5).

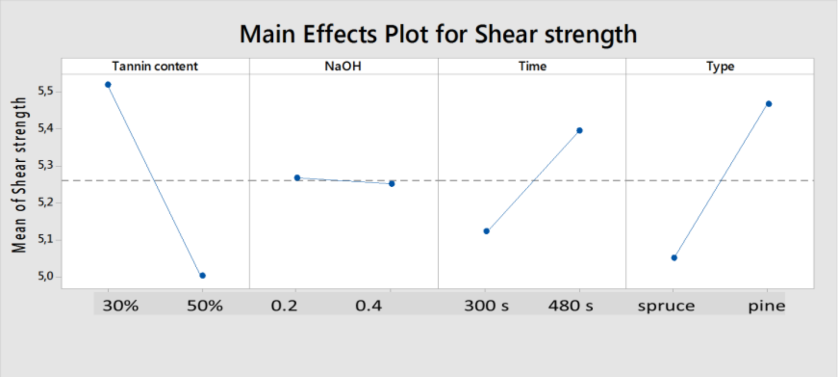

Figure 5. The effects of the different cooking parameters to shear strength.

Finally, shear strength of most promising experimental tannin resin was compared to commercial PF resin (Figure 6). Experimental tannin resin (30% pine tannin, 0.4 eq NaOH) displayed comparable results to reference, with shear strength of 6.1 N/mm^2 and 7.7 N/mm^2 with 5 w-% of commercial hardener added.

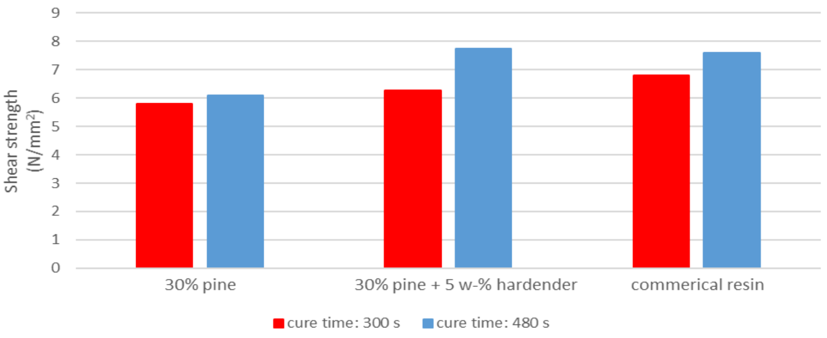

Figure 6. Shear strengths of most promising tannin PF resin and commercial PF reference with or without hardener.

Conclusion

We have shown than tannins can be extracted in reasonable amounts from bark of Scots pine and Norway spruce. In addition, proof of concept for utilization of tannins from Nordic softwood barks in phenol formaldehyde resins was demonstrated.

Acknowledgements

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A novel process for biomass extraction: The basis for a pine bark biorefinery

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Forest and agricultural biomass contain a high variety of interesting compounds, with unique properties and highly-valued applications. The commercial exploitation of this biomass requires extraction and concentration of specific fractions at reasonable costs. However, traditional solid-liquid extraction process cannot fulfill with these requirements.

In this context, the Technology Development Unit (UDT) of the University of Concepcion in Chile has developed and scaled-up to bench and pilot-plant level a new highly-efficient extraction technique to separate mainly water- and alcohol-soluble fractions from biomass. The technology is based on a sequence of two or more steps, each comprising the impregnation of biomass with solvent vapors with a liquid/biomass ratio of 2-2.5, followed by a subsequent mechanical pressing with a liquid/biomass ratio of 0.4-0.5. Such operation conditions result in: reduced processing times (from six or more hours in conventional countercurrent solid-liquid extraction, to less than one hour) and higher concentration of extracts in the liquors (at least two times), which allows the possibility of designing small extraction units with moderate investment.

A continuous demonstrative pilot plant of the mentioned “high-solid-extraction process” was implemented in UDT with a capacity of 150 kg of biomass/hour, to obtain tannins from *Pinus radiata* bark. The results of the production trial are very encouraging with high selectivity: tannin yields of typically 15 - 20% (based on dry biomass) and an exhausted bark with low moisture content, suitable to be burnt in industrial boilers. The water content was significantly lower than that of the original bark in winter. Extracted tannins are the main component of formaldehyde-free adhesives, applied by the Chilean wood-panel industry. Several other possible uses for these extracts are currently under evaluation, as well as higher-value applications for the exhausted bark.

The conceptual design of the extraction plant, the main results obtained at laboratory- and pilot-plant level and some applications for pine tannins will be presented. Based on our results, we speculate that the first bark-based biorefinery could be a reality soon.

Introduction

Tree bark contains highly specialized compounds, which allow it to protect the inner layers from predators, environmental oxygen, as well as extreme climates. Many of these structures also fulfill an important role in transportation of photosynthesis products.

In the case of pine bark, catechins, also known as condensed tannins, are particularly abundant. It is possible to extract between 10 and 25% of this type of polyphenols, depending on the type of bark, particle size, the solvent used, and the processing conditions. Although the extraction of pine bark has been extensively studied at laboratory-scale[1-5], its industrial use has only been carried out on small-scale processes and for limited periods of time. Such is the case of the company DITECO in Chile, which operated an extraction plant between 1992 and 1998, with a production capacity of xxx[6,7]. Similarly, the operation of small extraction units in France and New Zealand to obtain polyphenols with antioxidant properties for nutraceuticals have also been reported[8,9], as well small extractive plants in Australia and New Zealand for the production of adhesive resins[10]. Notwithstanding the above, the only commercial plants for obtaining condensed tannins are based on *Acacia mearnsii* bark, in Brazil and South Africa, and *Schinopsis balansae* (Quebracho) wood, in Argentina[11]. The production plants operate with old technology, which is based on a multi-stage countercurrent extraction of biomass with an alkaline solution of sodium sulfite (see Figure 1). The tannin generated thusly is used mainly as a tanning agent.

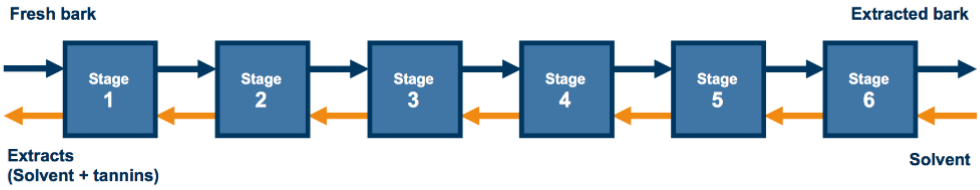

Figure 1. Countercurrent extraction.

Based on the same principle, the Technological Development Unit (UDT) of the Universidad de Concepción implemented a pilot plant for bark extraction. This is constituted by a 4 m^3 extraction unit and a liquor recirculation circuit, which is operated under a maximum pressure of 4 bar (see Figure 2).

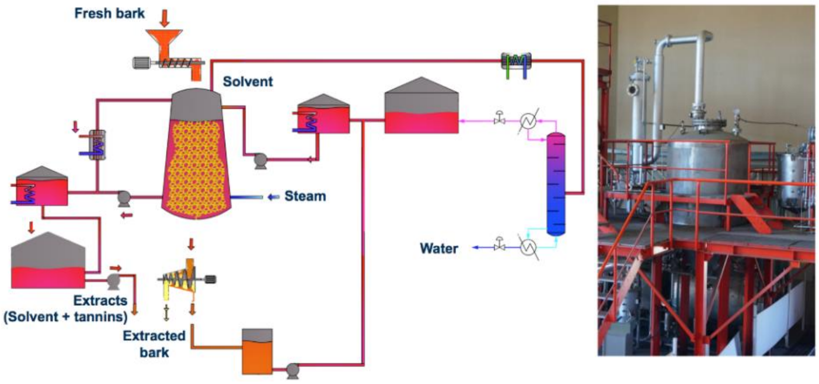

Figure 2. Outline and photo of the discontinuous bark extraction pilot plant.

The plant was tailored so the extraction solvent could be either water or methanol. In the latter case, it is possible to recover the organic solvent *via* stripping with steam followed by condensation of the resulting gases. We have carried out more than 400 extraction tests with different types of bark at different times of the year, evaluating product yields and variability of their compositions. We have also developed adhesives formulations for wood-based panels, considering the high reactivity and other characteristics of the extracts. Finally, we concluded that, for economic reasons, the traditional bark extraction process, based on a solid-liquid extraction, is not an appropriate technology to be implemented in the Chilean industry. Therefore, we developed a new extraction process bearing in mind the following considerations:

Plant investment: The process must be simple and must allow to process high flows of bark with low residence times. For this, solvent impregnation into the bark and diffusion of dissolved tannins from the bark must occur much faster than in conventional processes.

Yield: The price of the bark is not a relevant factor, since it is currently used as boiler fuel and the extracted material will be used for the same purpose with the advantage that its humidity level will be constant. Therefore, maximizing the extract yield is not a priority.

Liquor concentration: A conventional solid-liquid extraction process requires a liquid / solid ratio of at least 5/1. This means that tannins are obtained in a much-diluted way. To reverse this, specific solvent consumption must be decreased.

Experimental

Laboratory-level tests: The new developed process is based on impregnation of bark with water vapor and subsequent pressing of the material. The impregnation is carried out with saturated steam of 1 bar during different periods of time. The pressing, on the other hand, is carried out in a pressing device, provided with a sieve and a piston, at a pressure of 120-160 bar. In each test 100 g (dry basis) of bark is processed.

Pilot-level tests: The procedure is similar to laboratory tests, but using a continuous extrusion press, with a processing capacity of 100 kg of bark (dry basis) per hour (brand Vetter, Bv type). The impregnation of the bark with steam is done in the press-feeding chute.

Testing at the production level: The plant consists of a two-stage extraction process. Each extraction unit includes the following components: a 2 m^3 bark feed hopper; a steam impregnator, which consists of screw feeder with 15.4 cm internal diameter and 4 m long; and an extrusion press of the same characteristics as that of the pilot level[12].

Results and discussion

Laboratory-level tests: Regarding the most appropriate ways to impregnate and press the material, we determined that the optimal conditions are the following:

- Granulometry: less than 10 mm
- Steam treatment time: 15 min
- Water content of bark after steam treatment: 66%
- Water content of bark after pressing: 40-45%

Pilot-level tests: We verify the feasibility of using an extrusion press and establish that its effectiveness was similar to that achieved with the discontinuous laboratory press. We also observed that vaporizing the bark homogeneously with the desired granulometry is rather difficult, due to channeling. We conclude, therefore, that the impregnation should take place in continuous mode.

Testing at productive level: We recently started to operate the production plant. The main results are the following:

- Capacity: 200 kg of bark (dry basis) / hour
- Tannin yield: 15-20% (strongly dependent on the type of bark)
- Liquor concentration: 6-10%
- Stiasny Number of the liquors: 80-95

The tannins of the industrial plant are being used as a base for adhesive resins to manufacture plywood boards. Application tests at laboratory- and industrial-scale are being executed.

Conclusion

Our new bark extraction process, based on an impregnation of the raw material with steam and subsequent pressing, proved to be highly effective. It allows to obtain high extract yields and selectivity, in plants that can process low volumes of bark and that require low investment. At the same time, the extraction liquors are more concentrated than those of conventional processes, which facilitates further processing. We estimate that in the near future several plants will be installed based on our process in Chile.

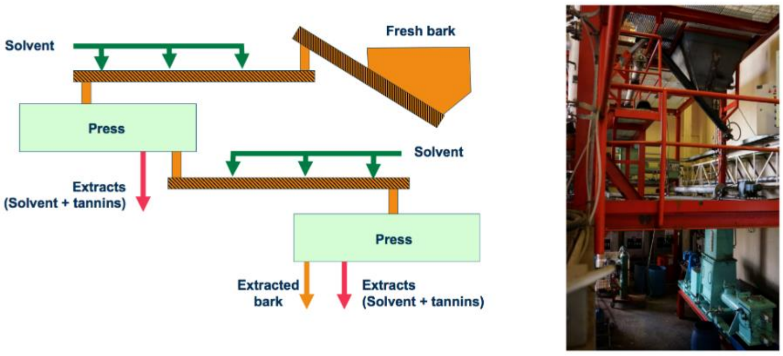

Figure 3. Outline and photo of the productive-demonstrative continuous bark extraction plant.

Acknowledgments

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Bark-based biorefinery for production of biocomposites

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Wood chips have been the primary feedstock for traditional pulp and paper mills and several forest biorefinery. However, barks from harvested logs are considered to be low value residue. This is partly because bark contains much lower polysaccharides than pulpwood, and, hence, has a lower potential for valorization via a sugar biorefinery platform. In addition, it is more recalcitrant, has a higher lignin content and its byproducts during pretreatment are known as fermentation inhibitors. In the thermochemical conversion biorefinery platform, barks are not considered to be of high value but only regarded as a cost competitive source of carbon. Consequently, barks are currently under valorized in the forest industry. In Canada, about 17 million m3 barks is distributed around forest operations and approximately 40% of it is used as a solid fuel in cogeneration systems or sent to landfills thereby incurring expenses. The objectives of this work was therefore to develop an innovative bark-based biorefinery concept and to demonstrate its technical and economic feasibility. Experimental work was combined with techno-economic analysis to demonstrate the products can meet the quality requirements of commercial alternatives and that integrated valorization can be economically viable. The proposed bark-based biorefinery concept consists of extractive removal, followed by lignin extraction and lastly the use of the bark extraction residue for low-cost biocomposite production. Tannin and lignin were extracted from yellow birch barks and used to produce polyurethane foam. Subsequently, the extraction residue was successfully extruded with thermoplastic polypropylene (PP) to produce biocomposite pellets. The biocomposite was then characterized to ensure conformity with market requirements. Specifically, the morphology, mechanical properties, the water sensitivity and the thermal stability of the obtained biocomposites were investigated with respect to the formulation. Different bark to PP ratios were tested with a coupling agent to improve the bark-matrix interface. Results obtained, using our patented thermoplastic composite formulation (US 7,041,716 B2) that is based on carboxylic acid anhydride grafted polypropylene as coupling agent, showed that for a 30 w/w% bark biocomposite, tensile modulus was 50% higher when compared to conventional biocomposite and 82% higher than unadulterated polypropylene. Tensile strength was 24% higher than for conventional biocomposite and only 8% lower when compared to unadulterated PP. Preliminary economic evaluation showed that the proposed production pathway of the biocomposites reduces the costs by about 25%.

Bio4Products: Unlocking the potential of biomass for a new range of bio-based products

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Bio4Products will demonstrate an innovative two-step conversion method to transform 4 different bio-resources into renewable chemicals and products. The project will show how these sustainable resources can replace fossil material in a wide variety of end products. The innovative approach of Bio4Products is to apply fast pyrolysis to enable the fractionation of these bio-resources, but keeping the key chemical functionalities in separate, depolymerized fractions. Within the project the process will be demonstrated in a 3 t/d demo-plant. Subsequently, Bio4Products will demonstrate the use of the resulting intermediate processing streams for the production of wood preservation products, foundry resins, phenolic resins and roofing material as cost-effective renewable alternatives for fossil resources in the conventional products (30-100% substitution). Each of the steps in the whole chain has at least been proven on bench-scale (TRL5) and should reach TRL 6-7 by execution of this project. The feedstock flexibility will be shown by demonstrating the complete chain for 4 different biomass resources representative for the majority of biomass resources available in Europe. Bio4Products will see a unique blend of organizations and expertise working together, led by BTG Biomass Technology Group from the Netherlands. Industrial partners from Belgium and Germany will demonstrate the viability of the new value chains, with support from expert partners in the United Kingdom and Belgium. The project, which started in September 2016 will run for four years, and is funded by the Sustainable Process Industry through Resource and Energy Efficiency (SPIRE) programme, under the EU framework programme Horizon 2020. In this contribution an update will be given on the progress of the project and the applications of the various fractions. www.bio4products.eu

Introduction

The overall objective of Bio4Products is to demonstrate the thermal fractionation of 4 different biomass resources, and to demonstrate the use of the fractions in 4 different applications supported by the techno-economic and environmental assessment of the whole value chain as illustrated in Figure 1.

Bio4Products will demonstrate the production of roofing material, phenolic resins, wood preservation products, and molding resins, using renewable alternatives to substitute fossil resources. Concrete resources which will be replaced with renewable alternatives include bitumen, phenol, creosote and foundry resins.

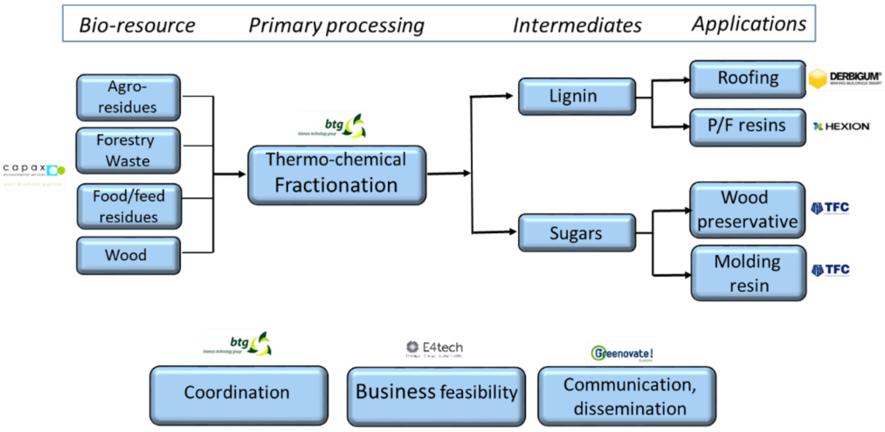
Bio-resource
Primary processing
Intermediates
Applications
Agro-residues
Forestry Waste
Food/feed residues
Wood
capax
btg
Thermo-chemical Fractionation
Lignin
Sugars
Roofing
DERBIGUM
P/F resins
HEXION
Wood preservative
TFC
Molding resin
TFC
btg
Coordination
E4tech
Business feasibility
Greenovate!
Communication, dissemination

Figure 1. Schematic representation of the 4x4 Bio4Products concept

The thermo-chemical fractionation used is a combination of biomass (fast) pyrolysis followed by pyrolysis oil fractionation. Pyrolysis is the thermal decomposition of a material under inert conditions. Biomass pyrolysis results in the formation of solid, liquid and gaseous products. When it is desired to maximize the liquid product, fast pyrolysis is applied. Typically temperatures around 500°C are used, and in order to maximize the liquid production rapid condensation of the vapour stream is required. For clean woody biomass (e.g. pine wood) up to 70 wt. % of a liquid product can be obtained. About 15 wt% of the biomass is converted into charcoal and the remaining 15 wt% to non-condensable gases. The obtained liquid is polar, acidic, contains water, and is a mixture of cracked components derived from the cellulose, hemicelluloses, and lignin components of the feedstock. The liquid can be easily separated in a pyrolytic sugar, pyrolytic lignin and a pyrolytic extractives phase. Subsequently, these intermediate processing streams can be used as renewable alternatives for a wide variety of end products. The pyrolysis oil fractionation will be scaled up in the project from a 12 kg/h bench-scale unit to a 3 t/d pilot plant.

In Bio4Products the given 4 end products were selected because of their high added-value and proven technical suitability (at least TRL 5). The potential to develop additional new innovative products from the renewable intermediates is very high. With the current development trajectory, these renewable intermediates will be produced in large quantities enabling the further development of innovative products.

The production process is flexible with respect to feedstock properties. All kinds of lignocellulosic bio-resources can be used. To demonstrate this flexibility, 4 bio-resources from different backgrounds are used as feedstock in Bio4Products; residues from agriculture (straw), forestry (forest residues and bark) and food/feed industry (sunflower husks).

Bio4Products approach essentially demonstrates 4x4=16 value chains simultaneously. By depolymerization of the biomass components, followed by separation of the functional groups, the chemical functionalities of the biomass are retained. The processing steps are of a thermo-chemical and physical nature, with high conversion rates and yields. By-products are used within the process to enables the production of value-added streams with minimal external resources, while avoiding the generation of waste streams.

Results and conclusions

In Bio4Products a range of biomass feedstock were tested in the thermo-chemical fractionation. The results of 6 of these feeds are illustrated in Table 1. The Table shows the yield of pyrolysis oil (FPBO) obtained and the amount of the pyrolytic fractions produced relative to the biomass input. The table also shows the extractives being produced. The extractives can be fractionated from the FPBO if necessary, but are not directly used as a raw material for further product development in the project.

Table 1. Amount of fractions obtained from different types of biomass via fast pyrolysis and subsequent fractionation

Biomass	FPBO Yield (%)	Relative to biomass input			Relative to FPBO input		
		P.Extractives (%)	P.Lignin (%)	P.Sugars (%)	P.Extractives (%)	P.Lignin (%)	P.Sugars (%)
Softwood	68	1.2	21.2	45.6	1.8	35.4	62.7
Olive stones	57	2.6	19.5	34.9	4.5	37.0	58.5
Flax	62	2.2	20.0	39.8	3.6	36.0	60.3
Sunflower	56	3.0	17.8	35.2	5.5	35.0	59.5
Poplar	61	1.5	16.4	40.1	2.5	34.6	62.9
Wheat straw	45	1.7	20.7	22.6	3.8	53.5	42.7

All the relevant fractions derived were further analyzed to determine the chemical reactivity, and with that the possible application in various products. Furthermore, the pyrolytic lignin has been tested in various resin applications replacing fossil phenol. Although the pyrolytic lignin is not as reactive as the fossil phenol, it showed to be much more reactive compared to other types of lignin such as natural or kraft lignin. Two types of promising pyrolytic lignin based resins were developed of which one has already been tested on a 200 kg+ scale and will tested on a 1000 kg+ scale at a customer in due course of the project. The use of pyrolytic lignin as a raw material in the production of waterproofing membranes at a high substitution level, showed to be difficult. The lignin cannot be processed at high temperatures (> 150 ° C) and it showed to be incompatible towards some of the other raw materials used. The use of the pyrolytic sugars in the production of foundry resins and formulations to modify/engineer wood showed to be very promising. A first 1 m3 pilot pressure/vacuum impregnation trial was performed with the most promising formulation and a second test is currently ongoing. The construction of the fractionation pilot-plant with a pyrolysis oil processing capacity of 3 t/d has almost finished. The pilot plant is now mechanical complete and will be commissioned within the coming months.

Acknowledgements

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Lignin 1:

Processing & tailoring properties

LigniOx lignins – High performance concrete plasticizers and versatile dispersants

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A simple and economic alkali-O_2 oxidation (LigniOx) process has been developed for the production of concrete plasticizers and versatile dispersants from technical lignins. Previously, soda and kraft lignin based LigniOx lignins have been shown to have great potential to serve the traditional lignosulfonate markets, and to compete even with more expensive synthetic products. Here, the latest results of successful use of kraft, organosolv and hydrolysis lignin based LigniOx solutions for mortar plasticization in comparison to several commercial lignosulfonates and synthetic superplasticizers are presented. To widen the range of applications of LigniOx lignins, high performance for dispersing of special carbon black into aqueous solutions, used e.g. in paints, inks and various coatings is demonstrated.

Introduction

Dispersants are widely used for suspending colloidal particles in cosmetics, paints, pharmaceuticals, oil drilling mud, cement, and ceramic applications. Besides lignosulfonates, mainly synthetic polymers are used as dispersants in these applications. For substituting the current non-biodegrable polymers with bio-based (less expensive) materials, technical lignins have been modified in several ways (e.g. by sulfomethylation, oxidation, carboxymethylation, grafting with PEG, hydroxymethylation/propylation and sulfonation, fractionation, enzyme utilization) to convert them into water soluble dispersants. Despite the encouraging results, the modification procedures seemed to be industrially unattractive and the property-performance relationships for lignin-based dispersants case dependent[1].

LigniOx technology, recently developed by VTT, is a simple and cost-efficient alkali-O_2 oxidation process for conversion of technical lignins to ready-to-use products for concrete plasticization, i.e. cement dispersing, or versatile dispersants[2,3]. The LigniOx process can be integrated into the biorefineries, or operated in stand-alone units e.g. by chemical industry. The oxidation is active toward phenolic hydroxyls (PhOH) and introduces acidic groups into the lignin polymer, while retaining its polymeric structure. Depending on the oxidation conditions, (especially pH), the negative charge and molar mass of lignin can be adjusted in a controlled way. The previous studies on mortar and concrete plasticization have demonstrated that the soda and kraft LigniOx lignins have great potential to compete with lignosulfonates in their traditional markets, and even with synthetic products. LigniOx lignins have also shown high dispersing performance of several inorganic pigments, such as TiO_2, colour pigment, and $CaCO_3$, used e.g. in paints[4,5]. Currently, the oxidation technology is optimized for several different lignin raw materials[6].

In this study the very recent results of applying kraft, organosolv and hydrolysis lignin based LigniOx lignins as plasticizers in mortar are presented. The adsorption tendency of the LigniOx lignins on cement surface is discussed. In addition, the dispersing performance of LigniOx lignins in special carbon black, used e.g. in latex paint pigmenting, conductive coating, water based inks, textile printing pastes, and aqueous graphite dispersions, is demonstrated.

Experimental

Industrial lignin raw materials provided by Metsä Fibre, CIMV and St1 were used (Table 1).

Table 1. Industrial lignin raw materials, characteristics, and sample coding.

Lignin	Origin	Characteristics	Coding
Kraft	Softwood	Rich in PhOH, low carbohydrate content	KL
Organosolv	Wheat straw	Relatively rich in PhOH	OSL
Hydrolysis	Softwood	Low PhOH, high carbohydrate content	HL

Oxidations of different lignin raw materials were performed under the range of conditions reported in [2,3].

The plasticizing performance of kraft, organosolv and hydrolysis lignin based LigniOx solutions was evaluated in mortar. Mortar was prepared using a standard sand mixture, Portland cement (CEM I, 52.5N, Megasementti by Finnsementti), and water. Plasticizer was added in the mix in the end of the preparation. Dosage of 0,6 wt% (active matter) of cement was used. Few drops of de-airing agent (Tributylfosfate, TBF) was used in all tests. The fluidity of the mortar was measured using Haegermann flow table (Ø 300 mm) method and a mold with a diameter of 100 mm. Flow value represents the spread (diameter) of mortar. Commercial polycarboxylate ether (PCE) and sulfonated naphthalene (SNF) based superplasticizers and lignosulfonate (LS) based plasticizers were used as references. Commercial products were dosed based on dry matter reported on the containers, LigniOx solutions based on lignin content measured by UV280.

Adsorption tendency of kraft lignin based LigniOx lignins on cement (CEM I, 52.5, Megasementti) surface was studied using a fast in-house method[7]. The method is based on quantifying the un-adsorbed amount of plasticizer by UV-measurement from the liquid phase separated from the cement paste (W/C 0.4) by centrifugation. Commercial sulfonated naphthalene (SNF) based superplasticizer and lignosulfonate (LS 2) were studied as references.

The dispersing performance of the oxidized kraft and hydrolysis based samples (LigniOx-KL 3 kDa, LigniOx-KL 7 kDa, LigniOx-HL 20 kDa) was evaluated in Special Carbon Black (CB) (Orion Engineered Carbons). The dispersion prepared using high shear mixing (Omni mixer Sorvall, OCI instruments) contained 10 wt% of CB pigment in water (including LigniOx solution or commercial products). Dispersant dosages 0,25 - 2,5 wt% (active matter) of pigment were used. The viscosity of the pastes was measured as a function of shear rate using AR-G2 rheometer (Texas Instruments) at 25°C. Commercial polyacrylic acid (PAA) and lignosulfonate (LS) based dispersants were used as references.

Results and discussion

Mortar plasticization

Strong dispersion capabilities of organosolv lignin (OSL) based LigniOx solutions was verified in addition to kraft lignin (KL) based LigniOx samples (Figure 1). Both the kraft and organosolv lignin based LigniOx solutions provided better plasticization performance compared to the commercial polycarboxylates (PCE) and sulfonated naphthalene (SNF) references. Hydrolysis lignin (HL) based LigniOx solutions were also showing rather good performance, and nearly comparable with some of the synthetic references.

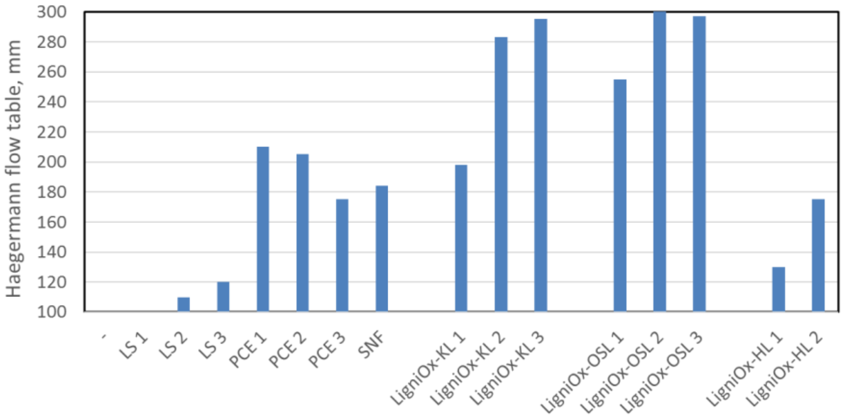

Figure 1. Haegermann flow in fresh mortar plasticized with commercial (super)plasticizer products (LS, PCE, SNF) and kraft, organosolv, and hydrolysis lignin based LigniOx. Dosing 0,6% (based on lignin content) of cement. Defoamer used.

Adsorption on cement particles

Concrete superplasticizers are reported to work either by electrostatic or steric repulsion between individual cement particles to achieve a full dispersion. The negatively charged functional groups of the superplasticizer, sulfonic and carboxylic groups, adsorb on the active sites (calcium aluminate) of the cement particles giving them a negative charge, which leads to the electrostatic repulsion between the particles. The branched structure of the PCE superplasticizer achieves steric repulsion by forcing the cement particles apart[8]. Steric repulsion is known to be more effective in dispersion compared to electrostatic repulsion. In the case of lignosulfonates, it is postulated that the dispersing effect is mainly due to the electrostatic repulsion between the cement particles[9].

In previous studies, it has been shown that alkali-O2 oxidation (LigniOx) of lignin yields highly carboxylated lignin[10]. To gain understanding of the working mechanism of LigniOx lignins, their adsorption on ordinary Portland cement as a function of dosing was quantified and compared to selected commercial plasticizers (Figure 2). Adsorption of sulfonated naphthalene based product (SNF) and lignosulfonate (LS 2), showed rather similar behaviour as a function of the plasticizer dosing: the adsorbed amount increased steadily as increasing the dosing up to 0,5%, where after it was still increasing in lesser extent as increasing the dosing up to 1,0%. In the case of the LigniOx plasticizers, the maximum adsorption was reached already with the dosing of 0,5% on cement. The adsorption behaviour of the studied plasticizers could be interpreted using Langmuir isotherm equation with rather high correlation[7]. Based on this initial study, it can be postulated that the working mechanism of LigniOx lignins is somewhat similar to that of the commercial plasticizers.

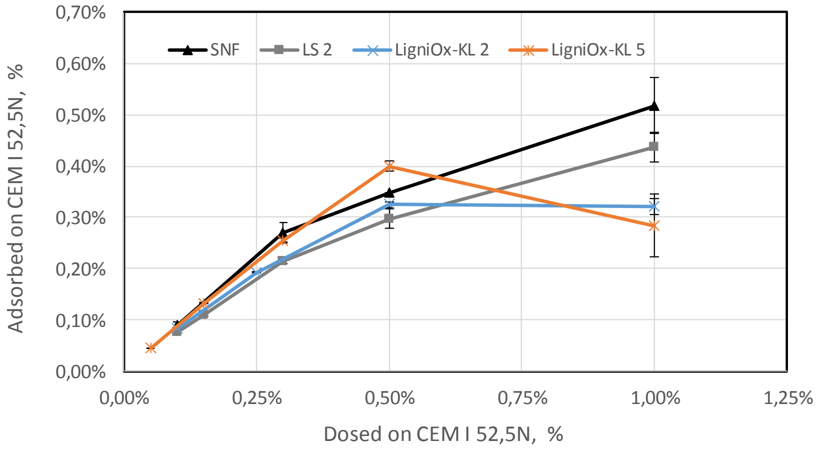

Figure 2. Adsorption of commercial plasticizers (SNF, LS 2) and kraft lignin based LigniOx on cement surface as a function of dosing.

Carbon black dispersing

LigniOx-KL samples with molar masses of 3 and 7 kDa and LigniOx-HL with Mw of 20 kDa showed all high dispersing performance in special carbon black when using dosing of 2,5% (Figure 3, left). The viscosity values were measured just after preparing the dispersion and after 7d.There was no changes seen after the storage period. Better dispersing performance of LigniOx lignins over synthetic commercial reference was supported also by microscopy and particle size analyses.

Differences in the performance between the tested LigniOx samples were seen when decreasing dosing down to 0,75% (Figure 3, right). The 7 kDa LigniOx-KL sample was still showing high performance, while the other LigniOx samples as well as the lignosulfonate reference (LS) could not retain the viscosity as low. To confirm that 0,75% was not overdosing for synthetic reference (PAA), 0,25% dosing was tested. At dosage of 0,25%, PAA showed even higher viscosity than at 2,5 or 0,75%.

The results highlight that the oxidation conditions must be optimized according to the specific end-uses to provide high-performance LigniOx products for each lignin type. Regarding the new end-uses of LigniOx lignin, performance in the actual formulated end-product (paints, coatings or inks), and the co-effect with all the other ingredients should be demonstrated.

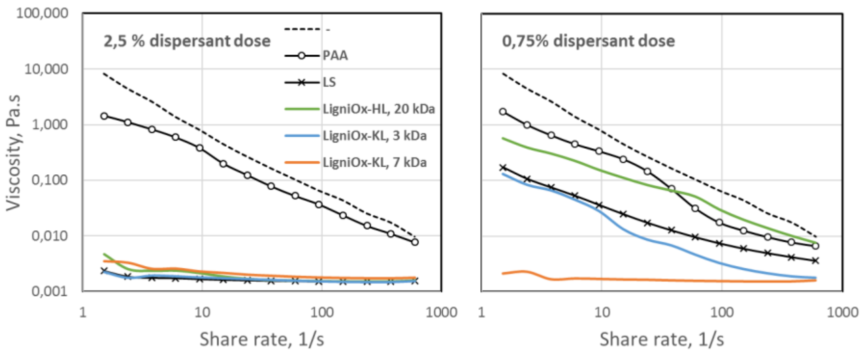

Figure 3. Viscosity of special carbon black dispersion with commercial dispersants (PAA, LS), kraft (LigniOx-KL 3 & 7 kDa) and hydrolysis lignin (LigniOx-HL 20 kDa) based LigniOx. Dosing 2,5 & 0,75% of carbon black.

Conclusions

LigniOx oxidation technology converts various industrial lignin raw materials to high-performing plasticizers and versatile dispersant. In addition to kraft lignin, it was shown that organosolv and hydrolysis lignin based LigniOx solutions have high dispersing performance in cementitious material. Kraft and hydrolysis lignin based solutions also efficiently dispersed special carbon black in water, which further opens new application possibilities for LigniOx lignins.

Acknowledgements

Biobased industries Joint Undertaking (BBI JU) under the European Unions Horizon 2020 Research and Innovation programme is acknowledged for funding the project (LigniOx - Lignin oxidation technology for versatile lignin dispersants, grant agreement No 745246). Juha Kaunisto, Jaakko Sippola and Ritva Heinonen are acknowledged for performing the oxidations and application testing. Jaakko Sippola is also thanked for the Bachelor thesis work.

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Aqueous solvent fractionation of kraft lignin - technoeconomical perspective

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Lignin is considered as one of the most promising future raw material in biobased products. However, kraft lignin has typically poor performance compared to oil-based materials. This is partly due to the very heterogeneous structure of lignin since it contains molecules of different sizes (high polydispersity), variable content of functional groups and branching. In addition, there may be variations in different batches of industrial lignins, making it a challenging to apply in products where well defined quality is required.

Recently, VTT developed a method to separate lignin into fractions with homogeneous structure[1]. The fractionation protocol is based on selective dissolution and precipitation of lignin in simple and green solvents, such as aqueous acetone. Each of the produced lignin fractions contains lignin molecules with uniform structure, which reflect into well-defined properties, such as solubility, reactivity and thermal properties. The structure and properties of the fractions are controllable by adjusting the solvent concentration in different stages of the fractionation process. In selected applications, the fractionated lignin outperforms the unfractionated lignin, e.g. the low molar mass lignin fraction is substantially better antioxidant in composite materials than the unfractionated lignin or a commercial reference.

This paper emphasizes on techno-economic analysis carried out for a production plant that fractionates 50 ttn of lignin/a into three fractions. Two scenarios were assessed: In the first one the fractionation process was integrated into a kraft pulp mill whereas the second was a stand-alone process. Regarding the overall cost breakdown, the main cost for the fractionation was the lignin feedstock followed by the solvent makeup. The production cost of fractionated lignin was ca 1.7 times the lignin feedstock cost in both integrated and standalone production plants.

This research was funded by BBI project SmartLi "Smart Technologies for the conversion of Industrial Lignins into Sustainable Materials"

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Enzymatic modification of lignin from a hydrothermal biorefinery concept and use thereof in polymer compounds

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The use of lignins as filler additives in polymer compounds has already been subject of research on numerous occasions. Early works applied lignins from pulping processes, due to their high availability and low economic value. With emerging lignocellulosic biorefinery concepts, new types of lignin can be isolated with hitherto unfound properties, which can supplement the still increasing application opportunities of lignins.

In this work, lignin from a biorefinery concept is used, which is isolated via hydrothermal pretreatment of lignocellulosic biomass with subsequent enzymatic saccharification of the solid fraction and solid-liquid separation of the remaining solid lignin fraction and sugar solution[1]. It has been found that the thus obtained sulfur-free lignin retained majority of the macromolecular nature[2], which show distinct differences to other lignins with respect to thermal properties and solubility.

The use of this aquasolv lignin as filler additive in different thermoplastic polymers has been studied and the properties were found to be comparable to literature values of other unmodified lignins. However, in order to improve the compatibility of the aquasolv lignin and the polymer matrix, the lignin has been modified. As an alternative to conventional chemical modification, fungal laccases have been applied to enzymatically catalyze an oxidative coupling of phenolic compounds onto the aquasolv lignin.

Motivation of which is the avoidance of organic solvents required for majority of chemical functionalization strategies. Additionally, the impact of overall water usage in the hydrothermal biorefinery concept can be reduced with the integration of the enzymatic modification into the process chain. The impact of the enzymatic modifications will be shown and evaluated in terms of solubility parameters proposed by Hansen as representation of compatibility and the properties of the lignin-polymer compounds themselves.

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Laccase pretreatment to decrease lignin-induced fouling in the membrane filtration of birch hot-water extracts

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Recovery of value-added materials from biorefinery streams to develop substitutes for fossil compounds is becoming increasingly important. Among the separation technologies, membrane-based techniques have gained great interest as selective, energy efficient and environmentally friendly option. However, fouling problems caused by lignin have been limiting the use of membranes. Laccase catalysed oxidation of lignin can change the physicochemical state of lignin to potentially less fouling form. Thus, the aim of this study was to find out if laccase pre-treatment can decrease adsorptive fouling and improve the filterability of a pressurized hot water extract made from birch chips. The extract was pre-treated with laccase before the adsorptive fouling and pressure-driven fouling experiments with commercial polyethersulphone membranes. Size exclusion chromatography (SEC) was used to analyse the average molecular weights (Mws) of the wood extracts. Furthermore, UV absorbance and total organic carbon (TOC) content of the samples were measured and membrane samples were examined with ATR-FTIR spectroscopy.

Laccase pre-treatment decreased adsorptive fouling. Moreover, the FTIR spectra showed that the pressure-driven fouling peak at 1515 cm^{-1}, which originates from lignin structure, was clearly smaller in samples used with the laccase treated extracts compared to those used with the reference extract. However, based on the changes in pure water permeabilities the pressure-driven fouling caused by the laccase treated wood extract was greater than fouling observed with the reference wood extract. The laccase treatment caused increase of Mw of lignin compounds (80%, from 680 Da to 1230 Da). The change in molecular size distribution might contribute to the pressure-driven fouling occurring as pore blocking, because after the treatment the Mw of the lignin compounds is closer to membrane cut-off value and they might cause more blocking of the inner membrane pores. Interestingly, it seemed that the laccase pre-treatment increased significantly filtration capacity in filtration of the wood extracts although it increased also pressure-driven fouling caused by the extract. Thus, changes in lignin structure due to the laccase treatment could influence beneficially to the structure of the secondary layer, which is formed on the membrane surface during the filtration.

Introduction

Modern biorefinery concepts target to exploit the full potential of lignocellulosic biomass via production of diverse high-value products such as platform chemicals, novel polymers and next generation biofuels from different components of biomass. Separation, purification and concentration of hemicelluloses, lignin and phenolics from process streams for further processing is essential in order to reach potential bio-based products[1,2]. Ultrafiltration has proven to be a very promising separation technique for the fractionation and recovery of lignin and hemicelluloses from wood extracts. However, the commercial membranes available are typically fairly hydrophobic and thus prone to fouling by lignin and wood extractives[2,3].

Laccase enzymes are copper containing biocatalysts that in the presence of molecular oxygen possess both polymerizing and depolymerizing reactions of phenolic substrates. The direction of the reactions depends on the size and chemical structure of the substrate as well as on the use of mediator molecules with laccases[1,4,5]. Besides modification of lignin molecular weight laccases have been applied also to break linkages between lignin-hemicellulose complexes and to increase the molecular size of hemicelluloses by crosslinking them via lignin side groups bound to them[6,7]. When combined to membrane filtration this kind of pre-treatment which either breaks the molecules to smaller compounds or aggregates them to larger compounds, might influence the flux favourably[3].

Especially linear, native like lignin, has a great tendency to adsorb on surfaces and thus cause fouling followed by flux decrease during membrane filtration of biorefinery extracts. Laccase-catalysed polymerization changes the physicochemical state of lignin and is thus expected to reduce its stickiness as the linearity decreases. Thus, laccase oxidation may decrease lignin tendency to foul membranes. (This hypothesis was tested in this study.)

In this study ultrafiltration was combined with laccase pre-treatment to explore how laccase treatment affects pressure driven and adsorptive fouling and filterability of the birch wood extract. Gathered knowledge on studied pre-treatment method and on mechanisms causing lignin originated fouling can be applied in the development of more efficient and economic filtration processes to fractionate and purify lignocellulosic streams.

Experimental

Pressurized hot water extract, rich in xylan (pH 3,5) was obtained by cooking birch chips at 160 °C for 90 min. Lignin concentration in the extract (3,5 g/l) was measured by UV280 (in 0,1 M NaOH) and taking into account the contribution of furfurals. Commercial M120 laccase *Trametes sp.* by Amano was used to treat the extract under 60 °C for 15 min. Laccase dosing of 500 nkat/g lignin was used. Laccase activity was determined against guaiacol (at pH 3,5) as previously considered relevant in the case of lignin substrates [8, 9] Alkaline size exclusion chromatography (SEC) was used to analyse the average molecular weights (Mws) of the wood extracts. UV absorbance and total organic carbon (TOC) were applied to study changes in retention.

Adsorption experiments were carried out using 4-cell cross flow filter (membrane area per cell 40 cm^2) equipped with peristaltic pump for running the adsorption step. Pressure-driven filtration experiments were carried out using a 350 ml nitrogen-pressurized and magnetically stirred dead–end Amicon cells (area ~38 cm^2). The commercial UH004 P polyethersulphone (PES) membrane (Microdyn Nadir GmBH) with cut-off values of 4 kDa was used in all experiments.

The pure water permeability was measured before and after the filtration and adsorption experiments to evaluate degree of fouling. ATR-FTIR spectroscopy was used as complementary method in fouling evaluation to characterize the changes caused by fouling and to compare amount of ligneous foulants on different membranes.

Results and discussion

Laccase-induced changes in the wood extract

The laccase treatment caused clear change in colour from light to dark brown and increase of molecular weight (Mw) of lignin compounds (80%, from 680 Da to 1230 Da). Laccase treatment caused also partial lignin agglomeration and further insolubilisation.

Adsorption experiments

Pure water permeability (PWP) results before and after adsorption varied considerably and thus the effect of laccase pre-treatment on adsorptive fouling was unclear based on the PWP measurements. However, ATR-FTIR spectra confirmed that the reference extract caused more fouling than the laccase treated extract.

Pressure-driven filtration experiments

Laccase treatment significantly improved the filterability of the extract with PES membranes. Filterability increased both at 25 and 60 °C as the result of laccase treatment. For instance, with the UH004P membrane (4 kDa) at 60°C, the flux of the laccase treated extract was on an average 550% higher compared to the reference extract (Figure 1.) Based on the UV absorption at 279 nm lignin retention increased slightly (about 10 and 20 % in 25 and 60 °C, respectively) as the result of laccase treatment. The increase in Mw can also partly explain the slight increase in the retention of lignin found after the laccase treatment.

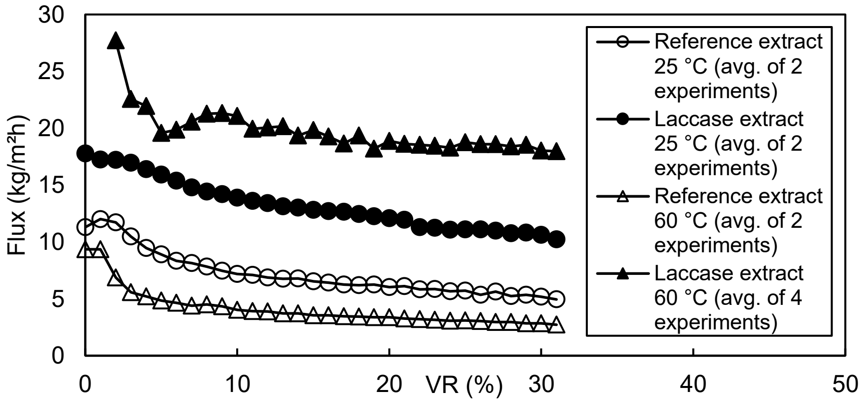

Figure 1. Average filtration capacity in pressure-driven filtrations of reference extract and laccase treated extract at 25 and 60 °C.

The degree of pressure-driven fouling was evaluated by comparing pure water permeabilities before and after fouling experiment. Laccase pre-treatment seems to increase pressure-driven fouling caused by the extract. Although, at 60°C the pure water permeabilities of the reference extract and laccase treated extracts were almost the same after fouling (Figure 2.) The reduced effectives of laccase treatment in decreasing lignin originated fouling at 60 °C could be explained by more significant role of other foulants such as extractives in higher temperatures.

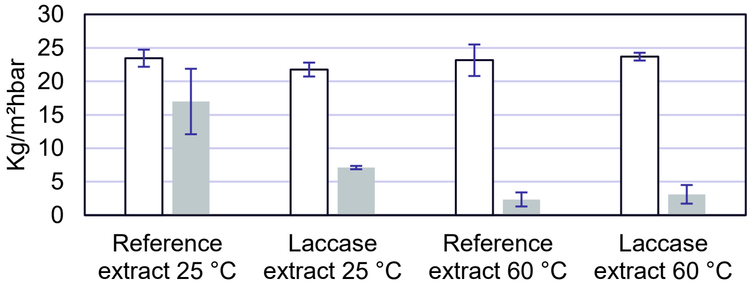

Figure 2. Pure water permeabilities before (white) and after (grey) pressure-driven fouling experiments.

It can be clearly seen in ATR-FTIR spectra in Figure 3 how laccase treatment decreases membrane fouling caused by lignin. The FTIR spectra showed that the pressure-driven fouling peak at 1515 cm^{-1}, which originates from lignin structure, was clearly smaller in samples used with the laccase treated extracts compared to those used with the reference extract.

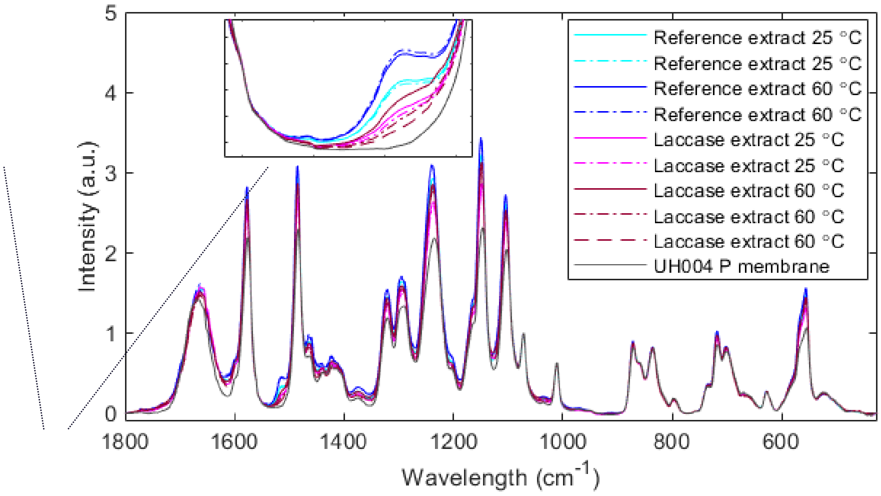

Figure 3. ATR-FTIR spectra for virgin UH004 P membrane and for membranes fouled in pressure-driven fouling experiments of reference extract and laccase treated extract at 25 and 60 °C.

Conclusions

This study applied laccase catalyzed oxidative pre-treatment to improve filterability of birch wood extract. The results of the study showed that catalytic pre-treatment of the extract lead to significantly better filtration capacity even though the irreversible pressure-driven fouling was unexpectedly increased based on the changes in pure water permeabilities.

Increased irreversible pressure-driven fouling can be possibly explained by molecular mass distribution changes caused by laccase pre-treatment. Lignin molecules with certain size range may enter the membrane skin layer and consequently block the pores of the membrane. Thus in the development of laccase pre-treatment processes, the matching of the membrane pore size and size of the resulting lignin molecules should be considered.

Contrary to results of pressure driven fouling experiments, the adsorptive fouling caused by ligneous compounds decreased as the result of laccase treatment. Thus laccase treatment probably changed physiochemical properties of lignin and modified lignin molecules to less sticky form that differs from the structure and/or size of native lignin. The changes in lignin structure might also alter beneficially the structure of the secondary layer, which is formed on the membrane surface during the filtration.

Acknowledgements

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Cyclic organic carbonates as reagents for the functionalization of lignins and hemicelluloses

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Cyclic organic carbonates are non-toxic components with high boiling and flash points and can be used as polar aprotic solvents or reagents to access new biobased and environmentally friendly polymer building blocks. This work focused on the use of different cyclic carbonates to extend the functionalities of lignins and hemicelluloses. Lignin polyols were successfully synthesized by an efficient, nontoxic and solvent free oxyalkylation procedure using commercially available organic carbonates (ethylene (EC), propylene (PC), butylene (BC) and glycerol carbonate (GC)). The applicability of oxyalkylation to a set of lignins from hardwood, softwood and annual plants and different processes (organosolv, kraft, soda) was investigated. To broaden the range of applications for lignin a simple environmentally friendly procedure was developed to prepare cyclocarbonated lignins, which could be used as synthons for the preparation of nonisocyanate polyurethanes. Since a growing interest in utilization and derivatization of hemicelluloses has emerged during the last decades the ability of propylene (PC) and vinyl ethylene carbonate (VEC) to etherify xylans was tested and the structure of products was analysed.

Introduction

The utilization of lignin and hemicelluloses for functional bio-based polymer materials is a highly desirable approach for the valorization of these renewable resources. To enhance their reactivity, processability and applicability in highly functionalized polymers the chemical modification is a key strategy for the utilization of lignin and hemicelluloses[1-5]. In particular, the aliphatic and, in the case of lignin, phenolic OH groups can be modified through alkylation or esterification reactions to extend chains or to introduce new active sites.

Chain extended hydroxyalkyl-lignins have been extensively investigated in recent years as precursors in “green” polyurethane (PU) applications[6]. The synthesis of these lignin-derivatives was usually achieved by chemical modification of lignin with different alkylene oxides, especially propylene oxide (PO), leading to more reactive lignin-based polyether polyols. However, the handling of PO carries substantial risks, due to its high vapor pressure, flammability, toxicity and carcinogenicity. As an attractive and promising alternative to epoxides, five-membered cyclic organic carbonates could be used for the etherification of lignins or hemicelluloses. Organic carbonates are characterized by low toxicity, high boiling and flash points, low vapor pressure, biodegradability and high solubility[7]. Due to these properties the applicability of ethylene (EC), propylene (PC), butylene (BC) and glycerol carbonate (GC) for the oxyalkylation of lignins from hardwood, softwood and annual plants and different processes (organosolv, kraft, soda) was investigated.

As a result of oxyalkylation with GC, a unified lignin is generated providing two adjacent hydroxyl groups in form of a 1,2-diol at the chain end. This product was used to develop a novel, efficient and green protocol to a lignin-based building block equipped with cyclic carbonate functionalities. Cyclocarbonated lignins could be able to act as crosslinking agent for the production of fully bio-based Non-Isocyanate PolyUrethanes (NIPUs)[8,9]. This route has become growing interest since regulations on chemical compound toxicity have become more strict and industries have to replace hazardous chemicals[10].

Hemicelluloses are another important sustainable feedstock which offers numerous possibilities in the fields of packaging, coating and biomedicine. However, new chemical pathways are needed for the synthesis of highly engineered hemicellulosic derivatives. Since xylan is one of the most abundant hemicellulose present in hardwood and perennial plants, xylan derivatives gain increasing importance as functional polymers or activated intermediates to produce materials with targeted properties[11-13]. To develop functional and sustainable xylan products from future biorefineries hydroxyalkylation of xylans from oat spelts was evaluated using propylene and vinyl ethylene carbonate. The structure of derivatized arabinoxylans was investigated by HPLC-MS detection after polysaccharide hydrolysis and reductive amination.

Experimental

Lignin extraction and lignin samples

Organosolv lignin was produced at the Thünen Institute of Wood Research using ethanol/water (1:1, w/w) pulping of beech wood (OL) with a liquor to biomass ratio of 4:1 (w/w) and 0.5% H_2SO_4. The technical lignin from kraft pulping processes was obtained from Suzano (spruce/pine, KL) and the soda lignin (wheat straw, SL) was purchased from GreenValue.

Extraction of xylan

Arabinoxylan (OX) was isolated from oat spelts by sodium hydroxide extraction as published previously[14]. SEC and monomer analysis yielded a molecular weight of M_w = 24 500 g/mol, a polydispersity of $Đ$ = 2.4 as well as a xylose content of approximately 62 mol% and an arabinose content of approximately 9 mol%.

Oxyalkylation of lignin

Lignin (1.0 g; OL: 5.17 mmol OH g^{-1}) was dissolved in 10 eq EC, PC and GC and 0.1 eq DBU was added. The mixture was allowed to react at 170°C for 3 h under stirring in N_2 atmosphere. After completion of the reaction the mixture was precipitated in the 10-fold amount of deionized acidified water. The crude product was filtered, washed with deionized water and then dried in a vacuum oven at 30°C over P_2O_5.

Transesterification of oxyalkylated lignin

To a solution of 200 mg of oxyalkylated lignin (1.01 mmol OH) and 5 eq. of DMC or EC in 0.5 mL DMSO, 0.2–0.4 eq. of K_2CO_3 was added. The mixture was stirred at 75 °C for 3–6 h in N_2 atmosphere. Afterward the precipitated product was washed with water and dried in a vacuum oven at 30 °C.

Oxyalkylation of xylans

For homogeneous synthesis 1.05 g xylan (5.02 mmol anhydro xylose) was suspended in 10.5 g DMSO (10% w/w) and stirred for 16 h at 50 °C. After the solution was heated to 100 °C, 10.5 g (102 mmol) propylene carbonate and 55 µL (0.35 µmol) DBU were added. Subsequently, the solution was heated to 140 °C or 160 °C, respectively. Reaction time was measured when the destined temperature was reached, with reaction times of 0, 40, 80, 160 and 240 min being examined.

NMR Spectroscopy

NMR spectroscopy was performed on a Bruker Avance 400 MHz spectrometer. ^{13}C NMR spectroscopy was performed following a procedure described by Capanema et al. (2004). 1,3,5-trioxane served as internal standard (IS). ^{31}P NMR spectroscopy was performed at 25 °C according to a published procedure (Granata and Argyropoulos, 1995). 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was used as phosphitylation reagent and cholesterol served as IS.

Xylan hydrolysis, reductive amination and chromatograhic analysis

The modified xylans were hydrolyzed into monomers by a solution of *trifluoroacetic acid* (TFA) using a microwave oven with a maximum power of 1200 W. Hydrolysis was carried out in Teflon vials with 50 mg dried sample material that was suspended in 5 ml of TFA solution and heating to 120 °C within 60 s and keeping this temperature for 30 s. The hydrolyzed sample materials were reductively aminated according to[13]. The chromatographic separation of monosaccharides after total hydrolysis and reductive amination was performed on an Agilent HPLC 1200 Series for mass spectrometric detection. Mass spectrograms were recorded with a Agilent 6224 ESI-TOF.

Results and Discussion

Depending on the reaction conditions and the nucleophile, carbonates can undergo two different reaction pathways: transesterification (Figure 1, a) or alkylation with release of CO_2 (Figure 1, b). As a result grafted chains of polyetherpolyols including carbonate linkages can be formed. The ^{31}P NMR spectra of the alkylated lignins showed that all of the phenolic hydroxyl groups fully disappeared regardless which carbonate was used (Figure 2). Simultaneously, new signals for aliphatic OH groups arose confirming the successful ring opening attachment of cyclic carbonates. The quantitative analysis of OH moieties revealed, that lignin polyols with up to 4.70 mmol g^{-1} (gOL) aliphatic OH groups could be synthesized. This corresponds to a hydroxyl index of 264 mg KOH g^{-1}, which is comparable to those of industrially used polyols. FTIR and ^{13}C NMR spectra of the lignin derivatives indicated the presence of some carbonate linkages. In the case of glycerol carbonate the signals corresponds to cyclic carbonate functionalized lignins due to partially transesterification reactions between the newly formed 1,2-diol and excess GC (c.f. Figure 3).

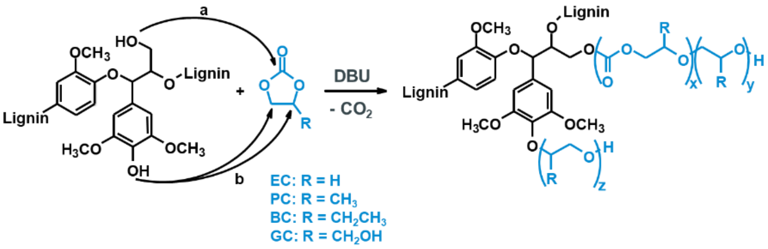

Figure 1. Oxyalkylation of lignin with cyclic organic carbonates

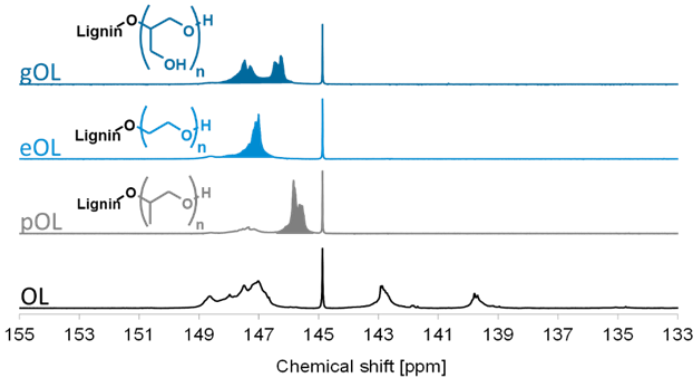

Figure 2. ^{31}P NMR spectra of organosolv lignin (OL) oxyalkylated with ethylene carbonate (eOL), propylene carbonate (pOL) and glycerol carbonate.

Despite of higher amounts of impurities of Kraft and Soda lignins the oxyalkylation with carbonates was almost quantitative. For all lignins an increased degree of substitution (DS) could be observed in the order BC < PC < GC < EC reaching a DS maximum of up to 0.96. After 3 h at 170°C the average length of the grafted chains was not more than 2.6 units per chain. As a result of oxyalkylation with glycerol carbonate 1,2-diol terminated lignin derivatives were formed.

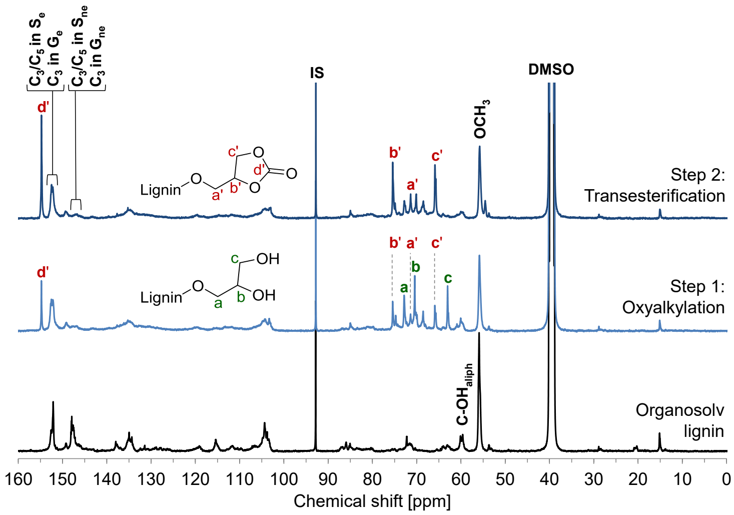

Figure 3. ^{13}C NMR spectra of unmodified, oxyalkylated and carbonated organosolv lignin [8].

In a second synthesis step the adjacent hydroxyl groups were converted to cyclic carbonates via transesterification with ethylene (EC) or dimethyl carbonate (DMC). According to the ^{13}C NMR spectra signals of the hydroxyl terminated carbons C_b (70.4 ppm) and C_c (63.1 ppm) in oxyalkylated lignin disappeared in favor of signals of etherified carbons in cyclic carbonate structures ($C_{b'}$ 65.9 ppm, $C_{c'}$ 75.4 ppm) (Figure 3). Additionally a signal for the carbonyl carbon $C_{d'}$ (154.8 ppm) appeared revealing the ring closure to cyclic carbonate function within the lignin. With dimethyl carbonate high conversions of up to 96% could be achieved under mild reaction conditions (75°C, ambient pressure) by using K_2CO_3 as catalyst.

Arabinoxylanes from oat spelts were similarly modified by propylene- (PC) and vinyl ethylene carbonate (VEC). In order to investigate the structure of derivatized xylans the products were analyzed by HPLC-MS after microwave assisted hydrolysis with trifluoroacetic acid and reductive amination (Figure 4). The chromatograms revealed the synthesis of a high variety of different isomers, caused by various hydroxyl groups, the elongation of the side chain and different possible reaction pathways. Xylan modification with vinyl ethylene carbonate showed a higher average molar substitution compared to PC. The differentiation of mono- and disubstituted xylose and arabinose units revealed that arabinose is by far the preferred reaction partner for cyclic carbonates.

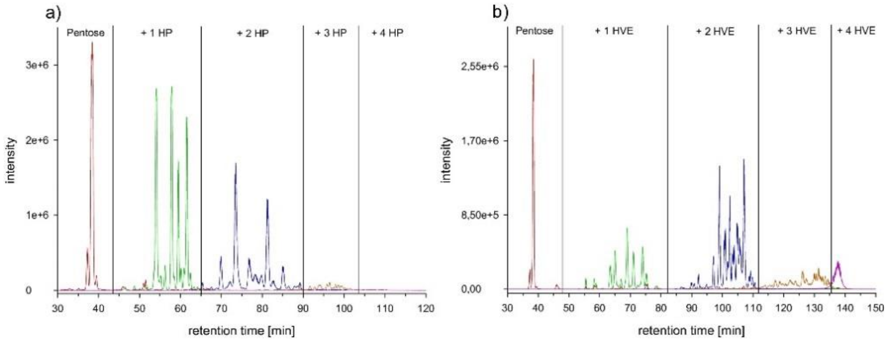

Figure 4. LC-MS chromatograms with mass traces for reductively aminated pentoses and the respective derivatives with 1,2,3, and 4 alkyl units (HP = hydroxypropylated pentoses, HVE = pentoses with hydroxyvinylethyl groups)[13].

Conclusions

Due to its easy handling, low toxicity, volatility and flammability, cyclic organic carbonates provide a convenient alternative to alkylene oxides for the preparation of lignin polyols and alkylated xylan derivatives. ^{31}P NMR spectroscopic analysis showed that the phenolic units and almost all of the aliphatic hydroxyl groups of lignins were oxyalkylated with EC, PC, BC and GC generating lignin polyols with exclusively aliphatic hydroxyl groups. The oxyalkylation could be applied for lignins from different feedstocks and pulping methods. A renewable lignin-based building block equipped with cyclic carbonate functionalities could be synthesized in a simple two step procedure under mild reaction conditions. An analytical method was developed for the detailed analysis of hydroxyalkylated arabinoxylan derivatives based on hydrolysis, reductive amination and chromatographic separation by HPLC.

Acknowledgements

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Lignin 2:

Applications

Designing kraft lignin based dispersants for clay suspensions

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Kraft lignin valorization is a crucial way to convert kraft pulping processes to biorefineries. Kraft lignin can be modified to function as a dispersant for various applications. To generate useful dispersants, it is important to identify the correlation between the properties of suspensions and dispersants. In this study, kraft lignin was modified by oxidation using nitric acid under varied conditions to produce oxidized lignin products with different charge densities and molecular weights. Then, the effect of anionic charge density (1.2-3.6 meq/g) and molecular weight (11,000-88,000 g/mol) of the lignin-based products on their dispersion performance was evaluated using different advanced techniques. It was discovered that the lignin-based product with the charge density of 3.6 meq/g and molecular weight of 30,000 g/mol was the most effective dispersant for clay suspensions. In this work, the adsorption of lignin-based dispersants on clay particles and the impact of adsorption on the particle size, zeta potential, relative turbidity and sedimentation of clay particles in different slurries will be discussed.

Lignin as novel renewable binder in pigment-based paper coating formulations

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Global paper coating industry uses over 1.8 Mio tonnes/year of petroleum-based binders valued at €4.3bn (https://www.icis.com/). Since future petroleum production is unlikely to meet our society's growing needs with current petroleum based products contributing 96 % of our chemicals and materials[1], bio-economy driven industry has been identified as the alternative solution. In line with circular bioeconomy, recently lignin is increasingly being considered as a possible raw material that can replace many fossil-based resources including paper coatings as summarized in Figure 1.

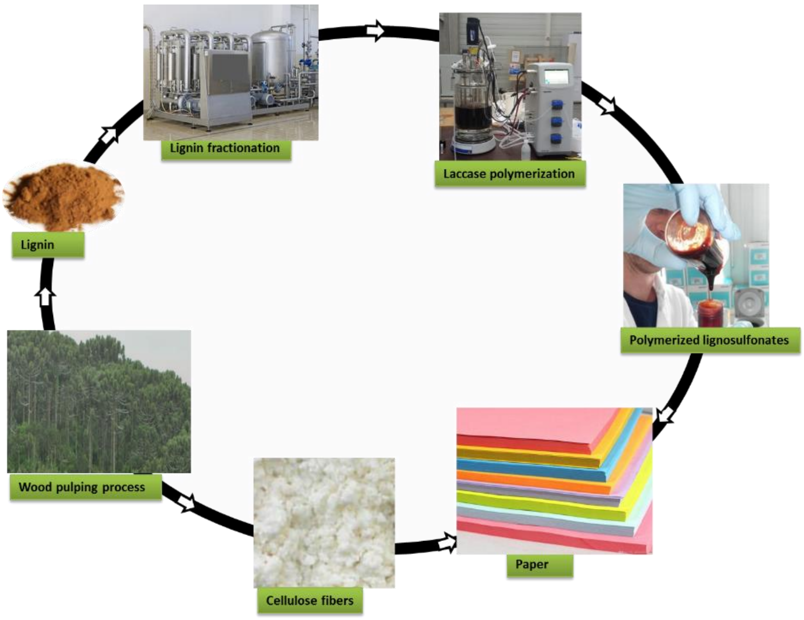

Figure 1. General overview of the scheme showing circular bioeconomy concept using lignin from the pulping process as a raw material in paper coating formulation.

However, lignin´s complex, heterogeneity, undesirable modifications introduced during the pulping process, impurities, strong inter- and intra-hydrogen-bonding, low reactivity and immiscibility has hampered its successfully exploitation, not only in coating formulations but many other potential applications. For example, sulfite pulping processes produces spent liquor containing lignosulfonates with average molecular weight [Da] ranging from 36 000–61 000 (softwood) and

5700–12 000 (hardwood), associated approximately 30 wt % hemicelluloses, 10 wt % inorganics and the remaining part residual pulping chemicals[2]. Lignin therefore requires processing to make it a suitable industrial raw material. Many physical, chemical, physico-chemical and enzyme based strategies, including purifying[3,4], modification of lignin end groups (hydroxyl, methoxyl, carbonyl and carboxyl groups)[5-7] or the use of plasticizers[8] have been intensely explored in order to make lignin suitable for industrial applications with limited success. In this study a combination of process i.e. lignin fractionation followed by laccase modification of the obtained lignin fractions is used to synthesize binders for incorporation into the paper coating formulation in order to replace oil-based styrene-butadiene (SB) or styrene-acrylate latex as a binder. Laccases (*p*-diphenol:dioxygen oxidoreductases, EC 1.10.3.2) are multi-copper oxidases that catalyze one-electron oxidation of a wide range of substrates including varied lignin substrates resulting in the generation of reactive species while simultaneously reducing molecular of oxygen to water[9]. The most attractive feature of laccase lies in their ability to generate reactive species that can cross-react among themselves or with other molecules in the surrounding milieu[7,9,] a property that makes them ideal biocatalysts for synthesizing large molecular weight polymers. Building on these discoveries, this study investigated the ability to exploit the lignin fraction and laccase polymerization processes for the synthesis of lignosulfonates based binders for incporation in paper coating formulation to replace oil-based styrene-butadiene (SB) or styrene-acrylate latex as a binder

Experimental

Laccase activity assay

A new putative laccase1 from *Aspergillus flavus* (AfLacc1) successfully engineered for improved activity on lignosulfonates by attaching a hydrophobic substrate-binding domain of polyhydroxyalkanoate depolymerase of *Alcaligenes faecalis*. Laccase activity was measured following the oxidation of spectrophotometrically according to the procedure described by Nugroho Prasetyo et al 2009, while monitoring the oxidation of 2,2-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) to its cation radical at 420 nm using a plate reader (Tecan, Infinite M200, Switzerland). The activity was expressed in katal (defined as the amount of enzyme necessary to convert 1 mole substrate per second). Unless otherwise indicated, all experiments were carried out in triplicates.

Laccase polymerization of lignosulfonates

The fractionated lignosulfonates incubated with laccase while monitoring oxygen consumption using a FireSting-O_2 device from *PyroScience* GmbH (Aachen, Germany) at pH 7 and 25 °C. To follow the oxygen consumption the sensor was placed in the reaction vessel containing 15 % TDS lignin sample. Lignosulfonate samples were first sparged with oxygen (*oxygenated*) reaching 100 % saturation before introducing 233 nkatal ml^{-1} laccase to start the reaction or simple left shaking (*aerated*). Samples (5 ml) were withdrawn regularly withdrawn for monitoring changes in molecular weight, fluorescence intensity and phenolic content.

Measuring changes in molecular weight measurement

Modified and unmodified lignosulfonate were analyzed using size exclusion chromatography (SEC) equipped with degasser, binary pump, auto sampler, a DAD (Diode Array Detector) and a RI (Refractive Idex) -detector system (Agilent Technologies 1260 Infinity). A guard column (Waters Ultrahydrogel, 200 Å, 6 x 40 mm, maximum pressure 3.93 MPa) was placed before the two separating columns (Waters Ultrahydrogel 500, 500 Å, 7.8 x 300 mm, 3.93 MPa and Waters Ultrahydrogel 250, 250 Å, 7.8 x 300 mm, 1.96 MPa) connected in series. The lignosulfonates were diluted with the mobile phase to a concentration of 1 mg*mL^{-1} before loading 100µl onto the column. The lignosulfonate samples were run on isocratic gradient using 0.1 M $NaNO_3$ solution as mobile phase. The standards used for size exclusion chromatography (SEC) were Polystyrene Sulfonate Sodium Salts with molecular weights ranging from 208 g/mol - 1188 400 g/mol.

Paper coating and printing tests

The coating formulations were prepared by mixing calcium carbonate, SB-latex, thickener from BASF and PVA and untreated and enzymatically modified lignosulfonate in ratio of 1:2. The paper coating was performed on pre-coated woodfree base paper using a laboratory reel-to-reel coater using a stiff blade at a speed of 15 m/min. Applied target coat weight was 7g/m^2 per side.

Results and Discussions

Laccase polymerization of lignosulfonates

Lignosulfonate fraction were incubated with laccase while either shaking (aerated) or oxygenated. The oxygen immediately dropped to undetectable levels in both shaking (aerated) or oxygenated reaction mixtures (Figure2-A). This shows that laccase immediately used the oxygen as the electron acceptor during the oxidation process[10-12]. In areated samples the oxygen remain undetectable during the whole incubation period (>300 min). However, in oxygenated samples, the oxygen level started accumulating after 50 min of incubation reaching over 360 % saturation after 1 h 30 min. This may be attributed to fact that all the oxidizable lignosulfonates had been modified. The decrease in oxygen concentration was also accompanied by decrease in phenolic content in both aerated and oxygenated samples, demonstrating successful laccase oxidation of the lignosulfonates. The oxidation was more pronounced in oxygenated samples than aerated samples emphasizing the importance of supplying enough oxygen in laccase reactions. Similarly, the changes in fluorescence intensity in both aerated and oxygenated samples were in agreement with the changes in the phenolic concentration. The changes/decrease in fluorescence shows modifications in conjugated biphenyl, phenylcoumarins, carbonyl, and stilbene groups in this case as a result of laccase oxidation[13,14]. During the laccase mediated oxidation process, the lignin aromatic hydroxyl groups are oxidized and reactive radicals are generated cross-react forming C-C and C-O bonds to form dimers leading to the formation long chain polymers. The average molecular weight increased from an average of 5.5 to 140 kDa in oxygenated samples and from an average of 5.5 to 83 kDa in oxygenated. The results clearly demonstrates the importance of oxygen supply in laccase catalyzed reactions.

The incorporation of the polymerized lignosulfonates as binders in paper coating formulations resulted in coated paper with improved printing properties (reduced picking compared to non polymerized lignosulfonates) similar to SB-latex coated paper (Fig 4). Although colour remains an issue, these results demonstrate the possibility of substituting fossil-based styrene-butadiene (SB) latex binders with on-site produced underutilized lignosulfonates traditionally used as low value energy source in the pulp and paper industry.

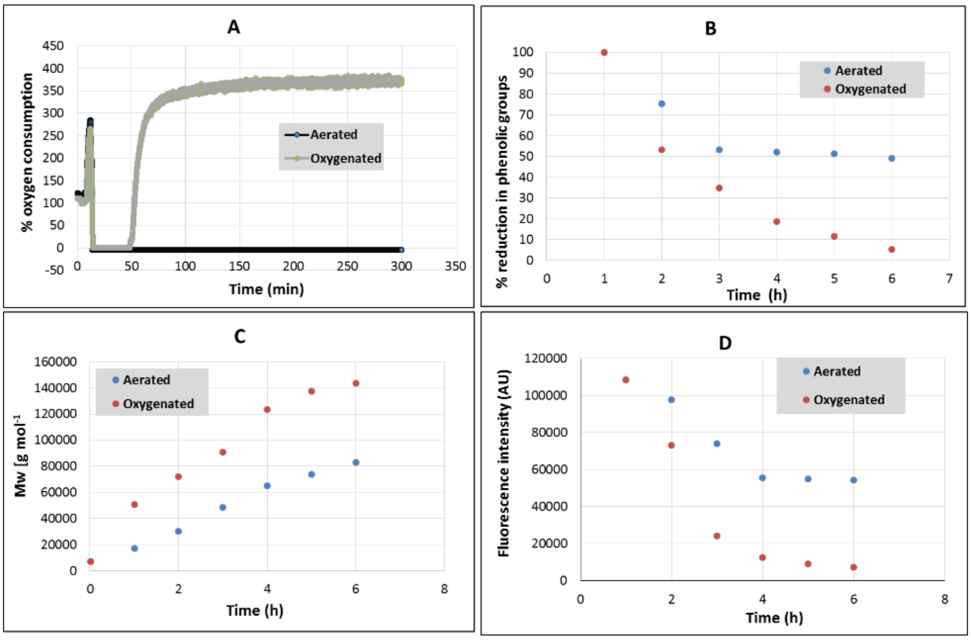

Figure 3. Changes in (A) oxygen consumption, (B) phenolic groups, (C) molecular weight and (D) fluorescence intensity during incubation of lignosulfonates with laccases in aerated and oxygenated samples.

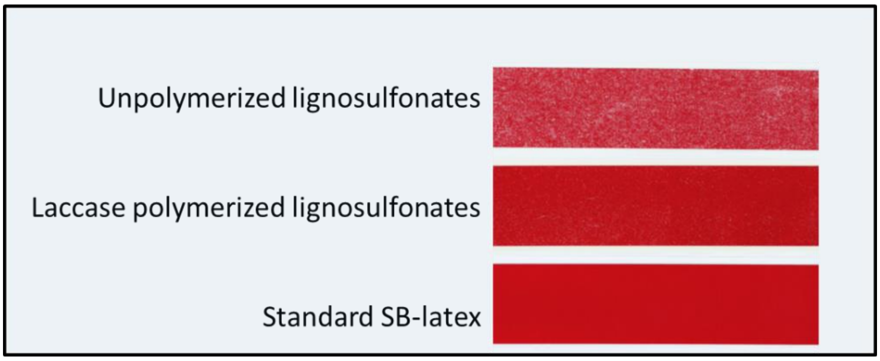
Unpolymerized lignosulfonates
Laccase polymerized lignosulfonates
Standard SB-latex

Figure 4. Printing results on paper coated with unpolymerized, laccase polymerized lignosulfonates and the SB-latex standard coating material.

Conclusions

Lignin fractionation and external oxygen supply are important factors to consider during laccase polymerization of lignosulfonates. Fractionated lignin and enzymatically polymerized lignosulfonates were successfully applied as partial replacement of SB-latex in paper coating formulations as evidenced by reduced picking during printing tests although brightness as expected remains a challenge.

Acknowledgements

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DES-lignin as a biobased hydrophilicity promoter in polyethersulphone (PES) membranes

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Polyethersulfone (PES) is one of the most commonly used polymeric material in manufacturing of ultrafiltration membranes. Its beneficial characteristics are high chemical and hydrolytic stability as well as good film-forming properties. However, it has a relatively hydrophobic nature, which makes it more susceptible to fouling in many applications, for example in the treatment of biorefinery streams and pulp and paper industry process waters. Thus, increasing the amount of hydrophilic functional groups on PES membrane surface can improve the antifouling properties of the PES membranes. This can be achieved by blending PES with more hydrophilic polymer or additives in the manufacturing stage. The additives typically used are oil-based organic compounds. However, lignin could be used as a biobased renewable additive in membrane manufacturing due to its rather inert and more hydrophilic nature compared to PES.

This study explores the use of lignin extracted from birch wood using deep eutectic solvent (DES-lignin) as a hydrophilic adhesion promoter in a polyethersulfone (PES) membrane. DES-extraction of lignin could be feasible for instance to the utilization of lignin, which is present in the harvested but nowadays under-utilized or waste wood fractions. The membranes were manufactured with phase-inversion technology with different DES-lignin contents (0.25%-1.0%) of the dope solution. The manufacturing conditions were optimized to enable the manufacturing of ultrafiltration membranes and influence of DES-lignin on the performance of the prepared membranes was evaluated based on pure water flux and polyethyleneglycol (PEG) retention. In addition, hydrophilicity and surface charge of the membranes were characterized. It was found that the increase of DES-lignin content in dope solution enabled the manufacturing of membranes with less negative charge and improved hydrophilicity. The DES-lignin did not leak out from the membrane. Thus, the results of this study demonstrate well the possibility to use DES-lignin as a biobased hydrophilicity promoter in PES ultrafiltration membranes.

Recent achievements in the valorization of technical lignins

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Conversion of lignins into high-value products is expected to dramatically influence the prospects of biorefineries and help to reinvigorate the forest industry and future commercialization opportunities. This requires lignins to be engineered for optimized product properties. Here we review new achievements in lignin valorisation, including lignin micro/nano-particles, the exploitation of lignin-cellulose synergisms and advances in valorisation of biorefinery lignins. The importance of efficient analytical methodology for successful lignin engineering through structure – performance correlation is highlighted.

Impact of lignin commercialization on biorefinery economy

Recent developments in the sugar-based "biorefinery" have faced significant economic challenges. The main focus of the current biorefineries is the production of carbohydrate-based biofuels and biochemicals, with lignins considered as low-value by-products. However, if they replace chemicals with prices in the range of $1500-2,500/t in market annual volumes of 1-200 Mt[1-3], lignin revenue contribution could be similar or even higher than that from carbohydrates. This could lead to the renaissance of the whole biorefinery and become a **game-changer rather than just a collateral "added value"**. However, such transformation requires for lignins to be engineered into high-value products suited to fulfil given property spaces.

In contrast to technical lignins from the pulping industry, where the range for lignin optimization is very narrow as the process conditions are locked to the properties of the required chemical pulps, the biorefinery allows much larger room for lignin optimization (Table 1). Variations in biorefinery process conditions affect mainly the yield of the sugars-based products, but should not affect their properties. This leads to a paradox conclusion: *to make sugar-based biorefinery economically successful, the main focus should be in lignin engineering*. This is in stark contrast with the current effort to optimize the biorefinery for sugar production only.

Table 1. Comparison of pulping and biorefinery lignins

Lignin source	**Potential production, Mt/y**	**Purity**	**Feedstock range**	**Process flexibility**	**Cost**	**Application value**
Pulping	5-8	med.-high	narrow	narrow	med.-high	med.-high
Biorefinery	>200	low	wide	wide	low	low-high*

*according to the current research

Recent developments in lignin valorisation

Lignin-cellulose synergism

It has been shown that the addition of cellulose to lignin make it possible to obtain fibres via wet-spinning from IS solutions, introducing viscoelastic properties to the lignin upon co-dissolution. An optimal lignin-cellulose ratio allows proper orientation or alignment for improved fiber strength and tenacity of the regenerated cellulose-lignin fibres[4]. Carbon fibers from gels of ligno-cellulose nanofibers (LCNF) containing up to 70% lignin showed increased carbon yield and conductivity after carbonization and very high electrical capacity[5].

The reinforcing effect of cellulose nanocrystals (CNC) when added at levels of up to 15% was observed in electrospinning of lignin mixed in aqueous suspensions with poly(vinyl alcohol) (PVA), which was used as plasticizer (75:25 and 80:20 ratios)[6]. The molecular mobility of the lignin−PVA matrix was hypothesized to decrease with CNC loading, and therefore, phase-separation was reduced (Figure 1). The thermal stability of the system increased owing to a strong interaction of the lignin−PVA matrix with the dispersed CNCs, mainly via hydrogen bonding. Moreover, the addition of CNC as the reinforcing solid phase significantly improved the thermomechanical properties of fibre mats and spin-casted films and stabilized the matrix against water absorption. These results highlight the role of molecular interactions as well as efficient stress transfer between the lignin:PVA matrix and dispersed CNCs.

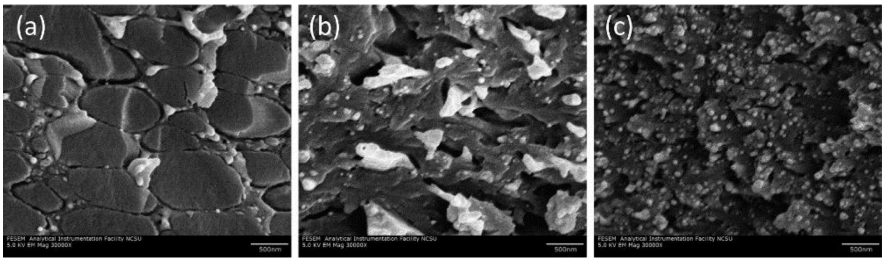

Figure 1. Scanning electron microscopy of the cross-section of solid thin films produced from lignin−PVA−CNC systems prepared by evaporation-casting. The lignin−PVA/%CNC composition included 75:25/0% (a), 75:25/5% (b), and 75:25/15% (c) (see Ref. [6] for details).

CNC was used to reinforce lignin phenol-formaldehyde resins (LPF) in liquid or powder forms[7]. The addition of CNC into LPF improved the wet bending strength and wet shear strength of the produced OSB and plywood, correspondingly.

The synergistic relationship between lignin and CNCs has also been observed as far as the optical, thermal, mechanical and antioxidant properties of lignin-PLA composites [8]. In addition, the combination of CNC and lignin showed to more effectively activate nucleation and crystal growth, with increased crystallinity. Furthermore, exploitation of lignin-cellulose interactions resulted in the best mechanical performance (tensile strength and elastic modulus) of a ternary system containing 1 wt% lignin and 3 wt% CNC[8].

Lignin micro- and nanoparticles (LMNPs)

Nano- and submicron particles (LMNPs) with given shapes and surface topologies enhance some typical lignin properties (such as antioxidant and UV-protection, antimicrobial, thermal stability) or provide opportunities to develop materials with new properties suitable for mechanical reinforcement, good miscibility with different chemicals, emulsion stabilizing effects, etc. Sub-micron lignin particles can be produced by a variety of methods[9]. Two scalable processes for LMNP production are given in Figure 2. Importantly, LMNPs can be produced from traditional lignins via the aerosol process at reasonable costs of 870-1,170 USD/t[10]. Such cost can be further reduced to $750/t if crude biorefinery lignins were used as feedstock. Thus, LMNPs are emerging as a strong alternatives to various lignin chemical modification processes (often utilizing hazardous chemicals) required for technical lignins to be successfully used in various applications[1,2].

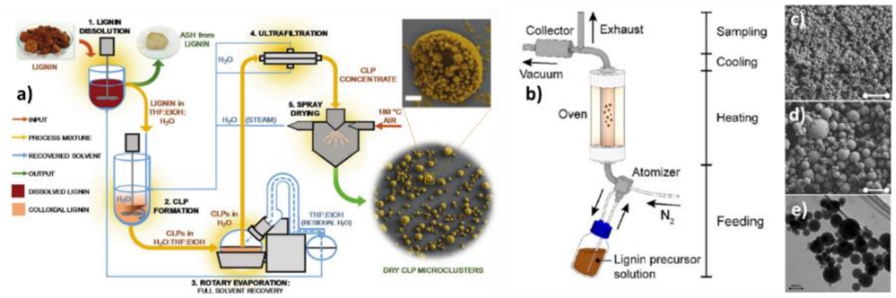
1. LIGNIN DISSOLUTION
LIGNIN
ASH from LIGNIN
4. ULTRAFILTRATION
a)
INPUT
PROCESS MIXTURE
RECOVERED SOLVENT
OUTPUT
DISSOLVED LIGNIN
COLLOIDAL LIGNIN
LIGNIN in THF:EtOH:H₂O
H₂O
H₂O (STEAM)
CLP CONCENTRATE
5. SPRAY DRYING
180 °C AIR
2. CLP FORMATION
CLPs in H₂O
CLPs in H₂O:THF:EtOH
THF:EtOH (RESIDUAL H₂O)
3. ROTARY EVAPORATION: FULL SOLVENT RECOVERY
DRY CLP MICROCLUSTERS
Collector
Exhaust
Vacuum
b)
Oven
Atomizer
N₂
Lignin precursor solution
Sampling
Cooling
Heating
Feeding
c)
d)
e)

Figure 2. Two process schemes for large-scale production of lignin particles: a) solvent shifting and evaporation[11], b) aerosol-flow process[10]. c) and d) SEM micrographs of solid lignin spheres as two out of the ten possible fractions via in-situ separation by size in the process shown in b). e) TEM micrograph of intact spherical lignin particles[9].

New achievements in valorisation of biorefinery lignins

Biorefinery lignins are usually considered as low-value products due to their low lignin purities. Their upgrade is taken as a must for higher value products and considered technically challenging and/or costly. Very recently, a new concept for the valorisation of biorefinery lignins has been suggested[12], showing their potential toward high-value products. Moreover, biorefinery lignins appear to be very suitable substrates to apply the lignin-cellulose synergism fundamentals and for LMNPs production in cost-effective efficient modes.

Superior performance of crude biorefinery lignins

Crude biorefinery lignins of low purity (containing 20-45% residual cellulose) can have superior performance in PF adhesive blends than the corresponding purified lignins and other technical lignins originated from different biomass (SW, HW, non-wood) and different pulping processes (kraft, soda, organosolv)[12] (Figure 3). This has been explained by the positive effect of the residual crystalline cellulose of given types on the lignin's performance, similarly to the lignin-cellulose synergism discussed above, but at much lower production costs (compared to CNC and CNF). The proportion of lignin to cellulose is not the only factor; cellulose characteristics (Table 2) have also a strong influence on the bond performance. Pilot trials on plywood and OSB panel production and testing showed that about 35% of glue can be replaced with SHR without any increase in the hot press time (the bottleneck in the mill operation)[13].

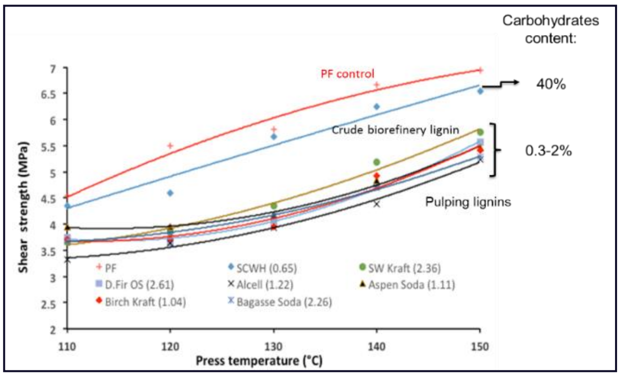

Figure 3. Bonding strength by Automatic Bond Evaluation System (ABES) (at 90 sec press time) of plywood PF blended with different technical lignins (70:30 w/w); the numbers in parenthesis are the amounts of the “reactive centers”, mmol/g.

Customized and functionalized lignins

If high value applications require upgraded lignins, they can be easily produced from crude biorefinery lingins by purification combined with fractionation using green and affordable solvent systems as well as by functionalizing extraction[12]. Moreover, these processes can be easily combined with LMNPs production.

Importance of analytical developments for lignin engineering

Practical importance of analytical methodology:

- To ensure consistency of lignin as feedstock supply for chemical industry.
- To generate IP on lignin structure for a specific process (see for example[14,15])
- To establish correlations between process conditions, lignin structure, lignin properties and its application performance.

An efficient analytical methodology is of primary importance for successful lignin engineering through structure – performance correlation. High flexibility of biorefinery (Table 1) also generates challenges related to a large number of lignin samples to evaluate. Therefore, an analytical approach should be not only reliable and informative, but also sufficiently productive.

Various NMR techniques (Table 2) fit well the requirements. Quantitative ^{13}C NMR is the core of a comprehensive quantification while 2D HSQC technique is excellent for lignin fingerprinting[14,16]. This approach was extremely useful for patenting of specific lignins[14,15]. ^{31}P- and ^{1}H NMR methods are very useful for high throughput lignin screening or/and express analysis of specific functionalities.

Table 2. Comparison of main NMR methods in lignin analysis

	^{1}H NMR	**^{31}P NMR**	**^{13}C NMR**	**2D NMR**
Numbers reported	5-8	4-5	>20	large
Fingerprinting	maybe	no	good	excellent
Molecular structure	no	no	some	excellent[1]
Functional groups	some	OH	comprehensive	no
Purity required	high	high	high-medium	any
NMR time	few min.	1-4 h	overnight/<1h[2]	overnight/<1h[2]
Qualification level	beginner	beginner	expert	expert
Best use	express	express	comprehensive	fingerprinting

[1]For the side chain structures; [2]For CryoProbe™ experiment

Small-scale performance evaluation methodology is the bottleneck in lignin engineering

The current approach for the evaluation of the lignin performance in various applications is often time- and labour- consuming, requires large quantities of lignin and therefore is of low productivity. Thus, development of low scale, fast screening methods is of primary importance to establish structure–performance correlations. ABES test[16] is a good example of a high throughput approach (Figure 3), being very efficient to evaluate lignin performance in wood (and potentially other) adhesives applications[13]. Similar small-scale high-throughput screening methods should be developed for other important potential lignin applications.

Lignin Structure – Performance correlations

Lignin-PF blends for adhesive applications are used as example. No correlation between the amount of "reactive centers" (free 5 and 3-position in phenolic moieties) or/and the molecular weight and the bond performance can be established (Figure 3)[12,13]. This indicates that these parameters are not (the only) important factors, and other characteristics (such as steric effects, flexibility of the lignin macromolecule, compatibility with the resin, etc.) may play a more important role in lignin-PF blend performance. In addition, extensive crosslinking between lignin and PF resins might not be required for good adhesion and lignin might just work an efficient extender. This further implies that simple modelling for lignin structure-performance correlations often used in the literature is obviously insufficient and more sophisticated models should be developed.

Concluding Remarks

Engineering of lignins for high-value applications requires serious analytical development including lignin structural analysis and, especially, high throughput methods for evaluation of lignin performance. For certain types of applications, the current lignin structure-performance correlations should be revised and further developed. Biorefinery lignins can be used, if applied correctly, in various high-value applications, beyond their fuel value. This can be addressed by systems comprising given amounts of crystalline cellulose or/and after green and cost-effective upgrading. These features allow a reconsideration of the value proposition and utilization of biorefinery lignins as high-value products in different applications. Overall, attempts to find a lignin "best-for-everything" or a "killer application" for lignins are unreasonable; each lignin type should find its best niche based on its performance in specific applications and production costs.

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Melt spun lignin-based carbon fiber from softwood kraft lignin: Effect of lignin pretreatment and fiber conversion conditions

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Softwood kraft lignin from LignoBoost process was used as precursor for making lignin-based carbon fibers. Different fractionation methods such as ultrafiltration and solvent extraction were used to improve spinnability and conversion process of lignin. Thermal properties and composition of lignin samples were analyzed. Heat treatments in vacuum oven or pelletizing by twin screw extruder were used for devolatilization and improving extrusion performance of lignins. Melt-spinning was performed using monofilament and multifilament extruders. The lignin fibers were stabilized and carbonized under different conditions include stabilization rate, carbonization temperature and tension during conversion. UV and plasma-assisted stabilization methods were applied to decrease the stabilization time. Tensile properties and morphological characteristics of fibers were evaluated. Lignins isolated using 150 kDa membrane filter and butanone solvent produced fibers with highest tensile properties. Tension during conversion significantly increased tensile properties of the produced carbon fibers. Both UV and plasma-assisted stabilization resulted in significant decrease in total stabilization time. Increasing the final carbonization temperature from 1000 to 1600°C resulted in slightly increase in tensile modulus but tensile strength decreased.

Introduction

Lignin as the second most abundant biopolymer is considered as a sustainable and low-cost precursor for manufacturing carbon fiber. The low-cost carbon fiber can expand application of these materials in areas such as automotive industry and construction. Kraft lignin with estimate annual production of about 70 million ton/year, as by product of pulp and paper industry, is the main source of the lignin in the world[1]. Developing LignoBoost process resulted in increased production capacity of pulp mills and producing lignin with higher purity compared to conventional kraft lignin recovery systems[2].

Melt-spinning is considered as a the most cost-effective method for fiber production. Lignin is required to have suitable melt and thermal properties to be melt-spinnable[3,4]. Efforts for improving spinnability of lignin mainly focused on blending lignin with thermoplastic polymers or chemical modification of lignin[5,6]. Immiscibility of lignin with many common thermoplastics is the main limiting factor. Lignin/lignin blend (plasticizing a non-fusible lignin with a fusible lignin) has been suggested as an alternative approach[7]. It has been shown that fractionation of lignin by solvent extraction or ultrafiltration could be an effective method for obtaining lignin with suitable purity and melt characteristics[8,9].

Conversion steps are important parts of carbon fiber manufacturing process. Slow stabilization rate and low tensile properties of the fibers are some of limiting factors in commercialization of lignin-based carbon fibers. Increasing the stabilization rate can significantly reduce the production cost of carbon fibers. Tension during conversion is another important parameter to increase the properties of commercial carbon fibers through increase in orientation along fiber axis. Also, final carbonization temperature can affect the structure and properties of carbon fibers by increasing the degree of graphitization.

The goal of this research is to find the suitable fraction of LignoBoost lignin for melt-spinning and carbon fiber production by means of different fractionation techniques include solvent extraction, pH-fractionation and ultrafiltration. In addition, devolatilization methods of lignin were used to improve continuous spinnability. UV irradiation and plasma treatment of lignin fibers were used to reduce stabilization time of lignin fibers. Effect of tension during conversion process and carbonization temperature on properties of the lignin-based carbon fiber were studied to find the optimum conditions for conversion process.

Experimental

Lignin isolation

All lignin samples were produced from a softwood kraft black liquor using the LignoBoost process[2]. A pilot scale N120 ceramic membrane filtration unit (Orélis) which was equipped with 38 membranes (150 and 15 kDa) was used to produce 150 and 15 kDa permeate lignins. The pH-fractionated lignin was isolated at pH 9.5-11. The solvent extracted samples were isolated from the standard LignoBoost lignin. Methanol and butanone (MEK) were used for solvent extraction and fractions soluble in these solvents were recovered by rotary evaporation. The yields of the methanol and butanone extractions were 69.5 and 51.0%, respectively. All recovered lignin samples were dried at 80°C for 24 hours prior to further processing or characterization.

Characterization of lignin samples

The ash and carbohydrate content of the lignin samples was determined using standard procedures (SCAN standard CM71:09, TAPPI Standard T211). Molar mass distribution of lignin sample was determined by size exclusion chromatography (SEC) using a Water SEC system. The mobile phase was a pH 12 buffer solution. Lignin sample was dissolved in NaOH solution (pH=13.5).

Thermal decomposition of lignin samples was studied using a TA Q5000 thermogravimetric analyzer (TGA). Lignin samples, approximately 10 mg, were heated from room temperature to 105°C at a heating rate of 10°C/min, held at this temperature for 20 min to remove moisture, and then heated to 1000°C at the same heating rate under a nitrogen atmosphere (25 mL/min).

Glass transition temperatures (T_g) were determined using a TA Q1000 differential scanning calorimeter (DSC). Each specimen, approximately 3 mg, was heated from 25°C to 85°C at a rate of 5°C/min under nitrogen (50 mL/min) and held at that temperature for 30 min to expel any remaining moisture in the sample. The sample was then cooled to 25°C and again heated to 260°C at the same heating rate. The second trace was used for the calculation of T_g and the corresponding heat capacity (ΔCp).

Devolatilization and spinning

Effect of different devolatilization methods on properties and spinning performance of the lignins were studied by heat treatment of the lignins in a vacuum oven or pelletizing by twin screw extruders. For heat treatment in vacuum oven, lignin samples were placed in aluminum tray and heated at temperatures of 180-240°C for 1-2 hours under vacuum. A LabTech Engineering LTE20-48 twin screw extruder at temperature profiles of 190-250ºC and screw speeds of 40-400 rpm was used to study devolatilization through compounding by extruder.

Melt-spinning of the lignins was performed using a monofilament MC15 extruder (Xplore Instruments) and a pilot-scale multifilament extruder (Alex James and Associates). The temperature profile of the extruder was adjusted based on the individual lignin's properties from 190 to 240°C.

Conversion process

Stabilization and carbonization

Lignin fibers were oxidatively thermostabilized by heating the samples to 250°C under air at different rates (0.05-2°C/min) and then holding the samples for 15-60 min at 250°C in a KSL-1200X-M Box Furnace (MTI Corporation). The stabilized fibers were carbonized in an ETF 70/18-III (Entech Energiteknik ABs) by heating from room temperature to 600°C at a rate of 1°C/min, heating from 600 to the final temperature at a rate of 3°C/min under nitrogen.

UV and Plasma-assisted stabilization

A Dymax 5000 UV system was used for UV-assisted stabilization study. Lignin fibers (200-300 mg) were exposed to UV light under different exposure times (300, 600, and 900 s). In each experiment the shutter was closed every 30 s, for a duration of 10 s, to avoid over heating the samples. The UV-irradiated fibers were stabilized and carbonized.

Lignin fibers were also stabilized using an atmospheric pressure plasma technique developed by RMX Technologies. Bundles of green fibers were stabilized at rates 0.14-4.5ºC/min which resulted in stabilization times of 2-6 hours.

Characterization of the fibers

The tensile properties of fibers were measured according to the ASTM standard (ASTM C1557-03) using a Dia-stron LEX820 tensile testing system (Dia-stron Ltd). A SU3500 Hitachi scanning electron microscope (SEM) was used to study the morphology of the fibers.

Results and discussions

Properties of lignins

Some of the important physical and chemical properties of the lignin are summarized in Table 1.

Table 1. Key characteristics of the lignin samples.

Lignin source	Carbohydrates (%)	Ash (%)	M_n (g/mol)	M_w (g/mol)	PD	T_g (°C)
LignoBoost	1.5	0.3	2100	5000	2.4	149
15 kDa permeate	0.2	0.2	1030	1830	1.8	122
150 kDa permeate	0.3	0.3	1250	2550	2.0	128
Methanol extracted	0.4	0.3	1230	2450	2.0	120
Butanone extracted	0.1	0.01	1150	2440	2.1	89
pH-fractionated	2.2	0.6	1250	2480	2.0	133

The original LignoBoost and pH-fractionated samples had the lowest purity. The purity was higher for samples from ultrafiltration (permeate samples) and solvent extraction. It is known that some of the impurities remains as insoluble part in solvent extraction processes or separate during ultrafiltration. In general, all samples had high purity and the ash content of the all samples was lower than what has been reported for regular softwood kraft lignin[10,11].

The molecular weight was the highest for standard LignoBoost sample and it was the lowest for the 15 kDa permeate lignin. Methanol and MEK are solvents which dissolve relatively low molecular weight fraction of lignin and the high molecular weight fraction will remain mostly as insoluble part. During ultrafiltration, the 150 kDa filter, due to its larger pore size, will pass larger lignin molecules. Therefore, the molecular weight of 150 kDa permeate is higher than 15 kDa permeate sample. The glass transition temperature of the lignins shows some correlation with molecular weight. However, the T_g was relatively lower in the solvent extracted samples which is mainly due to the plasticizing effect of the residual solvent.

Lignin pretreatment and fiber spinning

One of the major challenges during melt-spinning of lignin is formation of volatiles which interrupt continues spinning. Devolatilization, as heat treatment in vacuum oven, is a common process to decrease the level of volatiles in lignin[3]. Although this method can remove some of the volatiles, but absence of shearing can result in trapping some of the volatiles in the lignin. Therefore, pelletizing by a twin-screw extruder was used to have a more effective devolatilization in a shorter time.

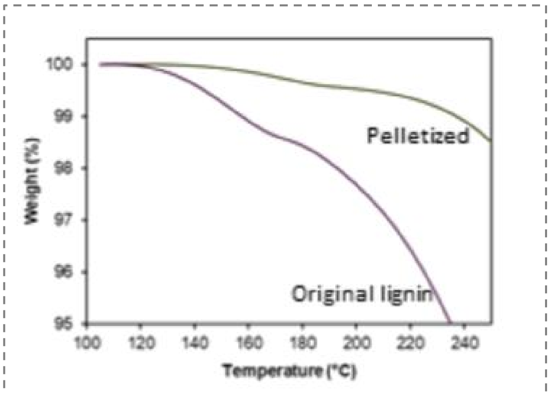

Figure 1. Thermal decomposition of methanol extracted lignin samples before and after pelletizing by twin screw extruder.

Figure 1 shows the initial thermal decomposition profile of the methanol extracted sample recorded by TGA before and after pelletizing in twin screw extruder. As it has been shown the sample pelletized in twin screw extruder has much lower volatiles in the melt-spinning temperature range. The optimum pretreatment condition was different for different sample. The melt-spinning of the pH-fractionated lignin was only possible without any heat treatment, and in monofilament extruder, which could be due to initial high T_g of this sample. The 150 kDa permeate lignin had the best spinnability when pelletized at 190°C with screw speed of 200 rpm. The 15 kDa permeate had better spinnability, in monofilament scale and without any pretreatment, compared to 150 kDa due to its lower molecular weight and T_g. Both solvent extracted lignins had very good spinnability in monofilament extruder. However, only the butanone sample heat treated for 1h at 230°C had good spinnability in multifilament extruder. Volatiles in methanol extracted lignin caused difficulty in multifilament spinning of this lignin.

Conversion and evaluation of fibers

The fibres from pH-fractionated lignin had the fastest stabilization rate (0.5°C/min) and fibres from the MEK extracted sample required slow stabilization rate (0.1°C/min). Results are consistent with molecular weight and T_g of the lignins as lignins with higher molecular weight can go faster under condensation/cross-linking reactions during stabilization. Plasma-assisted stabilization was tried for fibers from 15 kDa permeate lignin and it resulted in 9 h reduction in stabilization time (from initial stabilization of 11 h). UV-assisted stabilization was performed on fibres from methanol extracted and pH-fractionated lignins and according to the results it reduced the stabilization time to half.

The carbon fibers made form MEK extracted lignin and 150 kDa permeate lignin had higher tensile properties compared to other lignins in their optimized conversion process (Figure 2). The tensile properties of these samples are higher than what have been reported in peer-reviewed publications for carbon fiber from melt-spinning pure lignin[12]. These two lignins had high purity and good spinnability which resulted in producing fibers with less defects (Figure 3). The 15 kDa permeate and pH-fractionated lignin had the lowest tensile properties which for the 15 kDa lignin it could be due to lower molecular weight and difficulty in stabilization of this lignin and the pH-fractionated lignin had the highest level of impurities with poor spinnability. Having tension during conversion significantly increased tensile properties of the resulted carbon fibers (Figure 2). The non-linear and heterogenous structure of lignin limit orientation of its molecules along the fibers during spinning. However, tension during conversion can result in some orientation during conversion and increase the tensile properties of the lignin-based carbon fibers.

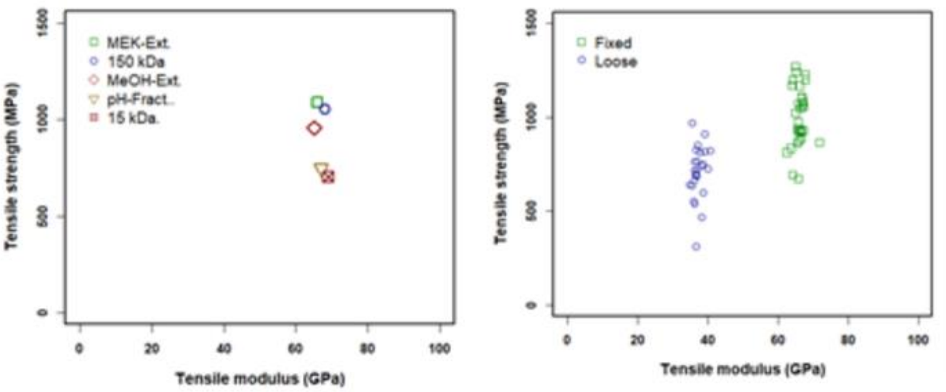

Figure 2. Tensile properties of lignin-based carbon fibers at their optimum conversion conditions: (left) carbon fibers from different lignin precursors and (right) carbon fibers from 150 kDa permeate lignin converted with and without tension (fixed and loose).

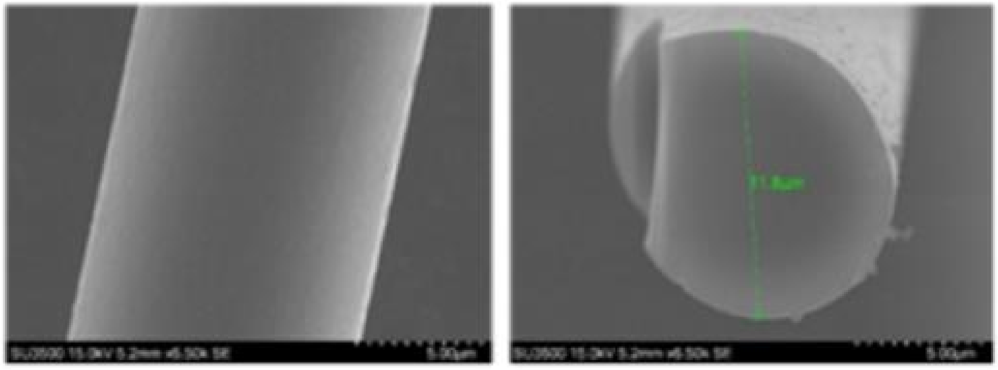

Figure 3. SEM images of carbon fibres made from 150 kDa permeate lignin.

Carbonization temperature is an important factor which can affect the properties of carbon fibers by formation of graphitic structure. Lignin fibers from 150 kDa permeate and methanol extracted lignin were carbonized at different carbonization temperatures. The tensile strength of fibers decreased by increasing the carbonization temperature and the highest values were observed at 1000°C (Figure 4). Different trend was observed for tensile modulus and the tensile modulus slightly increased by increasing carbonization temperature which were in the same range for carbonization at 1200 to 1600°C (Figure 4). This observation could be explained by increasing graphitization during carbonization at higher temperature which result in increase in tensile modulus. However, due to the lack of optimum orientation in graphitic structure and possible developing defects it resulted in decrease in tensile strength.

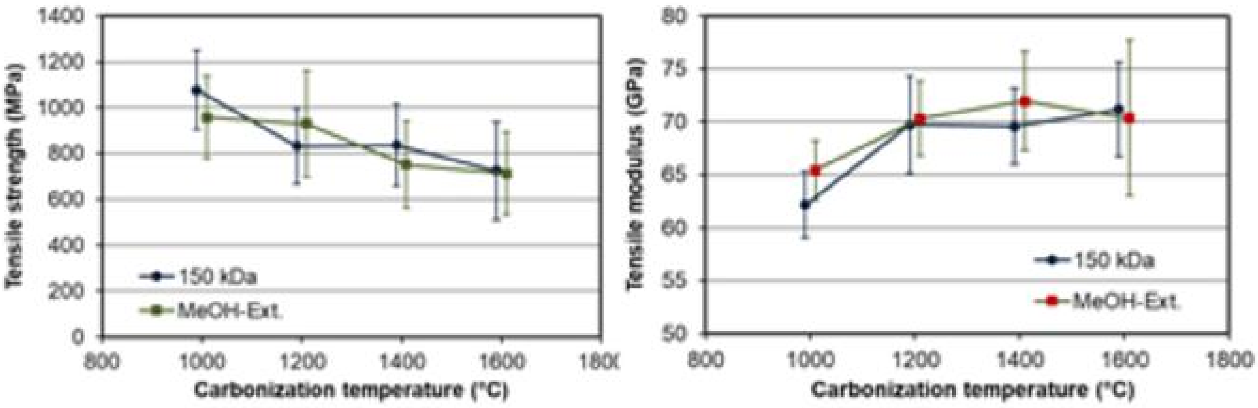

Figure 4. Tensile properties of carbon fibres made from 150 kDa permeate and methanol extracted lignins carbonized at different temperatures.

Conclusion

LignoBoost lignin was fractionated and extracted by different methods to obtain lignins with different properties as precursor for manufacturing carbon fiber. Both ultrafiltration and solvent extraction resulted in obtaining lignins with high purity which was higher than standard LignoBoost lignin. Different devolatilization methods include heat treatment in vacuum oven and pelletizing by twin screw extruder were tested and it was shown that twin screw extruder could be a fast and convenient way for devolatilization of lignin. The solvent extracted and permeate lignins had good spinnability in monofilament scale. However, only heat treated MEK extracted lignin had good spinnability in multifilament spinning. Slow stabilization rate is one of the challenges in commercialization of lignin-based carbon fibers. UV-irradiation and plasma treatment resulted in significant decrease in stabilization time. Tension during conversion improved properties of carbon fibers and resulted fibers had tensile properties higher that what have been reported for melt-spun carbon fiber from pure lignin. The carbonization temperature in the range of 1000-1200°C seems to be the optimum range for producing lignin-based carbon fibers with high tensile properties.

Acknowledgments

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Synthesis of bio adhesive from waste biomass from pulp and paper industry for wood based industry

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Phenol-formaldehyde (PF) resins are characterized by their high strength and moisture resistance. The cost of PF resin, the main factor limiting its use, has been the subject of considerable fluctuation, largely as a result of variability in the world oil market. But there is no trend indicating any long-term reduction of phenol costs. An alternative, cheaper source of phenols would be of great interest to all users of PF resin. There has been a great deal of research performed concerning lignin. An important field of application is in the wood-working industry, especially in plywood and particleboard production in which PF resins are almost exclusively used as the binder. Rice straw contains a high percentage of polysaccharide and lignin. Lignin is a polymer of phenyl propane units, which form a three dimensional network inside the cell wall. Substitution of phenol in PF wood adhesive is certainly the most widely explored avenue of lignin utilization. Lignin-PF formulations have been used in manufacturing particle board, plywood and fibre board. Under certain conditions, upto 40% of phenol in phenol formaldehyde resin can be replaced by lingo-sulphate lignin solids without deteriorating bond properties. To attain an acceptable final product, it is required that lignin react with PF in a high degree. The present paper highlights the efforts made by Indian Plywood Industries Research and Training Institute (IPIRTI) in utilization of lignin available as waste biomass from small agro based mills in producing lignin modified phenol formaldehyde resin (PLF). Lignin-phenol-formaldehyde (LPF) resins were produced by substituting phenol with rice straw lignin in various percentages. Wood adhesive is certainly the most widely explored avenue of lignin utilization. Phenol was replaced by various percentages of lignin to keep the phenolic to formalin weight ratio constant to 1:1.8. 10%, 20% and 30% replacement of phenol by lignin were adopted in making lignin phenol formaldehyde resin (LPF Resin). The plywood panels of 4 mm thick, 30cm X 30cm were made and the panels were subjected to test as per IS: 848:2006, specification for synthetic resin adhesives for plywood (Phenolic and Amino plastics). The results indicated that rice straw lignin was a feasible replacement for up to 30% of the phenol in PF resins.

ORAL

PRESENTATIONS

THURSDAY 25.10.2018

Woody biomass as a sustainable feedstock for biobased chemicals

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We live in a society with an increasing appetite for consumer goods but in a world that has limited resources. Our current linear economic model is based on the extraction of resources from the earth, processing to make articles and then use followed by disposal. Slowly but surely we are transferring our precious resources into environmental burdens - landfills and uncontrolled pollution such as plastics in the oceans. This is not an intelligent use of resources and is not sustainable. We must move to a more circular bio-economic model whereby renewable resources (ideally wastes) are used in green chemical processes to produce safe and effective products that are biodegradable and ideally recyclable.

Bio-wastes include those from forestry and wood-based industries including paper and pulp, as well as MSW and agricultural by-products. These can be seen as renewable resources and can form the basis of future bio-refineries gradually replacing petroleum-based refineries. To fully exploit the concept and make it widely useful while maintaining environmental advantage, we need to use the right technologies to extract the molecular value from the wastes and ensuring that future products from bio-refineries are genuinely green and sustainable. New, energy efficient green chemical technologies that can convert a wide variety of waste streams into valuable chemicals and energy include low-temperature microwave processing and benign solvent extraction and with bio-based platform molecules among the most important targets. Some of the most promising platform molecules have recently been identified and include the exciting new molecule levoglucosenone (LGO) that can be made in one process step from woody wastes. While LGO can be made from fossil resources, the costs of this make it at best a speciality chemical. Unusually, the bio-based equivalent is cheaper and has a lower environmental footprint. Its multiple functionality makes it an ideal platform for downstream chemistry to many possible products of which the dihydro-derivative is the most promising and is now traded under the name Cyrene. Cyrene is a versatile polar aprotic solvent with proven applications in chemical synthesis, polymer processing, cleaning and the production of advanced materials.

In this talk I will talk about Cyrene and some other promising platform molecules that can be made from woody biomass.

Processing 1:

Piloting & equipment design

Pilot scale pretreatment of lignocellulosic biomass: design considerations vs operational challenges

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Due to global warming caused by the use of mineral feedstocks for fuel, chemicals and materials, there is a large interest in processes using second generation renewable biomass feedstocks. In order to release the valuable compounds kept within the biomass, such as glucose and xylose, a certain kind of pretreatment followed by an enzymatic hydrolyzation is needed. Various pilot and demonstration plants have been put into operation around the globe, all aimed at de-risking the scale up to a commercial scale and shortening the time-to-market.

Each pilot plant focusses on different technologies depending on technology push or expected demands. The pretreatment pilot at the BPF can operate with a one or two-stage technology with high temperature / pressure and mild chemical treatment. The pilot unit is a scaled-down model based upon continuous paper and pulp digesters.

Examples of design considerations for this type of pretreatment technology are: Type of feedstock and supply chain; The use of the released C5 sugars and C6 sugars: are those preferably separated or is it ok to have a mixed C5-C6 stream; The efficiency and characteristics of the enzyme cocktail; The selected severity conditions in terms of chemical concentration, time, temperature and pressure; The use of co-solvents such as alcohols or ionic liquids; The setup of the pretreatment process; one or more stages, steam explosion or not.

The above considerations can give rise to several operational challenges, for example:

- Feeding a wet stream of biomass into a high pressure reactor;
- The release of biomass from high to atmospheric pressure;
- The presence of residual non-lignocellulosic material in the feedstock;
- Solid-liquid separations, of which the feasibility and selected separation technique depends on the pretreatment conditions.

Piloting is essential to recognize and mitigate operational challenges before encountering expensive issues at large scales. The relation between design considerations and BPF's experience on operational issues will be discussed in detail during the presentation.

Production of nanofibrillated cellulose reinforced nanopaper using pilot scale Experimental Paper Machine (XPM)

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Fabrications of NFC reinforced nanocomposites and improved properties of final dimensional structures were reported in literature[1,2]. Nevertheless the "centimeter size" of these fabricated dimensional products might be a hurdle to use them in real applications. Thus, in a current study upscaling of NFC reinforced nanopaper has been discussed. Highly flexible pilot scale machine (Experimental Paper Machine), having 150 mesh wire sheet (100 µm pore diameter) was used for the production of nanopaper. The bottleneck of nanopaper production was retention and dewatering of MFC. It was not possible to retain nanoscale NFC (5-30 nm in diameter) on wire sheet. Thus, two approaches were used for high retention and short drainage time, (i) NFC were mixed with pulp microfibers (25 µm in diameter) to increase the first pass wire retention percentage and (ii) cationic starch and silica microparticles were further used as additives. Effect of MFC loading (15-35%), additives (cationic starch and silica microparticles) and machine speeds (1.2-1.8 m/min) were studies. Highest retention, adequate dewatering time and best formation was recorded with the combination of 65% pine, 35% NFC, 1.2% cationic starch and 0.3% anionic silica. Compacted layered structure and aligned fibers towards machine direction were observed using SEM. The effect of aligned fibers on mechanical properties was further evaluated using tensile tester. Hg-porosimetry confirms decrease in average pore diameter after NFC and chemicals addition. This study show that it is possible to upscale the cellulose nanopaper using traditional paper making approach without losing desired characteristic and the fabricated nanopaper could be utilized in various value added real applications.

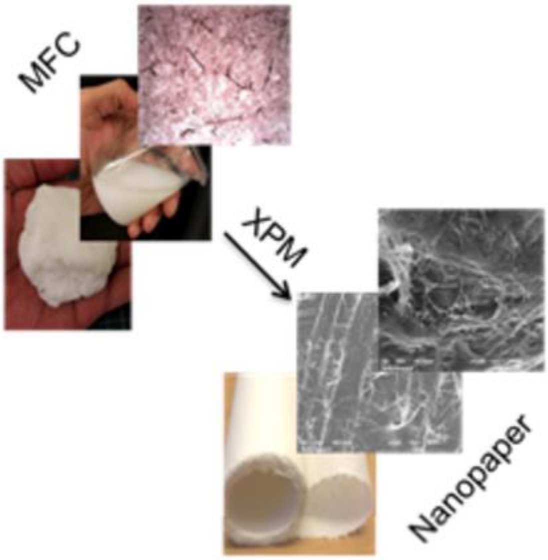

Figure 1.

Acknowledgement

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Increase accessibility for enzymatic hydrolysis of Norway spruce by organosolv pre-treatment in a novel reactor

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Organosolv pre-treatment of lignocellulosic biomass induces separation of high-purity cellulose with only minor degradation and causes lignin to break down by hydrolytic cleavage of alpha aryl-ether links into fragments that are soluble in the solvent system. Lignin removal is important for increasing the cellulose accessibility to enzymes for recalcitrant biomass, but once high cellulose accessibility is achieved, removing lignin is a much less impactful pre-treatment objective. Understanding of substrate characteristics after biomass pre-treatment and their relationship with enzymatic cellulose hydrolysis is important for decreasing costs associated with biomass saccharification.

Conventional pre-treatment reactors are normally limited by long heat-up times, low maximum temperature levels and no possibilities for displacing pre-treatment liquors at high temperature or pressure levels. At RISE PFI, a novel pre-treatment reactor system has been developed as a part of the Norwegian national research infrastructure project NorBioLab - Norwegian Biorefinery Laboratory. The reactor system is termed High Pressure Rapid Heating Displacement Pretreatment Reactor and the reactor system has been designed to overcome the major restrictions of conventional laboratory reactors. The reactor system is considered to be a unique tool for developing new pre-treatment technologies.

Thus, this study compared the organosolv pre-treatment of Norway spruce in a conventional pre-treatment reactor with a novel pre-treatment reactor, by using compositional analysis, enzymatic hydrolysis and scanning electron microscopy (SEM).

The results shows that increasing cellulose accessibility is a more important pre-treatment objective than delignification for effectively releasing sugars from recalcitrant lignocellulose at high yield. The effectiveness of increased cellulose accessibility is due largely to the reactor characteristics which facilitate efficient separation of components and overcome lignin reprecipitation problems by displacing the pre-treatment liquor at high temperature and pressure levels.

Degradation of cellulose by hydrogen chloride gas under elevated pressure in a custom-built reactor

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Acid-catalysed hydrolysis of cellulose was investigated in a custom-built reactor where dry HCl gas could be dosed at a pressure range between 0.1 – 1.0 bar. The mechanism of degradation proceeds by HCl adsorption on the fibre surface, followed by dissociation of HCl in a thin water layer covering the fibres, resulting in subsequent hydrolysis. The effect of water content was also investigated by conditioning the fibres in diverse relative humidity conditions prior to the hydrolysis. The degree of polymerisation (DP) dropped quickly to levelling-off degree of polymerisation (LODP) at room temperature, signalling that all disordered segments in cellulose microfibrils can easily be hydrolysed with HCl gas. Further hydrolysis presumably from the crystallite ends was detected at higher pressures at prolonged time periods (several days). Curiously, higher water contents (up to 10%) in the fibres resulted in significant humin formation from the glucose generated in cellulose hydrolysis. Such levels of humin are rarely detected from reaction mixtures with conventional aqueous acids. The results showed that behaviour of cellulosic fibres under pressurized HCl gas is fundamentally different from the well-established conditions in aqueous hydrolytic systems. By proper understanding on what governs the hydrolysis and its side reactions, HCl gas has potential to become a viable reagent in the future biorefinery. Moreover, gas is easier to recycle and the dry reaction product is easier to purify than in the case of aqueous systems.

Introduction

Degradation of cellulose has always been relevant for biomass related processes but recent trends have exposed two major reasons why degradation *per se* has become a topical subject: (i) for obtaining sugars or commodity chemicals[1] and (ii) for isolating nanocellulose, particularly cellulose nanocrystals (CNCs), from native fibres[2,3] . Many routes to cellulose chain scission exist especially via hydrolysis (Figure 1), with acid hydrolysis being one of the most researched pathways[4]. Concerning CNC production, it typically occurs in a solid fibres / liquid acid system in aqueous 64-65% H_2SO_4. The total hydrolysis of cellulose into glucose, on the other hand, requires 72% H_2SO_4 concentration. Because of such high concentrations, full recovery of the acid is nearly impossible and purification of the desired product from the reaction mixture can be cumbersome. Therefore, acid hydrolysis has generally not been viewed as an optimal industrial solution for cellulose degradation.

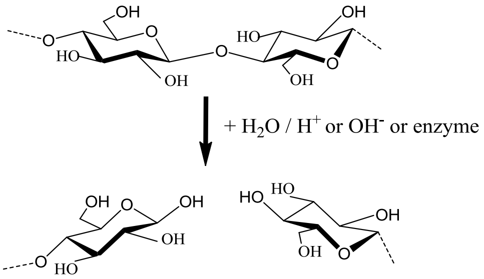

Figure 1. Hydrolysis of cellulose involves addition of water to the anhydroglucose units of cellulose, typically catalysed by acid, base, or enzymes.

Recently, our group published a method for degrading cellulose in a gas/solid system, utilizing HCl vapour or gas[5]. It is based on adsorption of HCl on the fibre surface which is always covered by a thin water layer at ambient conditions. The benefits of this approach were manifold. It is easier to separate and purify the hydrolysed products because the only mass transfer occurs due to HCl adsorption on the fibre and subsequent desorption after removing the sample from HCl atmosphere. The recycling of the gaseous acid is also more straightforward than that of a liquid acid which is virtually always confined in a mixture. We also demonstrated a proof of concept on how such system can be used to prepare CNCs with exceptionally high yields of >97%[5].

The aim of this proceeding is to sum up our recent work on cellulose degradation catalysed by HCl gas with an emphasis on a custom-built reactor for the purpose[5-9].

Experimental

*Materials***.** HCl gas (99.8 %, 10 dm^3, 6 kg) was purchased from AGA (Sweden). 50% aqueous sodium hydroxide, diluted to neutralise acid gas residues, was purchased from AKA Chemicals, Finland. Whatman 1 filter paper (Cat No 1001 150, 150 mm diameter) was used as cellulose source. Whatman 1 is a product of purified cotton linters (measured cellulose content > 99 %).

Reactor design. The reactor was designed to implement safe additions of HCl gas to cellulose samples (Figure 2). HCl gas is added at a default pressure to the glass bottle (Duran pressure plus bottle (-1 to 1.5 bar), Sigma Aldrich), which can be referred to as the sample reactor. Default HCl gas pressure was acquired with degassing process, i.e., releasing air/HCl mixture to flush line after HCl addition prior to the repeating HCl gas addition. Alternatively, vacuum in the sample reactor can be induced prior to the HCl gas addition. Sample bottle was detached after HCl addition. NSH coupling valves were applied for fast detachment/attachment and to ensure the preservation of the gas pressure in the sample reactor (Figure 2). Compressed air and nitrogen gas were used to thoroughly flush the gas lines (PTFE) after HCl gas addition. The HCl gas was eventually neutralized by a system consisting of two alkaline solution containers (the first container being closed). Sirai D105V31 (Asco Numatics Sirai SRI, Italy) dry solenoid valves (body material - PVDF) were applied to control gas flows (red colour in Figure 2). The gas release valve is a safety measure which releases the gas pressure at 4 bar.

*Characterization***.** All characterization methods have been described in detail in the relevant publications[5,9].

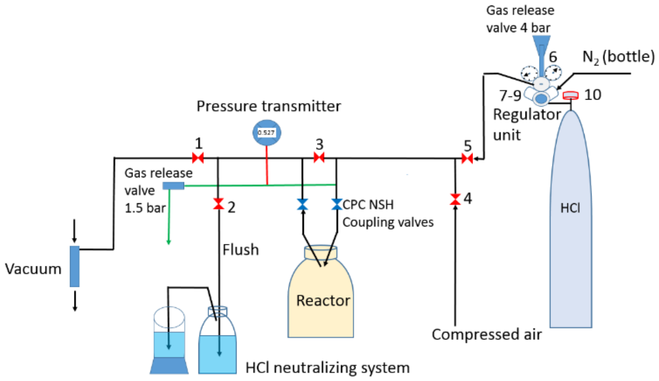

Figure 2. Schematic illustration of the cellulose degradation system with HCl gas. Solenoid valves: (1) vacuum valve, (2) Flush line valve, (3) bypass valve, (4) compressed air valve, (5) HCl gas valve. Control valves (6-9) are applied to adjust HCl gas pressure and to control N2 gas flow (applied to flush the gas regulator unit). The HCl gas bottle main valve is denoted as 10.

Results and discussion

The degradation behaviour under HCl pressure is similar to the reported trends in a liquid/solid system: first, a rapid decline in the degree of polymerization (DP) appears, after which the degradation nearly halts (Figure 3). The traditional explanation for the pattern lies in the semi-crystalline nature of the cellulose microfibrils: the more reactive disordered segments in the microfibril are cleaved at the beginning, followed by a so-called levelling-off DP phase (LODP) where only the recalcitrant cellulose crystallites remain[10]. We emphasize that the degradation takes place very fast: at 100 kPa pressure, the LODP is reached in just 2 hours *at room temperature*. Another major difference from the liquid/solid system is in the morphology of the cellulose substrate: the fibres are not broken into fragments but retain their integrity. In fact, even the paper substrate remains more or less intact after the process, although at after reaching the LODP it becomes very brittle and can easily break to larger pieces when touched upon.

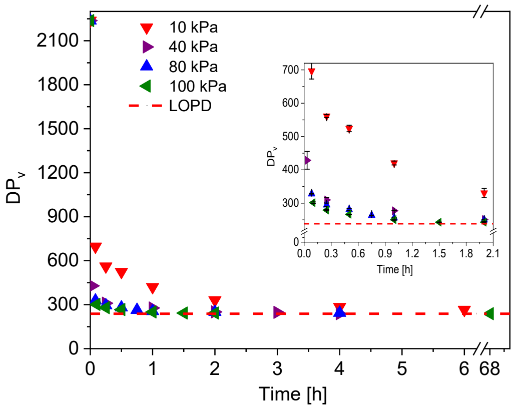

Figure 3. Reduction of the degree of polymerization determined by CED-viscosity (DPV) as a function of reaction time with different pressures. The dashed line represents the LODP determined for cotton linters with the novel method introduced here (lowest DPV with highest HCl gas pressure and practically unlimited reaction time).

The amount of HCl at high pressure (>60 kPa) amounted to 0.07 g HCl per a gram of fibre. The adsorption isotherm was of the Langmuir type, suggesting that a monolayer of HCl was eventually deposited on the fibres. When taking into account the amount of water on the fibres, the HCl concentration in water was at around 60 w-% which is far above the solubility limit. In other words, the water on the fibres had become a solution saturated with HCl with an insoluble reserve of HCl remaining adsorbed[5,9].

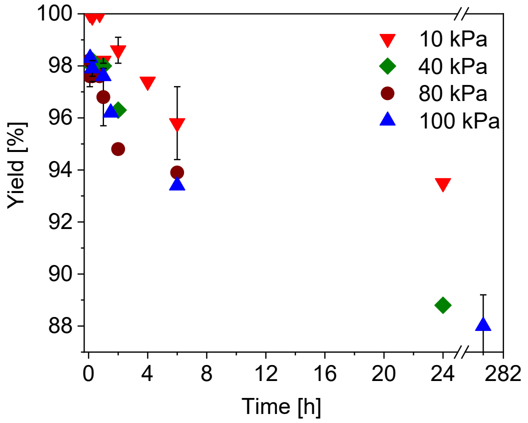

Figure 4. Yields of HCl gas degraded filter paper samples. After HCl hydrolysis (gas), all samples were washed with millipore water, dried overnight at RT, and homogenized prior to the yield analysis and DPV determination.

Although the DP value remains nearly constant after reaching the LODP phase (Figure 3), further degradation – too subtle for the DP measurement – can be detected by analysing the monosugars that are leached from the hydrolysed substrate and the corresponding yield after 15 min water immersion (Figure 4). Hypothetically, the hydrolysis continues at the crystallite ends after the LODP has been reached.

A striking colour formation was detected after prolonged exposures at high (100 kPa) HCl pressure. Figure 5b shows how just the hydrolysis to LODP does not change the colour, but a notable discoloration can be seen after 68 h exposure (Figure 5c). Curiously, added water content in the fibres amounts to almost blackened fibres after long hydrolysis times (72 h) at 100 kPa HCl pressure. The discoloration can be ascribed to the formation of highly chromophoric humins which form via complex pathways from monosugars like glucose[11].

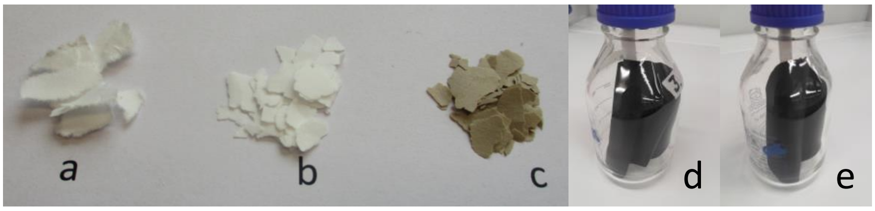

Figure 5. Cellulosic samples before and after degradation with gaseous HCl. a) Untreated Whatman 1 paper, b) Whatman 1 paper after 1.5 h treatment time with 100 kPa HCl pressure, c) Whatman 1 paper after 68 h treatment time with 100 kPa HCl pressure, d) Whatman 1 with 10 w-% water content after 72 h treatment, e) Whatman 1 with 20-% water content after 72 h treatment.

Conclusions

Efficiency and reproducibility of cellulose degradation by HCl gas was demonstrated in a custom-built reactor. The system offers a viable alternative to the conventional liquid/solid system where purification of the products and recycling of the acid is more laborious. Discoloration of the hydrolysed fibres due to humin formation is an issue with long hydrolysis times at high pressures but no colour formation was detected at shorter reaction times just to reach the levelling-off degree of polymerization.

Acknowledgements

We thank Academy of Finland for Key Project Funding (no. 305756).

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Cost-efficient sugar-based cellulase production

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Enzymes remain a significant operational cost in biochemical biorefining processes. Inexpensive streams of sugar are available at many potential biorefining sites, and these could be an optimal raw material for the on-site production of cellulase enzymes. However, simple sugars do not support cellulase production using conventional cellulase-producing strains, necessitating either process or strain improvements. Here we describe improved glucose-based enzyme production processes enabling industrially relevant cellulase production kinetics. Extracellular protein titers of up to 53 g/L could be reached in under 93 hours, representing an up to 260% improvement in productivity over previously reported results. Glucose-produced enzyme is also shown to perform well on pre-treated corn stover. Using the NREL biorefinery model, enzyme production costs are estimated to be $2,8 / kg protein or ¢ 6 / L produced ethanol. Additionally, we briefly discuss how organic nitrogen could be cycled in enzyme production, and how the described processes could fit into existing and emerging biorefining operations.

Introduction

Biochemical biorefining of lignocellulose is slowly but surely becoming an industrial reality, as illustrated by several commercial scale plants recently coming online in the Americas, Europe and China. These plants generally employ cellulase enzymes to hydrolyze the polysaccharide content of lignocelluloses into fermentable monomeric sugars. Enzymes have traditionally been seen as specialty products, purchased from specialty providers and with specialty chemical pricing. The bulk nature of biorefining processes, and the vast quantities of enzymes consumed, necessitate a shift in thinking whereby enzymes are instead seen as a low cost commodity. Many lignocellulosic biorefineries will be either integrated with or adjacent to industry processing sugary or starchy plant material into ethanol. Notable examples include facilities processing bagasse or straw from sugarcane industry, and corn stover from corn wet-milling industry. The 1G ethanol industry processes sugar streams such as molasses and corn starch, the net cost of which are very low to the producer. E.g. the net cost of corn starch to corn wet-millers has varied between $70 and $340 per ton during the past 10 years (average $170 / ton)[1]. Emerging biomass fractionation technologies also produce relatively pure glucose streams, which aim to compete in price with 1G sugars in the future. All these sugars could serve as carbon sources for the on-site production of low-cost cellulase enzymes. Simple sugars such as glucose, fructose and sucrose can be readily sterilized, and are taken up and metabolized rapidly by most microorganisms, potentially allowing fast bioprocess kinetics that are essential for minimizing operational costs. However, such sugars do not induce, but rather repress production of cellulase enzymes by typical fungal production strains such as *Trichoderma reesei*. This problem could be overcome using alternative process designs, such as the transglycosylation process proposed by Genencor[2] and included in NREL's 2011 technoeconomical model of a corn stover biorefininery[3], which modelled glucose-based production of low-cost on-site enzymes. Alternatively, we have shown that recently described transcription factor mutants[4] could be used to engineer *T. reesei* to secrete enzymes on low-cost sugarcane molasses as the sole carbon source[5]. However, to our knowledge, enzyme production kinetics on glucose matching those assumed by the NREL model have not been previously reported. Here we describe improved glucose-based enzyme production processes that reach the required kinetics and could serve as the basis for new on-site enzyme production systems.

Experimental

Bioreactor cultivations and nitrogen cycling

Bioreactor cultivations were carried out in 1L Sartorius Q-series vessels using *T. reesei* strains VTT-BR-C0020 and M2392, which overexpress a mutated XYR1_V821F transcription factor. VTT-BR-C0020 additionally overexpresses the TeCel3A β-glucosidase from *Rasamsonia emersonii*, and the enzymes from this strain were used in hydrolysis experiments. The cultivation temperature was maintained at 28-30°C, pH between 4.0 and 5.0 using 15% H_3PO_4 or 15% NH_4OH, dissolved oxygen between 30-50% using an agitation cascade (400-1200 rpm) and the reactors were aerated with 0.35 LPM compressed air. In all cases, the batch volume was 650 mL and feed containing 550 g/L glucose was fed at 2-4 mL/h after depletion of the batch carbon source. The standard basal medium contained KH_2PO_4 5 g/L, $(NH_4)_2SO_4$ 5 g/L, $MgSO_4$ 0,29 g/L, $CaCl_2$ 0,45 g/L, 3.7 mg/L $CoCl_2$, 5 mg/L $FeSO_4 \cdot 7H_2O$, 1.4 mg/L $ZnSO_4 \cdot 7H_2O$ and 1.6 mg/L $MnSO_4 \cdot 7H_2O$ and Strukol J647 antifoam (1 mL/L). The used nitrogen and carbon sources are indicated in the text. Corn steep solids were from Roquette and yeast extract from Sigma. When *T. reesei* cell mass was used as nitrogen source, washed mycelium from a separate cultivation was added to the batch medium to 2% on a dry-basis and autoclaved with the other components. The amino acid profile from a filtered boiled mycelial sample was analyzed by oxidizing with fresh performic acid and hydrolyzing in acidic conditions (6 N HCl). Subsequently, the samples were derivatized with 6-aminoquinolyl-*N*-hydroxysuccinimidyl carbamate (AQC) reagent and UPLC analysis was performed on an Acquity UPLC system (Waters, Milford, MA, USA) with an Acquity UPLCTM BEH C18 column (2.1 × 100 mm, 1.7 µm) and UV (260 nm) detection. In acid hydrolysis, Asn is converted to Asp and Gln to Glu and these amino acids are consequently reported together. Cysteine and methionine were determined as cysteic acid and methionine sulfone after the oxidation procedure. Total extracellular protein was routinely quantified from sample supernatants using the Lowry-based BioRad DC assay following acetone precipitation with BSA as standard.

Enzyme profile and hydrolysis performance

Enzymes produced using a XYR1_V821F overexpressing strain (M2392) were analyzed using LC-MS by the Proteomics Unit at University of Helsinki, and obtained the peptide-spectrum match (PSM) results compared to TrireV2_FilteredModelsv2.0 *Trichoderma reesei* assembly from JGI to estimate the relative abundance of secreted proteins. Hydrolysis of de-acetylated mechanically refined (DMR) corn stover (NREL)[6], steam exploded poplar (VTT) and α-cellulose (Sigma) was carried out for 72 hours at 45°C, pH 5.0 (100 mM Na-citrate + 0,02% NaN_3) at 10% dry matter as 1 g reactions in 2 mL tubes. The tubes were agitated using the Intellimixer (Elmi) at setting 16u32. The enzymes used were Novozymes Cellic CTec 2 and those produced by *T. reesei* VTT-BR-C0020 (overexpressing both XYR1_V821F and TeCel3A[5]) in glucose-based culture with corn steep solids as nitrogen source. Both enzymes were dosed at 8 mg / g dry substrate solids. The final contents were diluted 10-fold in water, boiled and the released glucose and xylose quantified by HPLC using refractive index detection, a BioRad Aminex HPX – 87H column and 5 mM H_2SO_4 as mobile phase at 0.3 mL/min, 55°C.

Technoeconomic analysis

Data from the NREL corn stover cellulosic ethanol biorefinery model[3] were updated to reflect 2018 prices using CEPCI indicators, and used to construct an Excel model providing as outputs enzyme production costs as a function of bioprocess parameters. The model was used to estimate the costs of producing a kilogram of enzyme protein and the operational cost it would represent to produce a liter of cellulosic ethanol, maintaining other variables as in the original study. The used parameters are described in Results.

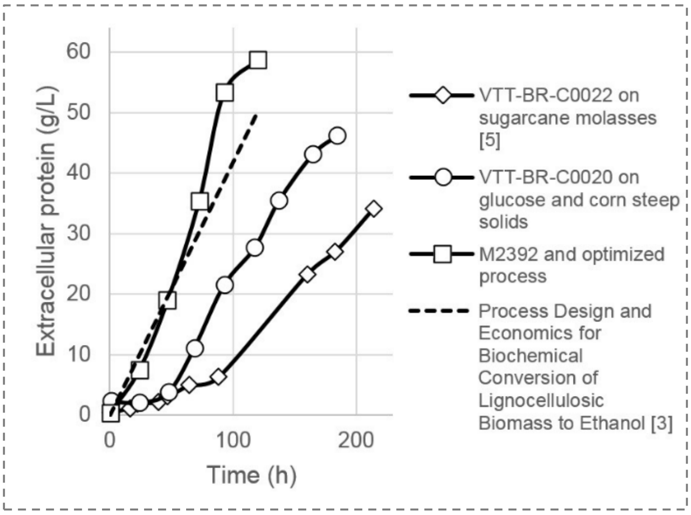

Figure 1. Improved protein production performance in laboratory bioreactor cultivation using XYR1_V821F overexpressing strains.

Results and discussion

Improved enzyme production kinetics on glucose-based media

We have previously demonstrated enzyme production on the low-cost ethanol feedstock sugarcane molasses using a *Trichoderma reesei* strain engineered to overexpress a mutated XYR1_V821F transcription factor under the constitutive *pdc1* promoter[5]. Here, the strain was cultivated in bioreactors on culture media containing corn steep solids (2%) and glucose (2%) in batch phase and using a concentrated glucose feed. Figure 1 shows the extracellular enzyme titer compared to that achieved previously on sugarcane molasses. Additionally, increasing batch phase cell growth (4% glucose, 4% yeast extract, high aeration) and feed rate (up to 2.5 g GLC l^{-1} h^{-1}), a similar strain was able to produce up to 53 g/L of protein in under 93 hours, representing a 260% increase in productivity compared to the results achieved previously[5]. High productivity is crucial for reducing capital and utility costs in enzyme production[3].

Nitrogen cycling in enzyme production

Industrial fermentations generally require a source of organic nitrogen such as corn steep liquor or yeast extract. Industrial processes employing genetically modified (GM) organisms also require a method to inactivate and treat spent GM cell mass. Fermenting Trichoderma reesei inevitably produces fungal biomass in addition to the desired extracellular enzymes. The cells contain a significant amount of intracellular protein, which could serve as an organic nitrogen source for subsequent cultivation batches. The use of spent T. reesei cell mass as an endogenous source of organic nitrogen was therefore explored. Figure 2A compares the relative proportion of amino acids found in commercial corn steep solids, yeast extract and an extract of water soluble protein prepared by boiling *T. reesei* cell mass in water and sterile-filtering the resulting solution. Only minor differences in amino acid frequency could be found between these samples. Bioreactor cultivations were then carried out comparing *T. reesei* cells as an organic nitrogen source directly to the use of corn steep solids and yeast extract. A reference cultivation without a source of organic nitrogen in batch phase was compared to cultures containing 2% of the listed nitrogen sources. The results shown in Figure 2B show that the *T. reesei* cells allowed comparable enzyme production performance to that achieved using corn steep solids and yeast extract.

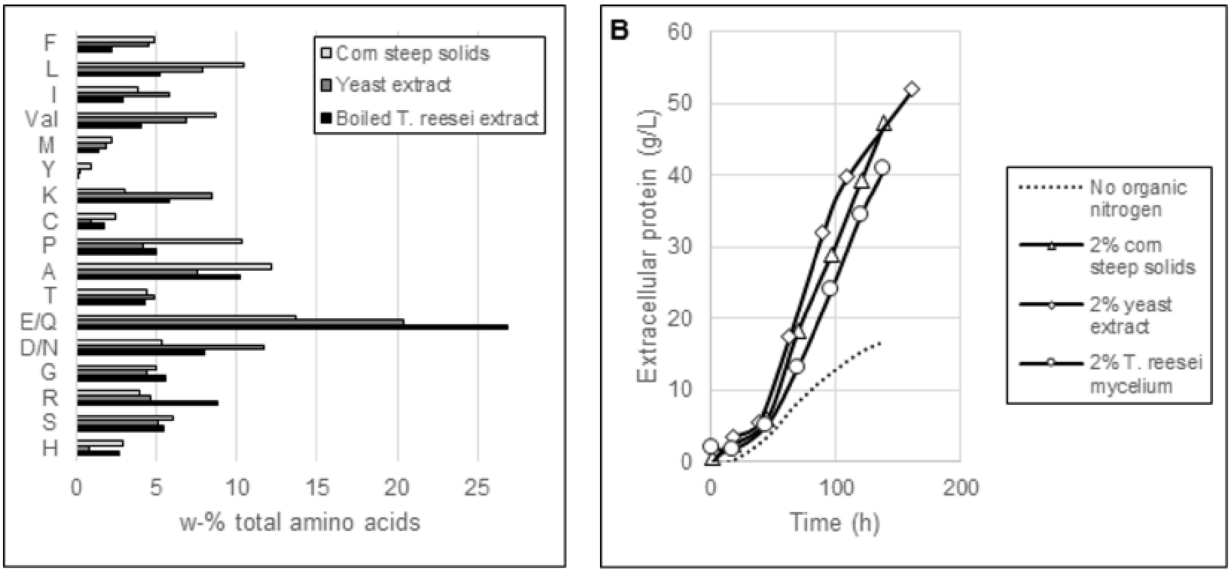

Figure 2. The use of spent T. reesei cell mass as an endogenous source of organic nitrogen. A) Relative amount of amino acids found in corn steep solids, yeast extract and a filtered extract prepared by boiling T. reesei mycelium in water. B) Extracellular protein production of a XYR1_V821F overexpressing strain (M2392) in bioreactor cultivation without organic nitrogen and with 2% alternative sources of organic nitrogen.

Profile of glucose-produced enzymes and performance in hydrolysis

The enzyme mixture secreted by strains overexpressing the XYR1_V821F transcription factor was previously found to contain elevated amounts of xylanase and β-xylosidase[5]. To gain further insight, the enzymes produced by M2932 on glucose and corn steep solids were analyzed by LC/MS (Figure 3) and the data used to estimate the relative abundance of specific proteins. The results indicated an abundance of enzymes involved in the degradation of xylan (shaded grey in Figure 3). Xylan-active enzymes accounted for over 40% of identified PSMs in the sample.

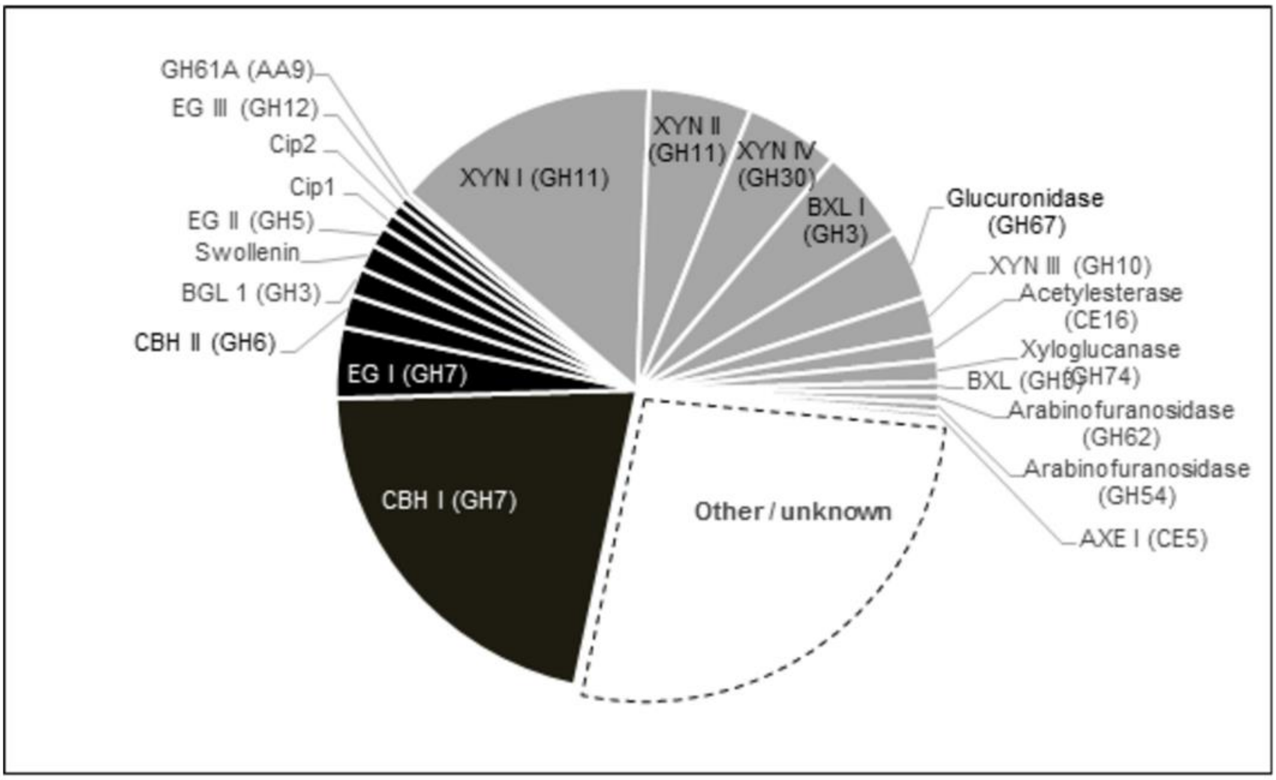

Figure 3. Relative abundance of proteins in the secretome of M2392 in bioreactor culture on glucose and corn steep solids. The supernatant sample was analyzed by LC-MS and the obtained PSMs used to estimate the relative abundance of cellulose-active (black) and xylan-active (grey) enzymes, by comparing the JGI T. reesei genome v.2.0 filtered model transcripts.

To understand the impact of this relative abundance of xylanolytic enzymes on hydrolysis performance, an enzyme mixture produced by the strain VTT-BR-C0020 overexpressing both XYR1_V821F and a beta-glucosidase essential for hydrolysis (TeCel3A) under the same conditions (glucose and corn steep solids) was compared using substrates containing high and low amounts of xylan. De-acetylated, mechanically refined (DMR) corn stover[6] was determined to contain 43,1% glucan, 24,5% xylan. For comparison, steam exploded poplar wood (VTT) and relatively pure commercial α-cellulose (Sigma) were also hydrolyzed. All substrates were hydrolyzed using the previously mentioned glucose-produced enzymes (VTT GPE) and Cellic CTec 2 (Novozymes). The results shown in Figure 4 indicate that the enzyme performed well compared to the commercial enzyme on the xylan-rich corn stover, but glucose yield was somewhat worse on the low-xylan poplar wood and notably worse on purer cellulose. A similar enzyme mixture was previously found to perform well on high-xylan sugarcane straw[5], suggesting that the enzyme is well-suited for grass substrates rich in xylan. Other substrates might require an increase in the relative amount of cellulose-active enzymes for improved performance.

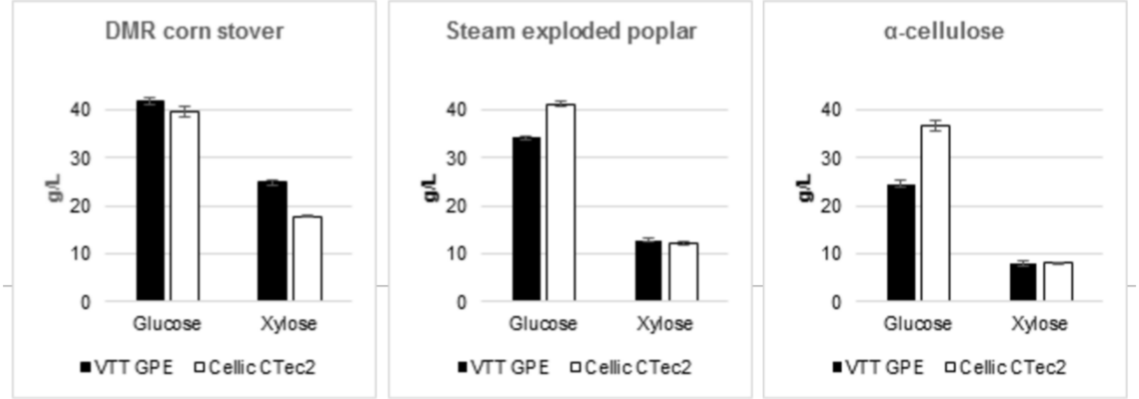

Figure 4. Hydrolysis of A) de-acetylated mechanically refined (DMR) corn stover B) steam-exploded poplar wood and C) commercial α-cellulose using a glucose-produced enzyme mixture (VTT GPE) and a commercial enzyme (Cellic CTec 2). All hydrolysis reactions were carried out at 45°C, pH 5.0, 72 h, 10% total solids.

Technoeconomic evaluation

Glucose-based enzyme production costs were estimated based on the NREL 2011 biorefinery model[3] and process parameters based on experimental data. The assumed input parameters are indicated in Table 1. Crucially, the glucose price was assumed to be the opportunity cost for an ethanol plant directing sugar toward enzyme production rather than the market rate for glucose syrup as assumed by the original model[3]. This value was set at $250 / t, well above the 10-year average net cost of starch for US corn wet-millers[1]. Enzyme yield on glucose (0.3 g/g) and fermenter productivity (0,3 g $l^{-1}h^{-1}$) were conservative estimates based on our experimental data. The latter Figure includes the 2-day reactor downtime associated with bioreactor cleaning and reload assumed in the original study. All other variables, such as those relating to hydrolysis and ethanol conversion, were maintained as in the original study. Besides nutrient, chemical and utility costs, the evaluation included fixed operating costs and capital expenses. The fixed costs included labor, supervision and maintenance costs and property overheads. The capital expenses included indirect and direct costs related to process equipment and site infrastructure and included contingencies.

Table 1. Modified parameters used to estimate enzyme production cost based on the NREL dilute acid corn stover biorefinery model [3], and costs per kilogram of enzyme and per liter of ethanol produced obtained as a result.

Parameter	**Value**	**NREL 2011 [3]**
Inputs		
Glucose price ($/t)	250	570
Enzyme yield on glucose (g/g)	0,30	0,24
Fermenter productivity (g l^{-1} h^{-1})	0,3	0,3
Outputs		
Enzyme production cost ($/kg)	2,8	4,34
Enzyme OPEX per liter EtOH (¢/L)	6	9

The estimate suggests a production cost of $2,8 per kilogram of enzyme, which in turn would signify a cost contribution of ¢6 / liter of 2nd generation ethanol. On-site enzyme production based on low-cost sugar may therefore be a very economical solution and decrease the operational cost of enzymes for biorefineries. Figure 5 shows the cost-breakdown of enzyme cost with the used parameters. Of note is that raw material costs no longer account for the majority of the overall enzyme production cost as in the original model. Rather, costs associated with financing (CAPEX) and operating (Utilities) the bioprocess unit account for more than 60% of total enzyme production cost. This point warrants emphasis – once carbon source price decreases beyond a certain point, bioprocess productivity, which determines the required fermentation volume, becomes the determining factor for enzyme production cost. Therefore, decreasing the cost of carbon source price even further e.g. by using lignocellulosics would have limited impact on enzyme production cost, and might have negative overall impacts if productivity is compromised as a result. The operational cost of enzymes to a biorefinery is obviously also highly dependent on enzyme performance. The performance of enzymes should be evaluated on a case-by-case basis and improved if necessary by engineering the secretome of the fungal strain.

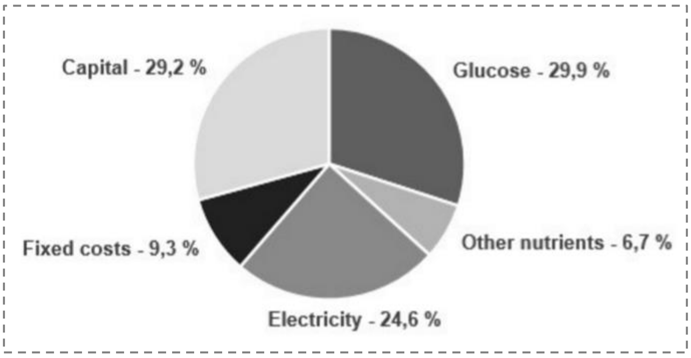

Figure 5. Cost breakdown for glucose-based enzyme production estimated using the parameters listed in Table 1. Raw materials (Glucose + other nutrients) account for 36,6 %, while the remainder is made up by costs associated with financing and operating the bioprocess.

Conclusions

In the present study, we show that *Trichoderma reesei* can be used to produce enzymes at high productivities using glucose as carbon source. The enzymes produced in this way can work well as such on xylan-rich biomass substrates, and could probably be tailored for improved performance on other types of biomass. This enzyme production model would be well suited for biorefineries with available low-cost sugar streams such as molasses or hydrolyzed starch, such as 1G ethanol facilities processing corn or sugarcane. The enzymes produced in this way have shown promise in the hydrolysis of sugarcane straw and corn stover. The use of biomass hydrolysates as carbon source instead would allow closing the carbon cycle for enzyme production, and C6 streams from fractionating pretreatments have been tested successfully for glucose-based enzyme production (data not shown). Sugar streams from standard dilute-acid or hydrothermal processes, on the other hand, are generally too toxic to be used as such in *T. reesei* culture. Nonetheless, the use of bought cheap sugar streams such as molasses could provide satisfactory process economics even to standalone lignocellulosic biorefineries. Here we also demonstrate that it may be possible to close the cycle for organic nitrogen, if spent *T. reesei* cells are inactivated and intracellular protein is recycled back into fermentation. This concept may be of particular relevance to biorefinery concepts that do not directly feed lignin into a boiler and that therefore lack a clear disposal route for genetically modified cell mass. Figure 6 summarized the proposed approach for sugar-based enzyme production.

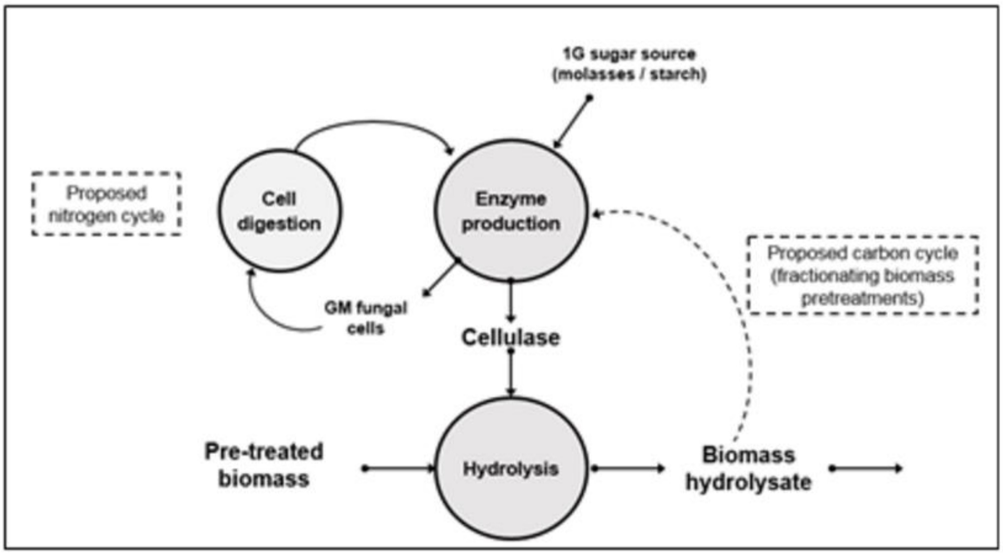
1G sugar source
(molasses / starch)
Proposed
nitrogen cycle
Cell
digestion
Enzyme
production
Proposed carbon cycle
(fractionating biomass
pretreatments)
GM fungal
cells
Cellulase
Pre-treated
biomass
Hydrolysis
Biomass
hydrolysate

Figure 6. Proposed on-site enzyme production using C6-sugars as carbon source

Acknowledgements

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Processing 2:

Fundamentals

Impregnation of wood chips for acidic processes and the influence of wood chips length

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Industrial-size technology for converting logs into wood chips is used by the traditional pulp and paper industry, but also by forest-based biorefineries. The dimensions of wood chips should be optimized to suite a particular type of process. The quality of the wood chips affects the impregnation with cooking chemicals and, for biorefining processes, pretreatment catalysts. The wood chips need be adapted for strongly alkaline processes, such as Kraft pulping, or for acidic processes, such as biorefining. Too small chips, fines and pin chips, and too big chips, overthick and oversized chips, are not useful in industrial-scale processes. The yield of accept chips is of major importance, as it determines how much of the feedstock that is used to make the desired products.

The length of the wood chips has a major influence on the strength of the pulp and the finished products. Industrial wood chips and wood chippers of today are designed for the Kraft process, and therefore for alkaline impregnation of long wood chips. Long wood chips are important for pulp with long fibres and for having as few fibre-shortenings as possible. In alkaline impregnation the thickness of the wood chips is important, as the thickness needs to be even due to that alkaline cooking liquid impregnates equally in every dimension. Too thick chips increase the reject fraction of the pulp.

For acidic processes, the impregnation in the fibre direction is more rapid than in other directions. The length of the wood chips has increased importance for acidic impregnation processes. The strength and, therefore, having a long fibre length is not the most important parameter of the pulp. Shorter wood chips can be beneficial for the impregnation process.

Wood chips for acidic processes were produced using a pilot wood chipper based on a novel modified drum-chipping technology developed for industrial use. Impregnation processes were studied using a specially designed reactor. The potential gains of using wood chips tailor-made for acidic processes will be discussed.

Lignin carbohydrate complexes studies on sulfite dissolving pulps

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Lignin cross-links with different monosaccharide residues in polysacharides forming different linkages in the wood thus providing important properties to the trees. The presence of these LCC (Lignin Carbohydrate complexes) bonds affects the easy separation of wood components during pulping and bleaching operations. The influence of alkaline kraft and acidic sulfite cooking conditions is found to have a different impact on the LCC bonds during the pulping process when producing paper grade pulp. The knowledge of LCC behavior during pulping operation for producing dissolving grade pulp is limited and there is a great scope to study and understand the impact of different cooking conditions on these LCC bonds. Dissolving pulp production using sulfite pulping is well known but studies relating to LCC on dissolving pulps with respect to delignification are limited. To verify the LCC behavior at different delignification rates, a study was carried out on 100% pine heartwood during acid sulfite processes. LCC fractionation was carried out using neutral pH protocol to in-depth investigate the LCC linkages in pine wood and subsequent bisulfite and acid sulfite pulps. From pulp industries perspective and biorefinery application, the LCC studies is a very useful tool which helps to fine tune the process parameters to get more value-added products.

Solubility and compatibility of various lignins in solvents and polymers: Experimental and computer-based evaluation

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Interest in the use of lignin to manufacture derivatives for a wide range of industrial applications has heightened over the past decade. The use of lignin in most cases require solubilization in solvents or dispersion in polymers. However, given the varied range of lignins that are available, decisions on their suitability is still primarily based on the lignin fractionation and recovery method followed by experimental validation. This approach is time and resource intensive and does not provide insights on the variability of lignin solubilities. To provide data to enhance the use of lignins, the behaviours of 45 representative lignin samples collected from Europe and North America were investigated in 20 solvents that were protic or aprotic as well as polar and non apolar. This work reveals the range of variability for solubility parameters that can be expected and illustrates how this knowledge can be used to support product development and lead to cost effective production of lignin derivatives.

Introduction

Several lignin processes and roadmaps have been developed to facilitate its use and to support market adoption for a wide range of applications. It has also been recognized that technical lignins are often crude and refining is necessary for use in many niche and high value applications. Some methods that have been employed to refine lignin include selective precipitation, black liquor ultrafiltration and organic solvent fractionation. The use of organic solvent is widespread and particularly advantageous because different solvents lead to different grade of refined lignins. However, the selection of solvents is mostly arbitrary and complemented with empirical laboratory assessments. In a similar manner, lignin based biocomposite formulations requiring blending of lignin are often prepared in an ad-hoc manner in twin-screw extruders and this is cost intensive. Common methods for lignin modification such as nitration, amination, alkylation, esterification, and phenolation[1], involve solid-liquid phase reactions. Hence, the solubility of a lignin cannot be ignored. Although some data are available on the solubility of various lignins, no evidence or interpretation seems available in open literature on the link between the solubility of lignin and its compatibility in polymers. Lignin solubility and compatibilities have been mainly investigated as isolated phenomena. Thus, there is a lack of available data to predict compatibility and solubility for early stage development of lignin derivatives. A method that can be used for quantifying the solubility and polymer compatibility of lignins is the Hansen Solubility Parameters (HSP), which can be estimated by combining experimental tests and computer-based simulation. The HSP is the mostly used parameter for determining the affinities between materials[2]. It is based on the premise that the total cohesive energy of a solvent is made up of three different intermolecular interactions, namely dispersion (δD), polar interactions (δP) and hydrogen bonding (δH) forces. The total solubility parameter (δT) of a compound can be determined from the three-dimensional solubility parameter using equation (1). All the parameters play a role in solubility and must be considered together. The solubility parameter difference (Ra) is used to compare two substances (within the Hansen space and is defined in equation (2). Lastly, another essential parameter known as the RED number is also used to characterise solute-solvent interactions and can be calculated using equation (3). The term R0 is frequently known as the radius of a Hansen solubility sphere.

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{1}$$

$$R_a = \sqrt{4\,(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + \ (\delta_{H2} - \delta_{H1})^2} \tag{2}$$

$$RED = \frac{R_a}{R_0} \tag{3}$$

Good solvents will have RED ≤ 1. A detailed explanation of HSP is available in the thematic Handbook [2]. Attempts have been made to determine the HSP of some lignins from experiment such as alkali lignin: $\delta_{D,}$ 17.21; $\delta_{P,}$ 12.35; and δ_H, 12.33, as well as genetic algorithm computation with $\delta_{D,}$ 21.71; $\delta_{P,}$ 14.18; and δ_H, 16.93[3,4].These values together with that estimated by Hansen to be $\delta_{D,}$ 21.9; $\delta_{P,}$ 14.1; and δ_H, 16.9 (Hansen, ultrastructure of wood,1998) are the most utilized for solvent selection, including the study by Duval on the fractionation of Kraft lignins[5]. A major drawback of previous HSP determination is that the influence of factors that affect lignin solubility are not taken into account. Lignin solubility is known to be influenced by the molecular weight, temperature, ionic strength and the ratio of numbers of phenolic hydroxyls to phenylpropane units in the macromolecules[6], which in turn depend on the biomass species, lignin extraction and recovery methods.

Therefore, generalization about lignin solubility parameter and its extension to applications should not be done without knowledge of the differences between technical and commercial lignins.

The objective of this work is to determine the HSPs with respect to lignin types and examine their compatibilities in polymers using computer-based evaluation.

Experimental

Materials

Lignins

The lignins used in this study originate from different biomass sources that were fractionated and recovered with different methods as illustrated in Figure 1. They include softwoods (26), hardwoods (11) and agricultural biomass (8). The fractionation methods employed for the lignin fractionation include Kraft pulping, bisulphite pulping, supercritical treatment, Organosolv.

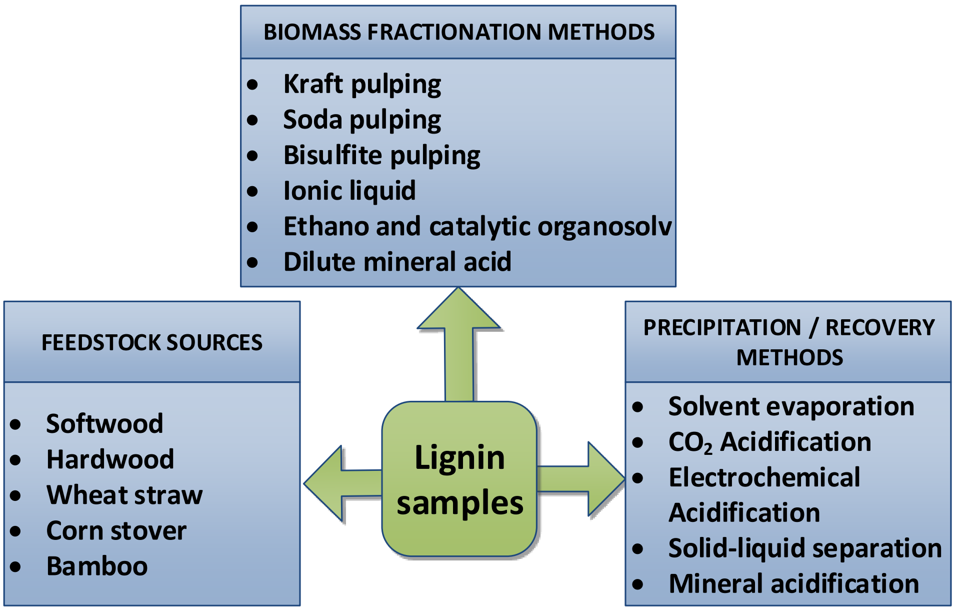
BIOMASS FRACTIONATION METHODS
Kraft pulping
Soda pulping
Bisulfite pulping
Ionic liquid
Ethano and catalytic organosolv
Dilute mineral acid
FEEDSTOCK SOURCES
Softwood
Hardwood
Wheat straw
Corn stover
Bamboo
Lignin samples
PRECIPITATION / RECOVERY METHODS
Solvent evaporation
CO2 Acidification
Electrochemical Acidification
Solid-liquid separation
Mineral acidification

Figure 1. Classification of lignins used for determination of Hansen solubility parameters

Solvents

The solvents used in the experiments were selected in a manner to ensure that those with Polar Protic (PP), Polar Aprotic (PA) and Non Polar-Aprotic (NA) were included. Importantly, solvents that have been used or reported for lignin solubilisation were included. The PP solvents were aniline, ethanol, methanol, 1-butanol, acetic acid, isopropanol, methyl isobutyl ketone and distilled water. The PA solvents are

dimethyl formamide (dmf), dimethyl sulfoxide (dmso), tetrahydrofuran (thf), dimethyl carbonate, acetic anhydride, acetone, acetonitrile, dichloromethane, ethyl acetate. Lastly, the NA solvents are chloroform, hexane and toluene.

Method

Experimental

Solubility experiments were conducted by introducing 250 ±1 mg of each lignin into separate Eppendorf tubes of 15 ml volume. Subsequently, 2.5 ml of the selected solvents are pipetted into the tube and it is closed up. To achieve a dissolution of the lignin, each of the tube is vortexed at a predetermined condition for 20 seconds. The tubes are then placed in a sonicator at room temperature for a minute prior to centrifuging at 10,000 rpm for 5 minutes. The tubes are then visually inspected and the condition classified as insoluble, partially soluble, majority soluble or entirely soluble.

Correlation method

The HSP computation method as well as the radius for each lignin is based on the qualitative description from the experimental procedure. The degree of interaction with the selected solvents whose HSPs, are known and reported in literature is tested and computer algorithms embedded in the HsPIP software applied to calculate the HSP and radius of each lignin. The centre of mass of the sphere is obtained from the in-built optimization method.

Results and discussion

Variability of HSP parameters

Significant variability exists in the computed HSP for the different lignins as shown in Figure 2. The dispersion (δD) parameter ranged between 1.78 and 24.18 MPa1/2, the polar interactions(δP) between 7.78 and 24.11 MPa1/2 and the hydrogen bonding (δH) parameter between 6.42 and 32.44 MPa1/2. The narrowest and widest radius are 5.1 and 19.9 MPa1/2 respectively. It was also possible to identify some trends such as similar HSPs for some lignins that originated from the same recovery process, this trend was also seen in some cases where the feedstock was changed e.g. lignin from a dilute mineral acid pretreatment process when wheat straw and bamboo where processed. All commercial softwood lignins had close dispersion (δD) parameters, with an average of 20.6 MPa1/2 ± 5%. However, the polar and hydrogen bonding terms had wider disparities. Lignosulfonate had the highest hydrogen bonding term (32.3 MPa1/2). The highest difference in radius observed for all the lignin samples from commercial scale processes was 8.5 MPa1/2. There also seem to be a consistent difference in radius between hardwood (HW) and softwoods (SW) for the commercialized lignin recovery technologies, i.e. RHW -RSW ≈ 3.5 MPa1/2.

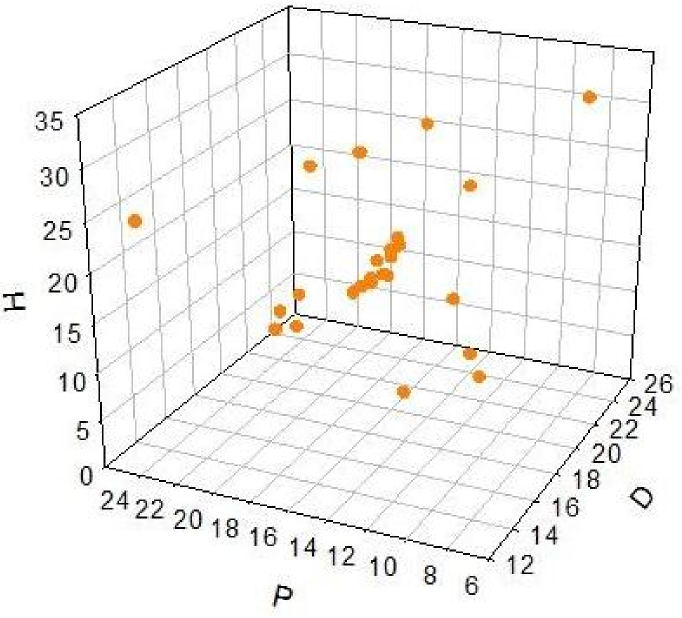

Figure 2. Variability of Hansen solubility parameters for the different lignins

An indication of the possibility to solubilize the lignin in the wide range of tested solvents is the radius. As expected, unwashed lignin exhibited higher solubility in polar solvents and it is necessary to ascertain if this is due only to the impurities alone or bounded sodium on the lignin molecules. Differences in the behaviour of the three selected lignins are illustrated in Figure 3.

The small radius exhibited by ionic liquid lignin is similar to other near native forms of lignins. To further determine the possible causes of differences in HSPs for lignins that are precipitated from the same black liquor, some experimental trials were performed. It was possible to that differences in precipitation agents could lead to differences in that of the solubility parameters (δD, δP, δH, R0): CO_2 precipitated (18.8;16.4;15.3;11.5); H_2SO_4 precipitated (19.5;12.4;14.1;10.0) and HCl precipitated (21.7;16.7;15.9;15.9).

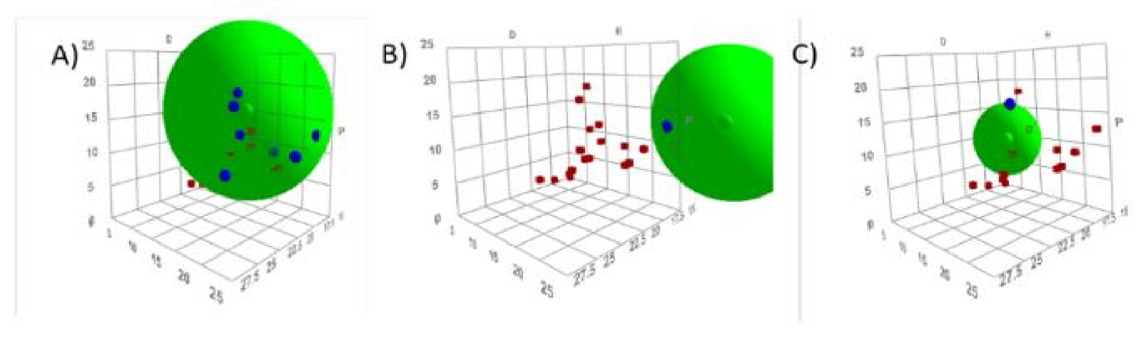

Figure 3. Differences in the sphere centre of mass and radius for A) Hardwood Kraft lignin B) Softwood Kraft lignin and C) Ionic liquid lignin.

Impact of Lignin HSP on a polymer application

Compatibility of lignin in polymer formulation for plastic applications can be seen from two different point of views that are interdependent. Firstly, the dispersion properties of lignin in the polymers must be suitable. Secondly, the glass transition temperature (Tg) of both the lignin and other constituents must be close enough to have an extrusion without the denaturation of any or chemical modification of the native form. A preliminary evaluation from the standpoint of dispersion was carried out by comparing the interaction radius of all the studied lignins with those for polypropylene (PP), Polyethylene terephthalate (PET) and polyethylene (PE). It was observed that the near native forms of the lignins had better compatibility (smaller interaction radiuses) with the three polymers. The calculated preferential order of compatibility with lignin is PET > PE > PP. It is also possible that prior modifications of the lignin could lead to differences in the order of their ranking.

Conclusion

This work has shown that determining the Hansen Solubility Parameters for a wide range of lignins can enhance the solvent selection process for fractionation as well as prediction of blendability of lignin in various polymers. In addition, the greatest variability arises from the hydrogen bonding term within the molecular structure of lignin. Even though overlaps exist in the 3D Hansen solubility space for different lignins, the interaction radius is wide enough in many cases to have a significant impact when producing derivatives.

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Digging in the structure and functionality of lignocellulosic raw material – from academic knowledge towards industrial applications

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The pulp and paper industry thrive upon well-established processes, which Incremental improvements has gradually changed toward higher quality and less environmental impact.

To make a paradigm change, exploit new fields of commerce and lay the ground for a sustainable cellulose based society, a deepened knowledge on the molecular and supermolecular behaviour of the materials is needed. Here we will present findings, and future pathways, in basic research leading towards new exploits.

In the last few decades solid state NMR has been vital to understanding the variations in supramolecular structure and crystallinity of cellulose. The deeper understanding of the supramolecular structure of the fibrous material has enabled us to develop new strategies for pulping, making it possible to tailor pulp properties for applications outside the realm of papermaking, for example increased cellulose solubility.

The exploitation of lignin as a raw material for high value products is not yet fully developed. It could be argued that critical properties of the material, and their linkages to analytical results is not fully understood. We aim at developing methods that provide analysis results that correlate with product properties, enabling tailored lignin qualities with desired properties for product development. The main analytical tool is solution state NMR spectroscopy, for which we are constantly applying new modes of measurements for a growing class of modified samples.

The next step in digging deeper into the structure and functionality of lignocellulosic raw material and products will employ the X-ray techniques SAXS and WAXS, recently installed at RISE Bioeconomy.

By combining analysis results describing the characteristic and behaviour of lignocellulosics in both solution and in the solid state, a better understanding of critical properties throughout the entire process chain for adding value can be obtained.

Results from initial measurements will be presented and future possibilities discussed.

Processing 3:

Separation, purification and recovery

Recovery of high-added value functional monomeric lignin derivatives from lignin oil: a comparison of separation technologies

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VITO's research activities are dedicated to valorization of biomass through conversion of lignocellulose into value-added bio-aromatics, primarily for use as building blocks within the chemical industry. Depolymerization of lignin typically results in complex mixtures comprising a wide array of phenolics, bearing a variety of oxygen-based functionalities and covering a broad range of molecular weights. However, in many cases, valorization of these lignols can only be pursued from well-defined fractions. In this context, the principal focus is the development and demonstration of membrane processes for fractionation and purification of lignins and lignin degradation fragments to enable the use of these molecules in chemical and materials applications.

VITO is co-initiator of Biorizon, an industry driven Shared Research Center, focusing on technology development for the production of functionalized biobased aromatics for performance materials, chemicals & coatings supported by a Roadmap, inspired by an **industry driven community. As the leading institute, VITO coordinates the development of lignin derived bioaromatics by its own technology and collaboration with many different technology providers (www.biorizon.eu).**

Valorization of biomass calls for development of new and/or optimized process technologies. Cost-effective separation processes are of utmost importance to separate biomass components on an industrial scale

Being involved in various national and international running initiatives in which different depolymerization processes of wood/lignin are envisaged, more insight is gained in the potential of membrane processes in the value chain of wood/lignin towards bio-based aromatics. The separation efficiency of commercial polymeric and ceramic membranes with carefully selected molecular weight cut-offs and surface affinity is evaluated and demonstrated at a larger scale aiming at a proof-of-concept of the membrane-based fractionation/purification, either to fractionate/purify mixtures of lignin derivatives or to recover reagents from waste streams back into the process. An important aspect using membrane separation technologies is to benchmark this technology with more traditional separation methods like distillation and extraction.

The lignin oil issued from the reductive catalytic fractionation of lignocellulose, the so-called 'lignin-first' biorefinery, as developed by KULeuven, contains a limited number of high-added value lignin-derived monomers, of which the functionality depends on the catalyst used. In this talk, membrane separation technology is compared with the more traditional separation technologies, i.e. extraction, distillation to recover the monomeric compounds from the lignin oil. Attention will be paid to quality of the products produced (purity, properties) and energy consumption.

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Hydroxy carboxylic acids from spent alkaline pulping liquors

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An efficient chromatography based process for the selective recovery of pure single hydroxy carboxylic acids from spent alkaline pulping liquors (black liquor) is introduced. All major acids are recovered as pure single compounds without need for any chemical modifications. This has not been achieved earlier, although purified hydroxy acid mixtures have been produced. Moreover, lignin and spent pulping chemicals are recycled back to the pulping process, and no chemicals that would interfere with the pulping process are needed.

Hydroxy acids (degradation products of polysaccharides) are formed during chemical pulping of wood under alkaline conditions and end up into black liquors. Annually, almost 200 Mt (as dry solids) of black liquors are produced; 10 % of this is sodium salts of hydroxy acids, the rest is lignin and spent pulping chemicals. Currently the acids are burned in the recovery boilers of the pulp mills. However, the acids have low calorific values and are valuable platform chemicals. Thus, their recovery would be highly beneficial. The main hydroxy acids are glycolic, lactic, 2-hydroxybutyric, xyloisosaccharinic, and α-glucoisosaccharinic acids.

In this work, the selective recovery of single hydroxy acids is done using chromatographic separation and ion exchange. No other separation methods, except for evaporation for feed concentration, are used. As first step, lignin and the spent pulping chemicals are separated from the hydroxy acids using chromatography. In case of soda black liquor the removal level is over 95 % for both. The hydroxy acid salts are then converted to free acids by means of ion exchange to enable their selective separation.

The chromatographic separation of single hydroxy acids from the acid mixtures is done using polymeric adsorbents and ion exchange resins as separation materials. Acids of high purity can be produced with good yields. Using batch chromatography and, for example, 95 % purity limits, the yields for glycolic, lactic, 2-hydroxybutyric, xyloisosaccharinic, and α-glucoisosaccharinic acids were 99 %, 99 %, 100 %, 50 %, and 90 %, respectively, in case of birch soda black liquor. Pure acetic and formic acids were also obtained.

These results demonstrate that single hydroxy acids with high purity can be recovered efficiently from black liquors without any chemical modifications. So far the process has been demonstrated with a batch process. Improved separation efficiency can be obtained with more advanced chromatographic process schemes.

A-Recovery+ - the next generation of chemical recovery cycle

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The chemical recovery cycles in kraft pulp mills are being closed to a greater extent for both economic and environmental reasons. This presentation introduces the novel A-recovery+ concept that allows for further closure of the cycle, while creating new opportunities for side-stream valorization and waste stream reduction by optimizing the Na/S-balance. The concept is justified with tangible mill balance examples and feasibility calculations.

Introduction

The A-recovery+ concept allows for further valorization of the side-streams in a kraft pulp mill through the creation of additional chemical cycles. The concept includes purification of raw methanol into commercial grade bio-methanol, sulfuric acid (H_2SO_4) from non-condensable gases (CNCG), and lignin recovery from black liquor.

In addition to internal production of concentrated commercial-grade sulfuric acid that can be used even in the demanding chlorine dioxide (ClO_2) generator, the sulfuric acid plant provides an environmentally and economically sound way of managing the Na/S-balance of a pulp mill. In mills with a sulfur surplus, the balance is currently corrected through dumping of recovery boiler fly ash. The ash consists mainly of sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3), which means that valuable sodium is lost in addition to sulfur. The lost sodium has to be made up with NaOH. When sulfuric acid is produced from CNCG, the sulfur that normally is returned to the chemical recovery cycle when the gases are combusted in the recovery boiler is removed from the cycle. Sulfuric acid production thus reduces or even eliminates the need for ash dumping.

The sulfuric acid plant can also be used to create spare sulfur capacity when more sulfur is removed from the cycle than enters it from other sources. Spare sulfur capacity enables optimization of make-up chemical use because internal Na_2SO_4 streams can be utilized as sodium make-up instead of purchased sodium hydroxide (NaOH).

Internal sulfuric acid production also allows the recovery of high-quality lignin without compromising the environmental performance of the mill as a result of dumping vast amounts of recovery boiler fly ash. The recovery process for high-quality lignin consists of lignin precipitation from black liquor with carbon dioxide, separation of the precipitated lignin through filtration, as well as acid washing and drying of the lignin. In the acid washing step, H_2SO_4 is used, and most of the added sulfur is returned to the evaporation plant together with the filtrates. Lignin recovery enables pulp mills to replace fossil fuels in the lime kiln or to achieve additional revenue by selling high-quality lignin to external customers as a raw material for advanced bioproducts.

Raw methanol originating from the kraft cooking process is currently used at the mill as a support fuel. With a patented advanced mineral oil based extraction process, the raw methanol can be purified into commercial-grade bio-methanol, which meets the high quality requirements set for the chlorine dioxide generator as well as for the global markets. The methanol currently used in the chlorine dioxide generator is the last fossil-based chemical limiting the establishment of a completely fossil-free pulp mill.

This presentation demonstrates the feasibility of integrating the A-recovery+ concept into a reference softwood kraft pulp mill.

Method

The chemical balances and feasibility calculations shown in this presentation are calculated for a reference softwood kraft mill with a pulp production of 1.4 MADt/a. The values are chosen to represent a typical modern softwood kraft mill. The Na/S balance of the reference mill used in the calculations is shown in Table 1.

Table 1. Na/S balance of the reference mill

Losses	**Na kg/Adt**	**S kg/Adt**	**Na kg/Adt**	**S kg/Adt**
Wash loss	3.24	0.31		
Dregs and Grits	0.29	0.08		
Flue gases	0.09	0.25		
Losses in ash dumping	5.19	3.51		
Make-up				
NaOH make-up			8.35	
AUX fuel (oil, gas, gasifier)			0.01	
Tall oil plant				3.76
$MgSO_4$				0.27
Wood			0.40	0.10
Water			0.05	0.02
Salt-cake make-up			0	0

In the chemical balance calculations, it is assumed that the recovered lignin is sold. If lignin is burnt in the lime kiln, part of the sulfur in the lignin is returned to the chemical recovery cycle as calcium sulfate. The Cl/K balance has been excluded when calculating the required amount of ash to be dumped.

The chemical prices and operating costs shown in Table 2 are used in the feasibility calculations, while the total investment costs (EPCC) shown in the results are estimates with an accuracy of ±40%. It is assumed that the lignin recovery debottlenecks the recovery boiler and thus the operating cost of the lignin plant does not include the loss of black liquor heating value. The same assumption holds for a greenfield mill, where the recovery boiler is sized smaller compared to the recovery boiler for the same pulp production without lignin recovery. However, the benefits of debottlenecking or revenues from increased pulp production for the complete mill investment have been excluded.

Table 2. Calculation basis for the chemical balance and feasibility calculations

Calculation basis		
ClO_2 process	R10	
By-product Na_2SO_4	t/d	55.90
H_2SO_4 consumption	t/d	108.46
ClO_2 plant	kg/ADt	10.50
Bleaching	kg/ADt	5.00
Tall oil plant	kg/ADt	12.00
Methanol purification	kg/ADt	0.82
CNCG amount	kg S/ADt	4.68
Raw methanol (20 % water content)	kg MeOH/ADt	8.80
Lignin recovery		
Capacity	tDS/d	200.00
H_2SO_4 consumption	kg H_2SO_4/ kg lignin	0.20
Lignin product sulfur content	w-%	1.70
Lignin product sodium content	w-%	0.10
Chemical prices		
NaOH	€/t	583
H_2SO_4	€/t	80
MeOH	€/t	400
Lignin	€/t	315
Ammonium sulfate	€/t	200
Operating costs		
Lignin recovery	€/ADt pulp	4.79
MeOH purification	€/ADt pulp	0.50
Sulfuric acid production	€/ADt pulp	0.35

Results and discussion

Chemical balance

Error! Reference source not found. shows the incoming and outgoing chemical streams at the reference SW kraft pulp mill. In the initial case, the excess sulfur is purged from the chemical cycle in the form of recovery boiler ash. Sodium hydroxide is used as a make-up chemical to replace the sodium that is lost due to ash dumping.

Figure 2 shows the Na/S balance of the reference mill after integrating a 200 tDS/d lignin recovery plant into the mill. There is a significant increase in the need for recovery boiler ash dumping from 70.36 t/d to 119.80 t/d. To replace the lost sodium, the increase in NaOH make-up would be 25.34 t/d.

The negative effect of the lignin plant on the chemical balance of the mill can be counteracted by integrating a sulfuric acid plant into the mill. Figure 3 shows the balance when a lignin recovery plant, methanol purification plant and a sulfuric acid plant are integrated into the mill. The methanol purification plant increases the CNCG release from the reference mill by 0.44 kg S/ADt to a total of 5.12 kg S/ADt. The sulfur content in the CNCG is larger than the sulfur input through lignin recovery, and thus the fly ash dumping and NaOH make up needs are decreased in comparison to the reference case.

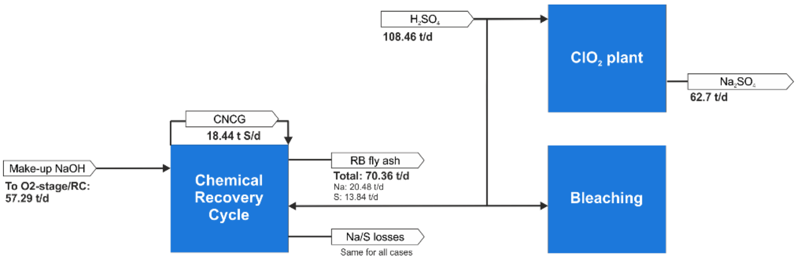
H$_2$SO$_4$
108.46 t/d
ClO$_2$ plant
Na$_2$SO$_4$
62.7 t/d
CNCG
18.44 t S/d
Make-up NaOH
To O2-stage/RC:
57.29 t/d
Chemical Recovery Cycle
RB fly ash
Total: 70.36 t/d
Na: 20.48 t/d
S: 13.84 t/d
Bleaching
Na/S losses
Same for all cases

Figure 1. Chemical balance of the reference soft wood kraft mill

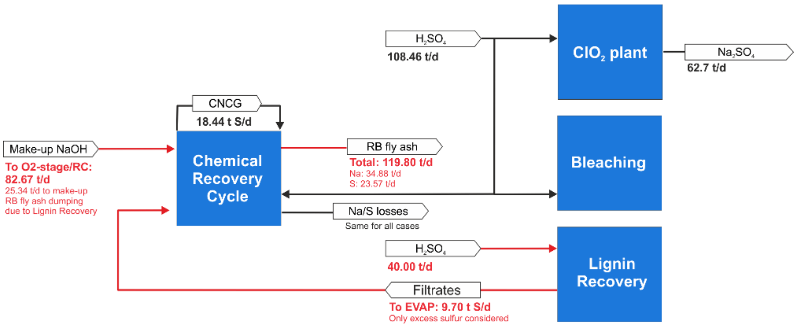
H$_2$SO$_4$
108.46 t/d
ClO$_2$ plant
Na$_2$SO$_4$
62.7 t/d
CNCG
18.44 t S/d
Make-up NaOH
To O2-stage/RC:
82.67 t/d
25.34 t/d to make-up
RB fly ash dumping
due to Lignin Recovery
Chemical Recovery Cycle
RB fly ash
Total: 119.80 t/d
Na: 34.88 t/d
S: 23.57 t/d
Bleaching
Na/S losses
Same for all cases
H$_2$SO$_4$
40.00 t/d
Lignin Recovery
Filtrates
To EVAP: 9.70 t S/d
Only excess sulfur considered

Figure 2. Chemical balance of the reference mill with a 200 tDS/d lignin recovery plant

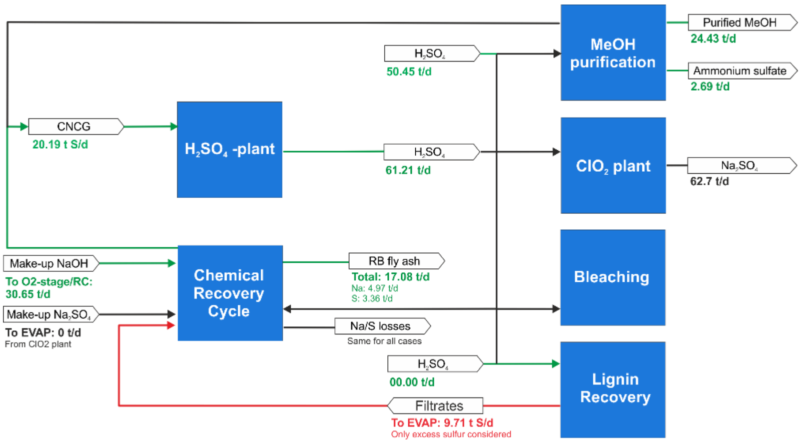
MeOH purification
Purified MeOH
24.43 t/d
Ammonium sulfate
2.69 t/d
H$_2$SO$_4$
50.45 t/d
CNCG
20.19 t S/d
H$_2$SO$_4$ -plant
H$_2$SO$_4$
61.21 t/d
ClO$_2$ plant
Na$_2$SO$_4$
62.7 t/d
Make-up NaOH
To O2-stage/RC:
30.65 t/d
Make-up Na$_2$SO$_4$
To EVAP: 0 t/d
From ClO2 plant
Chemical Recovery Cycle
RB fly ash
Total: 17.08 t/d
Na: 4.97 t/d
S: 3.36 t/d
Bleaching
Na/S losses
Same for all cases
H$_2$SO$_4$
00.00 t/d
Lignin Recovery
Filtrates
To EVAP: 9.71 t S/d
Only excess sulfur considered

Figure 3. Chemical balance of the reference mill with 200 tDS/d lignin recovery, methanol purification and sulfuric acid plant

Naturally, the need for purchasing H_2SO_4 is also reduced as a result of internal H_2SO_4 production at the mill. For the reference mill, this would mean that the amount of purchased H_2SO_4 would be reduced by more than half in comparison to the initial case. The H_2SO_4 production can be further increased if molten sulfur is used as raw material in addition to the CNCG.

Economic feasibility

Table 3 shows the economic feasibility of the separate A-recovery+ processes and the feasibility of the overall concept. Integrating a sulfuric acid plant into the reference mill results in significant savings in the NaOH make-up costs by avoiding sodium loss from ash dumping and because some of the sodium can be replaced with internally available sodium sulfate. The cost savings in make-up chemicals are larger than the savings from the reduced need to purchase H_2SO_4. In fact, the payback time of the investment is more sensitive to the NaOH price than to the H_2SO_4 price.

The economic feasibilities of methanol purification and lignin recovery are reasonably good considering the conservative prices used, global market price for fossil-based technical methanol (400 €/t) and 315 €/t for lignin.

Table 3. Feasibility of A-recovery+ processes.

INVESTMENT COSTS	WSA	A-Lignin	MeOH purification	A-Recovery+	
Lignin recovery		3.32		3.32	€/ADt
WSA	1.35			1.35	€/ADt
MeOH			0.81	0.81	€/ADt
TOTAL	**1.35**	**3.32**	**0.81**	**5.48**	
REVENUES					
Steam generation	1465			1465	k€/a
NaOH -savings	9755			5514	k€/a
Lignin		22365		22365	k€/a
H2SO4 -savings	1579			1729	k€/a
Ammonium sulfate			191	191	k€/a
MeOH			3469	3469	k€/a
TOTAL	**12799**	**22365**	**3660**	**34732**	
OPEX					
NaOH makeup		5253			k€/a
Lignin recovery		6678		6678	k€/a
H2SO4 -plant	446			446	k€/a
MeOH purification			698	698	k€/a
RB steam generation lost	641		894	1535	k€/a
TOTAL	**1087**	**11932**	**1592**	**9358**	
SIMPLE PAYBACK	**1.49**	**4.15**	**5.08**	**2.81**	**years**
NPV (15 years)	**84.80**	**47.88**	**7.56**	**150.39**	**M€**
WACC	**8 %**	**8 %**	**8 %**	**8 %**	
IRR	**67 %**	**23 %**	**18 %**	**35 %**	

*Investment costs are expressed as €/ADt with 15 year payback time using the defined WACC as interest rate

Conclusions

The A-recovery+ concept presents tools for further closure of the chemical cycles as well as further valorization of side and waste streams in kraft pulp mills. Integration of a sulfuric acid plant into the mill, not only provides the mill with commercial quality concentrated sulfuric acid, but also reduces the amount of ash dumping and/or enables the use of internally available sodium sulfate as make up chemical, depending on the mill's initial Na/S balance. A sulfuric acid plant can also enable the integration of a lignin recovery plant into the mill because it counteracts the negative impact of adding sulfur containing filtrates from the lignin recovery process to the chemical recovery cycle by extracting sulphur-rich CNCG and converting it to a valuable product. Lignin can be used at the mill as a lime kiln fuel or generate additional revenue for the mill when sold to external customers as a raw material for advanced bioproducts. Purification of raw-methanol to high quality biomethanol enables kraft mills to replace the fossil-based methanol currently used in ClO_2-generators, and become completely fossil-free if the lime kiln is operated with biofuels.

It is utmost important to note that the A-Recovery+ concept feasibility is very good even with the extremely conservative product prices used in the calculations. In the future, when lignin markets develop, and the environmental consciousness towards both the origin of methanol and the importance of Na/S-balance management raises, the integration benefits of A-Recovery+ will increase both the environmental and economic feasibility even further.

Possibilities of membrane filtration processes in recycling of Deep Eutectic Solvents (DES)

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Deep eutectic solvents (DES) are known to be able to fractionate lignin directly from wood. Moreover, they can be produced from biodegradable and non-toxic substances. Thus, they are an attractive solvent option for future biorefinery processes. However, without a feasible solvent recycling process the DES based fractionation processes cannot be implemented cost-efficiently. In this study the possibility to use ultra- and nanofiltration membranes in recycling of a DES used for lignin recovery from wood is examined. Both the stability of the membranes in DES and the filtration performance of the membranes in purification of the used DES is studied. The experiments are performed with commercial polymeric and ceramic membranes. The results of the study show the potential of membrane technology in recycling of deep eutectic solvents in biorefinery processes.

POSTER

PRESENTATIONS

Development of vertical laminates board from bamboo for interior house application

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Key words

Soft wood, Wood Composite, Bamboo, Bamboo laminates.

Bamboo is one of the fastest growing plants and has mechanical properties similar to timber. Bamboo has been commonly used for many years as a traditional construction material for low rise houses, foot bridges, roofs and construction platforms, especially in Asia and other parts of the world. The main reasons for the popularity of bamboo in construction can be attributed to its low cost, local availability and adequacy of simple, local tools and skills for fabrication. Application of bamboo in construction is, however, normally limited to low cost housing and temporary structures due to a number of factors including irregular shapes, hollow circular cross sections and durability issues. This report presents the results of an investigation into production of an engineered bamboo lumber product. Bamboo culms were cut into smaller strands and were re-constituted into rectangular sections by gluing and pressing at 140 C -145 C. This approach overcomes the presence of the inherent hollow core and randomises the inter-nodes and other growth characteristics found in bamboo. In this study, 300 number of Bambusa bambos were utilized and detailed investigation were carried out with the objectives of development manufacturing technology of Vertical Laminates which includes primary processing of bamboo, preservation and trained the manpower; resin formulation and process parameter for development of Vertical Laminates with the supplied bamboo; and standardisation of the process parameter for Board making from Vertical Laminates through edge lamination process. It was infered that vertical laminate board having good strength properties can be made with Bambusa bambos species using urea melamine formaldehyde adhesive and Epoxy resin. The laminates Bonded with UMF and Epoxy resin withstand immersion in warm water cycle of three cycle (each cycle consisting of 3 hours at 60 ± 2 C in water and thereafter drying at 65±2 C for 8 hours) as per IS:848, 2006. The laminate Boards are good with following dimension 3’X4’X15mm. if we increase the span area then it may not hold self-weight and causes delaminate from the edge hence it need further research in this line for future study

Effect of coagulating agents on lignin and sugar contents in acid prehydrolysis liquor obtained in the production of dissolving pulp from poplar residual slabs

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Prehydrolysis adding acid can aid in removing as much hemicellulose as possible from the cellulose fiber compared to traditional prehydrolysis without acid addition in the poplar residual slab kraft-based dissolving pulp production process. In the acid prehydrolysis process, a portion of lignin also dissolves, along with the hemicelluloses. The presence of lignin fragments in acid prehydrolysis liquor (APHL) is detrimental for the separation of value-added bio-products such as sugar in APHL and subsequent fermentation purposes, and so it is advantageous to remove it. This study focused on lignin removal from APHL with three coagulating agents, namely aluminum sulfate (alum), polyaluminum chloride (PAC), and polydiallyldimethyl ammonium chloride (pDADMAC). It was found that the removal of lignin increased as the dosage of the alum, PAC, and pDADMAC increased. Additionally, both the higher retention of total monomeric sugars and higher lignin removal in the APHL occurred at dosages of 120 mg/L for pDADMAC, PAC and alum.

Introduction

Prehydrolysis is an important step in the kraft-based dissolving pulp production process, as it helps remove as much hemicellulose as possible from cellulose fibers before the material is subjected to the main delignification operation, i.e. the pulping process. Earlier publications have shown that the main components of the pre-hydrolysis liquor (PHL) are mono- and oligo-saccharides, lignin, furfural, and acetic acid[1]. The prehydrolysis liquor (PHL) from the kraft-based dissolving pulp production process contains mainly oligosugars with a minor amount of monosugars[2]. To obtain fuels and chemicals from the PHL, further acid hydrolysis of PHL will be an essential step in converting polysaccharides to monosaccharides. This will lead to the complexity of the fermentation process for obtaining ethanol or butanol from the PHL.

Prehydrolysis adding acid in the kraft-based dissolving pulp production process can aid in removing as much hemicellulose as possible from the cellulose fiber compared to traditional prehydrolysis without acid addition, and result in obtaining low pentosan content dissolving pulp. Loyd et al[3] treated corn stover with dilute sulfuric acid, the results indicated that dilute-acid pretreatment can not only solubilize hemicellulose but also convert solubilized hemicellulose to fermentable sugars. Theoretically, sugars in acid prehydrolysis liquor (APHL) from the kraft-based dissolving pulp production process will be existed in monosaccharide forms.

To facilitate the further utilization of fermentable sugars in acid prehydrolysis liquor (APHL), lignin contaminants have to be removed specifically and completely due to its high toxicity to fermentation microorganism[4]. In the literature, the efficiencies of activated carbon, polyethylene oxide, surfactant/calcium oxide, acidification/PEO, chitosan, and laccase treatments for removing various components of the PHL have been comprehensively investigated.

This study mainly considers the effects of alum, polyaluminum chloride (PAC), and polydimethyldiallylammonium chloride (pDADMAC) on the monosaccharide, total sugar, and lignin contents in acid prehydrolysis liquors (APHL) obtained in the production of dissolving pulp from poplar residual slabs. Due to their strongly positive charged nature and relatively low molecular mass, the three additives considered in this work can be regarded as coagulants. The removal of lignin and the retention of total monomeric sugars in the APHL were assessed at various dosages of alum, PAC, and pDADMAC. The objective of the present study was to simultaneously obtain a high removal of lignin and high retention of total monomeric sugars from APHL.

Experimental

Acid Prehydrolysis Procedure

Acid prehydrolysis liquor (APHL, pH=1.64) was collected from the acid pre-hydrolysis stage of a dissolving pulp made from poplar residual slabs[5]. Acid prehydrolysis was carried out in an electrically heated stainless steel digester (15 L) that rotated at a rate of 1 rpm in our laboratory. The acid prehydrolysis was carried out at a constant cooking temperature of 160 °C, and it was heated from room temperature at a heating rate of 8 °C/10 min. The time at cooking temperature was 120 min, with a liquor-to-wood ratio of 6:1 and a sulfuric acid dosage of 1.0%.

Materials

Alum and PAC were chemically pure agents and dissolved in distilled water of 10.0 g/L prior to being used. Polydiallyldimethyl ammonium chloride (pDADMAC), 200 to 350 kDa, was purchased from Aladdin Co., Ltd., Shanghai, China and applied without further purification.

Addition of Coagulating Agents to APHL

The APHL was filtered using a 0.45-μm nylon syringe filter prior to the coagulating agent addition. Various amounts of alum, PAC, and pDADMAC were subsequently added to 100 mL of the APHL at a temperature of 28 °C , unadjusted pH value of 1.64 and stirring at 500 rpm for 60 min. Afterwards, the complexes were isolated by centrifuging at 3000 rpm for 5 min. The lignin and sugar contents in the APHL supernatant before and after alum, PAC, and pDADMAC addition were determined. In addition, optimal amounts of alum, PAC, and pDADMAC were added to 100 mL of the APHL at a temperature of 28 °C , adjusted pH value from 1.64 to 7.91 by adding NaOH solution and stirring at 500 rpm for 60 min. Afterwards, the complexes were also isolated by centrifuging at 3000 rpm for 5 min. Then, only the lignin content in the APHL supernatant before and after alum, PAC, and pDADMAC addition were determined.

Analytical Methods

The concentration of sugars in the APHL was determined using ion chromatography with a pulse amperometric detector and CarboPacTM PA20 column (ICS-5000, MA, USA). A mixture of 80% ultrapure de-ionized water and 20% of 10 mM NaOH was used as an eluant with a flow rate of 0.5 mL/min. To measure the oligomeric sugar in original APHL, an additional acid hydrolysis was conducted on the APHL, under conditions of 4% sulfuric acid at 121 °C for 1 h in an oil bath. The samples were filtered (0.22 μm) and diluted prior to analysis. The monomeric sugar contents in the post-acid hydrolysate represented the total saccharides in the acid prehydrolysis liquor. The sugar contents in oligomeric form in the acid prehydrolysis liquor were calculated by taking the difference in the monomeric sugar contents, both with and without the post-acid hydrolysis. The acid-soluble lignin content in the APHL was measured a UV/Vis detector (Agilent 8453, USA) at a wavelength of 205 nm (TAPPI UM 250).

Results and discussion

Properties of APHL

The various APHL properties, such as sugar and acid-soluble lignin contents, are listed in Table 1. The contents of monomeric arabinose, galactose, glucose, xylose, and mannose were 0.47, 0.68, 5.78, 9.17, and 0.92 g/L, respectively. It was obvious that monosaccharides, which accounted for more than 95% of the total sugars, were the main sugar in the APHL. This indicated that the APHL has the potential to be used as a direct source of fuels and chemicals. The lignin content (10.7 g/L) in the APHL was relatively higher than that (10.2 g/L) of the PHL from the dissolving pulp industries in Canada[6]. The isolation of lignin in APHL is a problem that obstructs the recovery and utilization of total monomeric sugars from the APHL.

Table 1. Dissolved Sugars and Lignin Concentration in APHL

Acid-soluble Lignin (g/L)		10.7
Arabinose (g/L)	Monomeric	0.47
	Oligomeric	0.01
Galactose (g/L)	Monomeric	0.68
	Oligomeric	0.01
Glucose (g/L)	Monomeric	5.78
	Oligomeric	0.02
Xylose (g/L)	Monomeric	9.17
	Oligomeric	0.57
Mannose (g/L)	Monomeric	0.92
	Oligomeric	0.01
Total Sugars (g/L) (Monomeric+Oligomeric)		17.6
Total Sugars (g/L) (Monomeric)		17.0

Optimization of Alum Dosages

The lignin and monomeric sugar contents in the APHL treated with various dosages of alum are presented in Table 2. As can be seen, as the alum dosage increased, a downward trend in the lignin content of APHL appeared, indicating that the removal of lignin increased with the increased alum dosage. After increasing the alum dosage, the monomeric arabinose content in the APHL reached a maximum at 80 mg/L alum, monomeric galactose content reached a maximum at 80 mg/L alum, monomeric glucose content reached a maximum at 120 mg/L alum, monomeric xylose content reached a maximum at 120 mg/L alum, monomeric mannose content reached a maximum at 200 mg/L alum, and total monomeric sugars content reached a maximum at 120 mg/L alum. These results show that the highest retention (near 85%) of total monomeric sugars occurred at dosages of 120 mg/L alum.

Table 2. Effect of Alum Dosage on Main Components in APHL

Alum Dosage (mg/L)	0	40	80	120	160	200	240
Acid-soluable Lignin (g/L)	10.7	10.6	9.80	9.18	8.89	8.62	8.42
Monomeric Arabinose (g/L)	0.47	0.31	0.32	0.29	0.24	0.24	0.26
Monomeric Galactose (g/L)	0.68	0.51	0.53	0.52	0.40	0.39	0.39
Monomeric Glucose (g/L)	5.78	5.12	4.97	5.51	3.41	3.59	3.39
Monomeric Xylose (g/L)	9.17	7.18	7.60	7.61	5.06	5.63	5.30
Monomeric Mannose (g/L)	0.92	0.58	0.64	0.52	0.90	0.91	0.91
Total Sugars (g/L) (Monomeric)	17.0	13.7	14.1	14.4	10.0	10.8	10.2

Optimization of PAC Dosages

The lignin and monomeric sugar contents in the APHL treated with various dosages of PAC are presented in Table 3. As can be seen, the lignin content in the APHL slightly decreased with an increase in PAC dosage. With increasing PAC dosage, monomeric arabinose content in the APHL reached a maximum at 80 mg/L PAC, monomeric galactose content reached a maximum at 80 mg/L PAC, monomeric glucose content reached a maximum at 120 mg/L PAC, monomeric xylose content reached a maximum at 40 mg/L PAC, monomeric mannose content reached a maximum at 160 mg/L PAC, and total monomeric sugars content reached a maximum at 40 mg/L PAC. Although the highest retention (near 93%) of total monomeric sugars occurred at dosages of 40 mg/L for PAC, however, the lignin removal was very low. So the optimal dosage of 120 mg/L PAC was selected for the next experiment, both the higher retention (near 87%) of total monomeric sugars and the higher removal of lignin occurred at the dosage of 120 mg/L PAC.

Table 3. Effect of PAC Dosage on Main Components in APHL

PAC Dosage (mg/L)	0	40	80	120	160	200	240
Acid-soluable Lignin (g/L)	10.7	10.4	9.76	9.36	9.15	9.02	9.00
Monomeric Arabinose (g/L)	0.47	0.30	0.38	0.34	0.22	0.24	0.21
Monomeric Galactose (g/L)	0.68	0.50	0.55	0.52	0.38	0.38	0.37
Monomeric Glucose (g/L)	5.78	5.67	4.72	5.70	3.40	3.81	4.18
Monomeric Xylose (g/L)	9.17	8.69	7.51	7.58	5.12	5.97	6.58
Monomeric Mannose (g/L)	0.92	0.59	0.70	0.64	0.91	0.88	0.90
Total Sugars (g/L) (Monomeric)	17.0	15.8	13.9	14.8	10.0	11.3	12.2

Optimization of pDADMAC Dosages

The lignin and monomeric sugar contents in the APHL treated with various dosages of pDADMAC are presented in Table 4. As shown, the lignin content in the APHL decreased with an increase in pDADMAC dosage. After increasing the pDADMAC dosage, the monomeric arabinose content in APHL reached a maximum of 80 mg/L pDADMAC, monomeric galactose content reached a maximum of 120 mg/L pDADMAC, monomeric glucose content reached a maximum of 80 mg/L pDADMAC, monomeric xylose content reached a maximum of 40 mg/L pDADMAC, monomeric mannose content reached a maximum of 200 mg/L pDADMAC, and total monomeric sugars content reached a maximum at 40 mg/L pDADMAC. Although the highest retention (near 93%) of total monomeric sugars occurred at dosages of 40 mg/L for pDADMAC, however, the lignin removal was very low. So the optimal dosage of 120 mg/L pDADMAC was selected for the next experiment, both the higher retention (near 89%) of total monomeric sugars and the higher removal of lignin occurred at the dosage of 120 mg/L pDADMAC.

Table 4. Effect of pDADMAC Dosage on Main Components in APHL

pDADMAC Dosage (mg/L)	0	40	80	120	160	200	240
Acid-soluable Lignin (g/L)	10.7	10.5	10.3	10.0	9.73	9.07	8.55
Monomeric Arabinose (g/L)	0.47	0.30	0.35	0.34	0.23	0.18	0.19
Monomeric Galactose (g/L)	0.68	0.51	0.53	0.54	0.34	0.34	0.34
Monomeric Glucose (g/L)	5.78	5.57	5.58	5.12	3.07	3.20	3.02
Monomeric Xylose (g/L)	9.17	8.85	8.57	8.43	4.76	5.07	4.37
Monomeric Mannose (g/L)	0.92	0.55	0.60	0.62	0.80	0.84	0.82
Total Sugars (g/L) (Monomeric)	17.0	15.8	15.6	15.0	9.20	9.63	8.74

Conclusions

The APHL from the pre-hydrolysis stage of dissolving pulp, made from poplar residual slabs, could potentially be a direct source of fuels and chemical because of its high monosaccharide percentages of total sugars, as well as its relatively low lignin content.

The removal of lignin all increased with increasing dosages of alum, PAC, and pDADMAC. Both the higher retention of total monomeric sugars and the higher removal of lignin occurred at dosages of 120 mg/L for alum, PAC and pDADMAC.

Acknowledgements

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Carbon negative pulp industry

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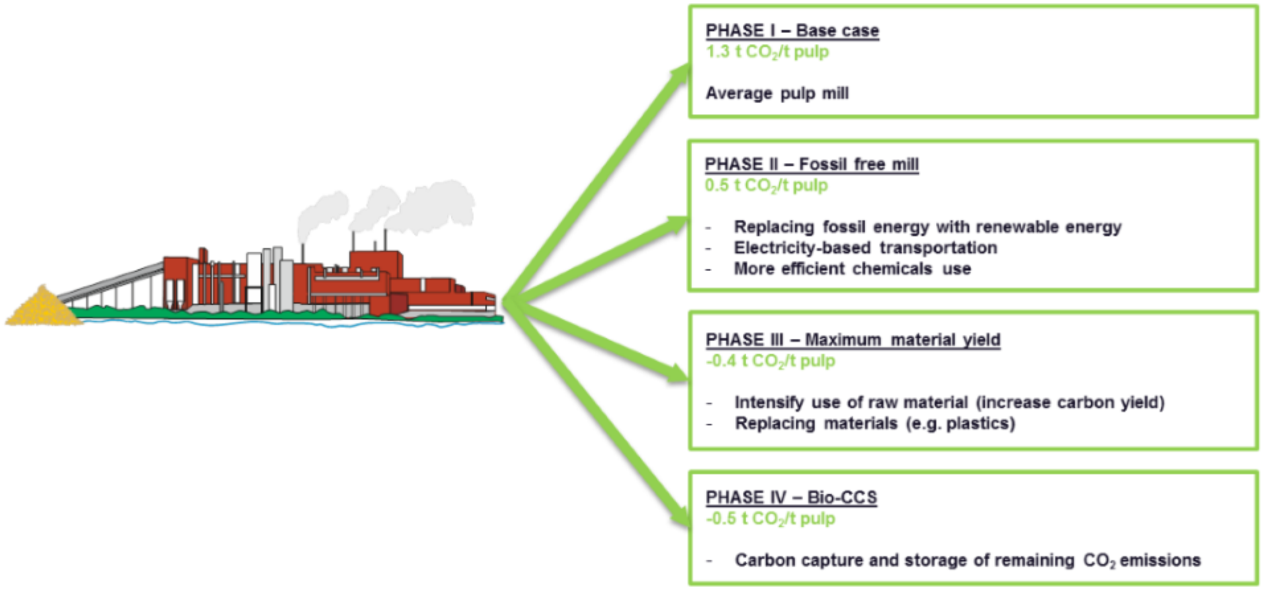
Capturing and permanently storing CO_2 originating from biomass (biogenic CO_2) is currently the only large-scale technology for reducing atmospheric CO_2 emissions. Utilizing biomass for raw material, the forest industry is one of the sectors with the largest technical potential to realize negative CO_2 emissions and thus remove larger amounts of CO_2 from the atmosphere. Acting as a carbon sink, the forest industry would have the potential to offset both historic CO_2 emissions and CO_2 emissions from sectors that are more challenging to decarbonize, for instance the transportation sector and certain industry sectors that currently are dependent of fossil carbon such as iron and steel production and cement production. However, carbon capture and storage (CCS) currently comes with a significant additional cost that increase the price of pulp by up to 40%, depending on the prevailing policies on CO_2 emissions and incentives for renewable electricity production[1]. This paper identifies a strategy consisting of three individual phases for reducing CO_2 emissions per unit product from a pulp and paper mill and compares the impact of this strategy to an average pulp and paper mill.

Phase I represents a modern reference pulp and paper mill without specific measures to reduce CO_2 emissions. The typical average CO_2 emission from this mill is 1.1–1.3 t CO_2/t pulp. In Phase II use of fossil energy resources is eliminated through replacement with renewable energy. In transportation of raw materials, chemicals and products electric alternatives, mainly railroad, are applied instead of transportation utilizing fossil fuels. In addition, chemical circulation at the mill is intensified, especially in chemicals recovery. Furthermore, energy efficiency of the mill is improved by bark gasification. In Phase II the mill is close to zero net CO_2 emissions, but still not operating as a carbon sink. In Phase III the use of raw materials is intensified in order to maximize the carbon flow from the raw material to the products. This can be done for instance by producing special pulps to replace plastic products and recovering carbon monoxide from the recovery boiler flue gases to be used use as a feedstock for other products. Taking into consideration the entire lifecycle of the products, there is already a potential to reduce the CO_2 emissions below zero in this phase. Phase IV introducing CCS is the last option to further reduce the CO_2 emissions after all other options are implemented. In Phase IV, the CCS investment would be significantly lower compared to Bio-CCS without implementing phases II and III as the amount of CO_2 to be captured would be significantly smaller. The phases are illustrated in Figure 1.

This work illustrates that a modern pulp mill can operate with below-zero emissions even without Bio-CCS and thus create negative CO_2 emissions without being dependent on costly CCS technology. By directing more of the carbon from the raw material into the products, switching from fossil to renewable energy sources and replacing fossil intensive materials with bio-based materials the mill could reduce CO_2 emissions by up to 140% compared to the base case. This implies that a modern pulp and paper mill can produce products that function as pure carbon sinks without Bio-CCS technology.



PHASE I – Base case
1.3 t CO_2/t pulp

Average pulp mill

PHASE II – Fossil free mill
0.5 t CO_2/t pulp

- Replacing fossil energy with renewable energy
- Electricity-based transportation
- More efficient chemicals use

PHASE III – Maximum material yield
-0.4 t CO_2/t pulp

- Intensify use of raw material (increase carbon yield)
- Replacing materials (e.g. plastics)

PHASE IV – Bio-CCS
-0.5 t CO_2/t pulp

- Carbon capture and storage of remaining CO_2 emissions

Figure 1 Stepwise reduction of CO_2 emissions at a pulp and board mill

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Real-time analysis of syngas quality for feedback control of torrefaction

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Key Words

Torrefaction, fluidized bed gasification, willow, model predictive control, lignocelluloses

Predictive control strategies have the potential to improve operability and therefore the economics of gasification for production of chemicals and fuels from biomass. This work proposes an advanced control methodology for control of syngas quality using process parameters and feedstock characteristics (lignocellulosic composition). In addition, exploratory work on the effect of torrefaction extent on syngas quality is presented. The work hypothesizes that an integrated torrefaction process could be controlled directly to manipulate downstream gasifier syngas quality. The experimental results prove that there is the potential to incorporate biomass characterization data into an advanced control strategy. In this research work, willow (*Salix* spp.) was harvested, torrefied, and characterized by TGA. The torrefied willow was gasified in a laboratory fluidized bed gasifier. A process mass spectrometer was used to measure syngas composition and tar species of the syngas. The mass spectrometer was found to reduce measurement lag time to virtually real-time compared to other gas analyzers. In addition to gas composition, the parent ion peak intensities of benzene in syngas from torrefied and non-torrefied willow were measured. The ion intensities in the syngas are correlated to the hemicelluloses fraction in the torrefied and non-torrefied willow.

Introduction

In the context of biorefining, biomass gasifiers present a challenging control problem. The constraints required to produce multiple value-added products combined with the complex interactions between biomass and gasifying media complicates the operation of a thermal reactor. Stepwise thermal treatments (i.e., torrefaction followed by gasification) have been shown to improve syngas quality and could be used directly in a process control strategy.

Computational modeling is useful for optimization studies and control. Typical dynamic models for gasification have recently been categorized into (i) thermodynamic equilibrium models, (ii) kinetic models, and (iii) artificial neural network models (ANN)[1] with many successful applications. Despite the development of accurate and precise models, feedstock variability continues to be a significant limitation. Sunkopha et al.[2] recently used an ANN to model oxidation behavior of biomass. They were able to demonstrate that changes in chemical composition affect the kinetic parameters (activation energy and frequency factor) of the reaction system. In particular, when modeling is used in control applications, the continuous disturbances introduced by the properties of the biomass can saturate control functions. Mikulandric et al.[3] recently demonstrated a 25% improvement in gasifier performance using an advanced control approach. However, the researchers also identified biomass chemical composition as a significant unmeasured disturbance.

Torrefaction is a low temperature thermal treatment where biomass is heated to between 200 and 300 °C in an inert environment. The process volatilizes hemicelluloses and initiates reactions that change the chemical composition and physical structure of the resulting char. As a pretreatment of biomass for gasification, torrefaction has been found improve gas quality and operation of the gasifying reactor[4-6]. Separation technology for light aromatics from syngas motivate greater study of torrefaction's effects on production of benzene[7,8].

In this research work, it is hypothesized that torrefaction conditions can be correlated to syngas contaminants. The objectives are to investigate the effect of torrefaction on syngas species (benzene), and evaluate the potential to use torrefaction in a predictive control system. A mass spectrometer (MS) was used for real-time analysis of gas and vapour composition of syngas produced in a 75 mm diameter fluidized bed reactor. The mass spectra were used to investigate the concentration of chemicals in syngas from torrefied and non-torrefied coppice willow.

Materials and Methods

Apparatus

The details of the 75 mm diameter fluidized bed (FB) reactor used in the work are presented in Woytiuk et al[9]. In this work, modifications were made to the gas sampling system to integrate the mass spectrometer (Extrel Max300 EGA, US). Steam and air are used as gasification media for the untreated and torrefied samples. Table 1 shows the design and actual experimental conditions used in the research.

Analysis

The mass spectrometer software (Questor 5 v2.1, Extrel, US) is equipped with a survey scan mode of analysis. The survey scan mode measures the ion intensities across a specified range of currents to produce a spectra of m/z ratio based on the intensity of the most abundant peak. The m/z ratio of the parent peak is used here as a proxy for concentration.

Table 1. Design and actual gasification conditions of three torrefied willow samples and the control sample. Design conditions are based on biomass characterization data with actual conditions (in brackets) determined following each experiment.

Parameter	**Untreated**	**@240°C**	**@260°C**	**@280°C**
Feed rate, dry basis (g/s)	0.100*(0.098)*	0.100*(0.099)*	0.100*(0.096)*	0.100*(0.096)*
Bed Temperature (°C)	900*(899)*	900*(894)*	900*(896)*	900*(893)*
Steam (g/s)	0.044	0.049	0.049	0.048
Fluidization Air (g/s)	0.094	0.087	0.089	0.092
Fuel bound Oxygen (g/s)	0.041	0.041	0.039	0.036
Nitrogen* (g/s)	0.138	0.140	0.140	0.139
Equivalence Ratio	0.100*(0.102)*	0.100*(0.102)*	0.100*(0.104)*	0.100*(0.104)*
*the sum of compressed gas and atmospheric nitrogen				

Results and Discussion

Experimental Study

A fast-growing willow cultivar was harvested and cut into 25 mm long billets as described in the previous work[9]. A high resolution TGA method was then used to quantify lignocelluloses composition of the untreated and torrefied samples[10,11]. The extent of torrefaction is defined here as a significant decrease in hemicelluloses relative to the untreated biomass. Table 2 shows the decrease in hemicellulose fraction as a result of increased peak torrefaction temperatures. No significant change in cellulose or lignin fractions were observed under the conditions in this study, consistent with the thermal stability of these species at temperatures below 300 °C reported by Bergman et al[12].

Table 2. Lignocellulose composition of torrefied and non-torrefied SV1 willow determined by HR-TGA[10][(% dry weight). Reprinted from Woytiuk et al.[9] [9].

	Cellulose		**Hemicellulose**		**Lignin**		**Ash**	
Untreated	43.2	+/-2.1	18.5	+/-0.2	26.8	+/-0.9	1.9	+/-1.3
@ 240 °C	44.9	+/-3.5	15.5	+/-0.1	28.5	+/-3.8	2.3	<0.1
@ 260 °C	48.2	+/-1.1	10.9	+/-1.3	29.4	+/-0.6	2.4	+/-0.3
@ 280 °C	49.7	+/-0.1	3.4	+/-0.4	33.9	+/-1.5	2.4	+/-0.7

Figure 1 shows the average ion intensities from mass spectra for the parent ion peak for benzene (m/z 78) against the fraction of hemicelluloses in the biomass samples. The reduction in ion intensity of the parent ion peak at m/z 78 implies a reduction in benzene concentration in the syngas as a result of increasing torrefaction severity

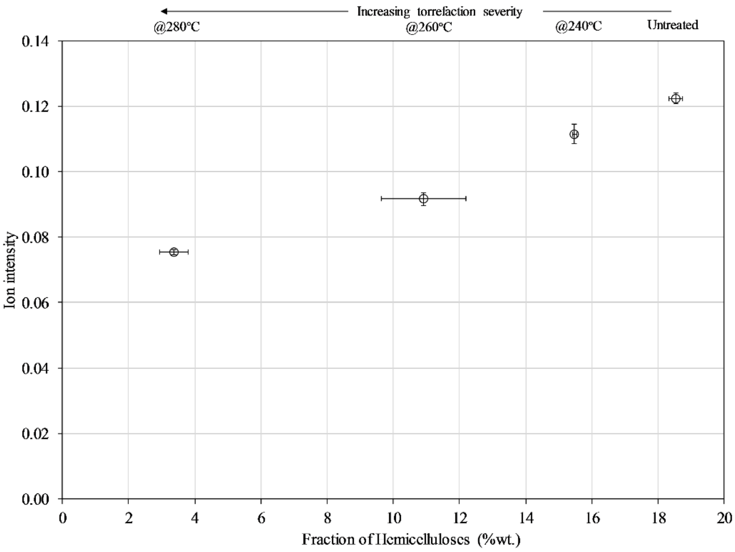

Figure 1. Ion intensity of benzene's parent ion peak (m /z 78) in syngas from torrefied and non-torrefied SV1 willow compared to hemicellulose composition of the biomass. Error bars indicate random uncertainty at the 95% confidence level

Application to predictive control

Figure 2 shows a predictive control schematic for gasification of char pretreated by torrefaction. Willow biomass is input to the system to produce syngas for downstream upgrading and refining. The torrefaction control schematic is similar to the torrefaction control loop proposed by Campbell and Evitts[13] where downstream process measurements may be used to manipulate torrefaction severity by adjusting peak temperature or residence time for a horizontal moving bed torrefaction process.The manipulated inputs to the gasification system (G_{sp}) include biomass feedrate, air and steam input, char removal among others. The responding outputs include gas quality (heating value, H_2/CO, CO/CO_2, CH_4 concentration, tar concentration, and tar species concentration), temperature, pressure, and particulates. Applications have frequently failed to meet setpoints as a result of feedstock variability. For example, in the second round of the ALSTOM benchmark challenge for coal gasification control, most solutions met all constraints except the coal quality disturbance test of +/-18%[14,15].

Moving bed torrefaction control, on the other hand, is relatively simple with only two main manipulated variables (temperature and residence time) represented by T_{sp} in Figure 2. The system also has potential for an accurate predictive model[13,16]. The reactor requires a short torrefaction residence time (5-10 minutes) compared to most torrefaction systems and is therefore well suited to a transient control application.

In this research work, the TGA method used to measure feedstock properties significantly reduced typical analytical time and complexity compared to standard laboratory procedures (for example NREL/TP-510-42618). However, for most gasifier optimization problems (pressure and temperature optimization for example), the 30 minute lag time introduced by TGA testing is too long. Campbell and Evitts[13] have demonstrated the potential to correlate several feedstock properties to a single variable measurable in-situ. Therefore integrating the torrefaction controls directly into the FB gasifier predictive model could be used for syngas quality optimization.

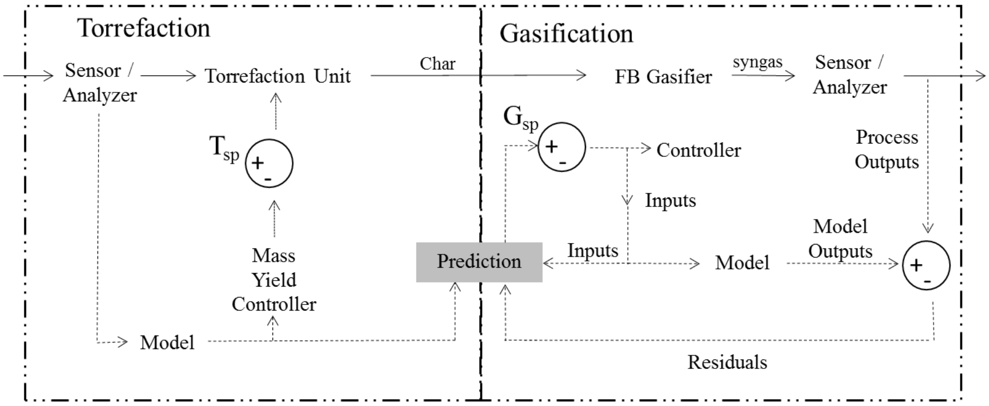

Figure 2. Predictive control schematic for a fluidized bed gasifier (FB Gasifier) and a torrefaction unit adapted from Seborg *et al.*[17] [17] and Campbell and Evitts[13] [13].

Conclusions

Syngas from fluidized bed gasification of coppice willow was analyzed in real-time by mass spectrometry.

The characteristic volatilization of hemicelluloses associated with torrefaction correlates positively with alkyl tertiary tars in syngas represented by benzene.

It was found that the ion intensity values for benzene in syngas, measured by mass spectrometry, have a positive linear correlation with the fraction of hemicelluloses resulting from torrefaction of coppice willow measured by TGA.

A generalized control schematic for combined torrefaction and gasification is proposed.

Acknowledgments

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Wood fractionation and lignin valorization by prehydrolysis alkaline cooking with phenols

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Pulp is largely produced by kraft pulping of wood chip. Prehydrolysis before kraft pulping could remove hemiecllulose to give oligo-saccharides, monomeric sugars or furfurals. High-purity cellulosic pulp could be obtained after the following kraft cooking. To valorize lignin in this process, we propose to impregnate monophenol into raw wood and to adopt prehydrolysis soda cooking. Hydrothermal treatment at 180 °C was carried out for p-cresol-impregnated wood meal followed by soda cooking at 150 °C. Delignification was significantly promoted, indicating that p-cresol successfully prevented self-condensation during autohydrolysis. Kraft lignin is generally difficult to be dissolved in water or organic solvents, however, our process increased the solubility of lignin to tetrahydrofuran.

Introduction

Prehydrolysis kraft process is a modified kraft pulping before which hydrolysis is added (Figure 1). Some kraft mills have been changed into prehydrolysis kraft mill due to increasing demand of dissolving pulp[1]. First, hemicellulose is removed by prehydrolysis and then the residue containing cellulose and lignin is delignified by kraft cooking to produce cellulose with high purity, so called “dissolving kraft pulp”. Dissolving kraft pulp can be a raw material of viscose, cellulose acetate, microcrystalline cellulose by further chemical treatment. Furthermore, it can be used for other functional materials such as cellulose nanofiber or substrate for enzymatic saccharification. Decomposed hemicellulose in hydrolysate can be converted to furfural and so on. The process fits into the biorefinery concept because functional materials could be obtained from both cellulose and hemicellulose except that kraft lignin is difficult to be used as a functional material. Although many researchers have been struggling to utilize kraft lignin, it has still been difficult. For example, sulfur in kraft lignin poisons catalysts used for further chemical conversion.

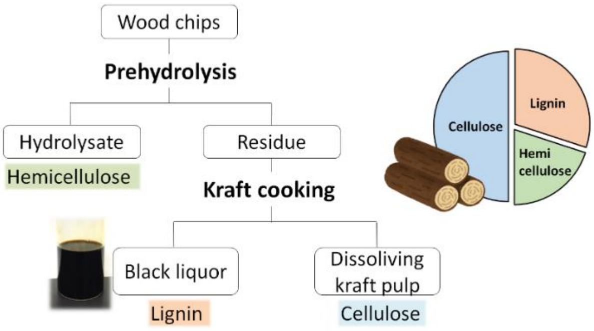


Figure 1. Kraft-based dissolving pulp production

In order to valorize lignin in this process, we propose “prehydrolysis soda cooking of monophenol-impregnated wood”. Autohydrolysis or mild dilute acid hydrolysis was carried out for monophenol-impregnated wood meal to hydrolyze hemicellulose and to phenolate lignin, then, the hydrolysis residue consisting of cellulose and lignin was soda-cooked to dissolve lignin leaving cellulose. *p*-Cresol was selected as a monophenols in this study. Our process is also advantageous from the view point of early industrialization because it could be managed on an existing prehydrolysis kraft mill.

Theory

Under acidic conditions, cation is formed in reactive benzyl positions of lignin aromatic nuclei, and “self-condensation” between lignin molecules (Figure 2) occurs[2,3]. Because lignin structure is changed to more condensed rigid one, “hydrolysis lignin” is generally difficult to be dissolved in any organic solvents and is not thermoplastic.

On the other hands, in the presence of monophenol, it could chemically link to the benzyl cation of lignin[2,3] (phenolation of lignin, Figure 3), preventing the self-condensation. Wayman and Lora studied impregnation of 23 aromatic compound to prevent the self-condensation of lignin during the autohydrolysis of aspen wood chips (175 °C, 90 min)[4]. They obtained pulp by extraction of the residue after autohydrolysis with dioxane-water (9:1) solution. It was reported that 2-naphthol was the most effective compound to increase the amount of extractable lignin. Timilsena *et al*. treated 2-naphthol-impregnated wood meal under autohydrolysis condition and obtained pulp by organosolv pulping of the hydrolysis residue[5]. Effective delignification during organosolv pulping was reported. Hussin *et al*. confirmed that lignin with high antioxidant activity is able to be recovered from black liquor during organosolv pulping of autohydrolyzed 2-naphthol-impregnated wood meal[6]. From these reports, it is clear that prehydrolysis of monophenol-impregnated wood followed by pulping is effective on increasing solubility of lignin into organic solvents.

Funaoka treated *p*-cresol-impregnated wood meal with concentrated sulfuric acid at room temperature[7]. It was successful to obtain functional lignin named lignophenol. It was proved based on NMR analysis that many benzyl positions of lignin were stabilized by *p*-cresol. We have tried dilute acid hydrolysis of *p*-cresol-impregnated wood meal using 1.1 % sulfuric acid at 180 °C for 60 min. Glucose, levulinic acid and formic acid were main products in the hydrolysate and the solubility of hydrolysis lignin to organic solvents was highly improved due to partial phenolation of lignin by *p*-cresol[8].

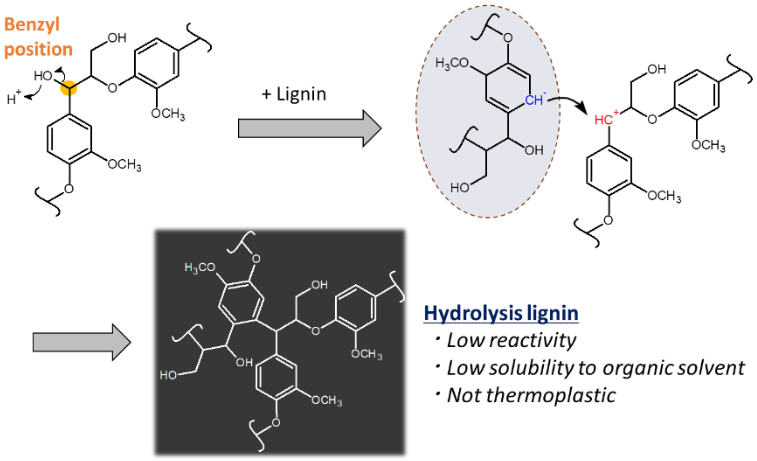
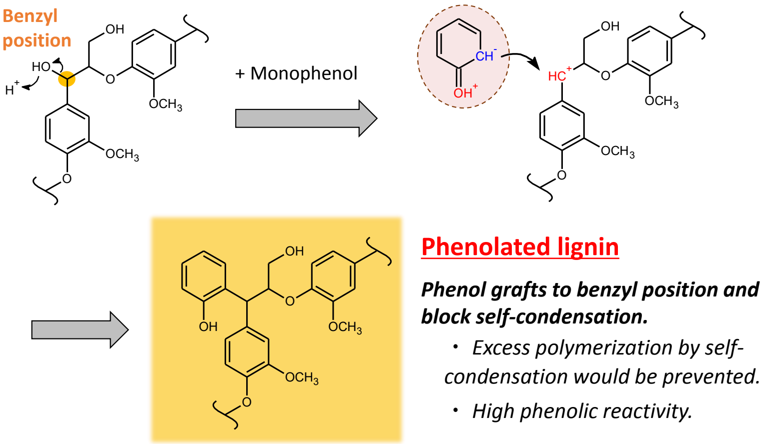


Figure 2. Self-condensation of lignin under acidic conditions



Phenolated lignin

Phenol grafts to benzyl position and block self-condensation.

- *Excess polymerization by self-condensation would be prevented.*
- *High phenolic reactivity.*

Figure 3. Phenolation of lignin under acidic conditions

Experimental

Preparation of p-cresol-impregnated wood meal

Wood meal from softwood (cedar, lignin content: 34.9 %) was extracted with an ethanol-benzene (1:2, v/v) solution using a Soxhlet extractor. *p*-Cresol (3 g) was dissolved in acetone and added to 2 g of extractive-free wood meal. After waiting for the acetone solution to infiltrate into the wood meal overnight, acetone was air-dried by stirring the solution in a draft chamber to leave *p*-cresol-impregnated wood meal.

Prehydrolysis of p-cresol-impregnated wood meal

Autohydrolysis of *p*-cresol-impregnated wood meal was conducted with 14 mL of distilled water in an oil bath set at 180 °C for 120 min under nitrogen using a 20 mL stainless steel batch-type reactor. After cooling the reactor, the mixture was filtered and the residue was washed with deionized water, freeze-dried, and weighed to calculate the yield. The control experiment was carried out using raw extractive-free wood meal.

Soda cooking of prehydrolysis residue

1 g of freeze-dried hydrolysis residue was cooked with 10 mL of 0.5 N NaOH under nitrogen at 150 °C for 90 min using a 20 mL stainless steel batch-type reactor. The reaction mixture was filtered and the soda pulp was washed with the same NaOH solution. The soda pulp was further washed with deionized water, acetic acid, and deionized water in sequence and then oven-dried.

Results and discussion

Figure 4 shows the yields of hydrolysis residue and soda pulp without impregnating monophenol (control experiment) and with *p*-cresol. Without monophenol, the yield of hydrolysis residue was 78.7%. The main reaction during autohydrolysis at 180 °C for 120 min is hydrolysis of hemicellulose. Only less than 3% of the hydrolysis residue was soluble in tetrahydrofuran (THF). Soda cooking did not delignify the hydrolysis residue well, resulting in 55.8 % soda pulp with high lignin content. The colour was deep brown.

By impregnation of *p*-cresol, the yield of prehydrolysis residue was increased from 78.7 % to 85.5 %. This trend is consistent with that of our previous report treated at 180 °C with 1.1 % H_2SO_4 [8], indicating that *p*-cresol successfully bound to reactive benzyl position of lignin during autohydrolysis. 22.1 % of the hydrolysis residue was soluble in THF. It means that 18% (= 85.5 % x 22.1 %) of wood, mostly lignin, became extractable by THF. High solubility to organic solvents would give advantage to lignin for resin, gel or film production. *p*-Cresol highly promoted delignification of hydrolysis residue during soda cooking, leaving soda pulp with much lower lignin content in a yield of 38.6 %. The colour was light brown.

The lignin content and compositional sugars of hydrolysis residue and soda pulp are planned to be measured based on the typical two-step sulfuric acid hydrolysis method[9]. The compounds in the hydrolysate will be analyzed using HPLC equipped with an ion exchange and size exclusion chromatography column (Shodex SH1011) with 2 mM sulfuric acid as the eluent. Based on these data, we will show how nicely our process could fractionate softwood components.

The lignin is recovered from the black liquor to evaluate the functionality. The molecular weight distribution is analyzed using gel permeation chromatograph compared with polystyrene standards. The amount of *p*-cresol linked to lignin can be estimated by integration of the methyl proton on NMR analysis. Thermal decomposition and fluidity are measured by thermogravimetric analysis (TGA) and thermomechanical analysis (TMA).

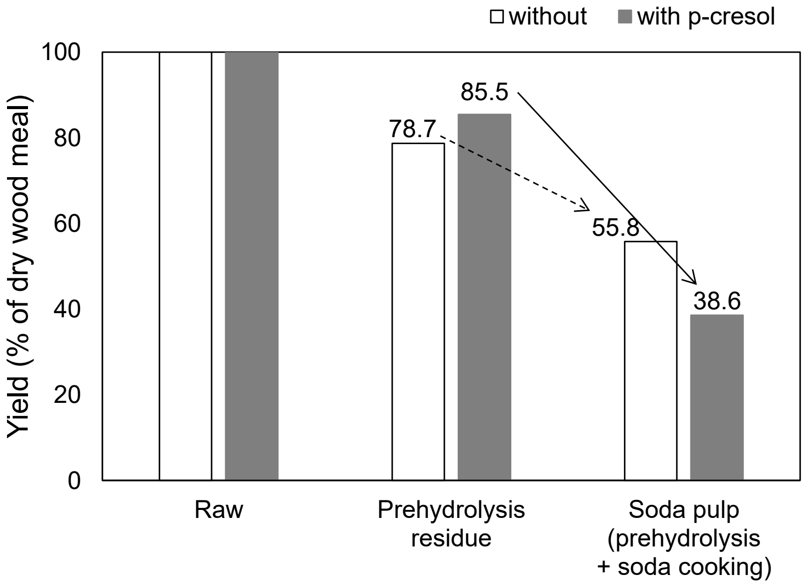


Figure 4. Yield of prehydrolysis residue and soda pulp without or with p-cresol

Conclusion

Autohydrolysis at 180 °C was carried out for *p*-cresol-impregnated wood meal followed by soda cooking at 150 °C. By impregnation of *p*-cresol, the yield of hydrolysis residue was increased and delignification was significantly promoted, indicating that *p*-cresol successfully prevented self-condensation during autohydrolysis. The solubility of lignin in THF increased. Lacked data is presented at the conference.

Acknowledgements

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Novel reaction systems and catalysts for producing aromatic hydrocarbons from lignin

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Lignin is a high-volume, wide-spread renewable resource with a strong potential as a feedstock for products to replace petroleum based products. However, the conversion of lignin to low-molecular products with well-defined chemical properties is challenging. Especially for the production of hydrocarbons, the high content of oxygen in the lignin polymer and the prevalence of phenolic functional groups make the upgrading technologies established for petroleum feedstocks unsuitable. Conventional hydrogenation catalysts do not give optional product compositions, since aromatic rings, which preferable should be retained, are hydrogenated before the phenol groups are reduced. The processes also require high temperatures and pressures.

Here, we will present recent efforts in developing catalytic systems that produce low molecular weight aromatic and/or cycloalkane compounds from lignin or depolymerized lignin at mild conditions, i.e. below 200-300 °C and at low hydrogen pressure/hydrogenation agent concentration. We will compare novel catalysts that have been employed and have given promising results with conversion routes utilising more conventional heterogeneous hydrogenation catalysts. The catalysts that have been tested comprise both homogeneous and heterogeneous systems, and provide alternative pathways for production of fuel range hydrocarbons from lignin. Results based on lignin model compounds and complete lignin oil feedstocks will be presented and compared, and the most promising systems for upscaling will be identified.

CERES Competence Center for the Materials Bioeconomy: A Flagship for our Sustainable Future

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The CERES Flagship funded by the Academy of Finland is the joint effort of Aalto University and VTT. It aims at building a sustainable future for the bio-economy materials and applications with a solid scientific foundation. One of the goals of CERES is the future success of the Finnish forest industry renewal. CERES addresses some of the most urgent global megatrends such as resource sufficiency, climate change, and quality of life, by turning these megatrend challenges into opportunities, and further into potential solutions that are built on scientific discoveries.

The technical and scientific objectives of CERES are (a) gaining deep knowledge on the nature of the interactions that exist between lignocellulosic systems and water; (b) developing methods for lignocellulose disassembly; (c) using new tools and methodologies to facilitate creation of next generation materials based on sustainable resources.

The CERES Flagship will create a unique foundation for new bioeconomy innovations in Finland. The purpose is to develop new materials, in particular based on lignocellulose and forest biomass, for industrial scale production of packaging, textiles and separation systems, as well as semiconductors, composites and solutions for energy storage.

Lignin analytics: Variability, challenges with the methods, and opportunities

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The reported global production of lignin stood at about 100 million tonnes/year as of 2015, with a market size of about USD 732.7 million. There is also a fast growing demand for lignin utilization in both large volume markets (e.g. adhesives, flocculants, dispersants, filler in thermoplastics, phenol replacement, blended lignin-polyurethane, etc.) and niche markets (e.g. carbon fiber, cosmetics, etc.) because it is a sustainable alternative to non renewable feedstock. It also has the advantage that it is not sensitive to oil price fluctuation and can reduce products cost. To respond to this demand trend, various feedstock (e.g. Kraft black liquors, softwood, hardwood, agricultural residues, etc.) and a variety of recovery processes (e.g. LignoBoostTM, LignoForce SystemTM, SLRPTM, organosolv, supercritical hydrolysis, etc.) are used to recover lignin. However, each feedstock-recovery process system results in lignin with differences in chemical, physical, thermal and functional proprieties. This implies diversity and variability in the molecular structure and functionality of lignins. It also offers opportunities to develop new chemistry that could support better understanding of lignin reactivity and to explore new approaches to transform lignin into high-value bio-based products. The objective of this study was to enhance knowledge of lignin properties and their variability, as a step towards identification of best-suited lignins for a wide range of applications. Furthermore, this knowledge is applied to develop a series of standardized methods for seven groups of properties, namely: characterize general chemical composition, size and morphology, structure and functional groups, thermal properties (glass transition, decomposition temperature, thermal stability) and other properties (solubility, pH, conductivity, colour, toxicity). About 120 lignin samples have been collected from different organizations in Europe and North America, and screened down to 45 for comprehensive characterization using a funnelling approach that was based on the following criteria: feedstock availability (e.g. agricultural residues, softwood and hardwood), different recovery processes (e.g. Kraft lignins, biorefinery lignins), technology readiness level, and relevance for lignin users and manufacturers. The limitations of established characterization methods during analysis of various lignins using were determined and, where necessary, alternative analytical protocols for enhancing knowledge on lignin were developed. The results were used to build a functionality fingerprint that was correlated to the corresponding feedstock-recovery process system by means of principal components analysis, a descriptive data analytics technique.

Electrospun lignin-based carbon fibers for energy storage application

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Electrospinning is a simple and efficient method for producing sub-micron diameter fibers. The electrospun fibers have a wide range of applications such as biomedical, textile and filtration. In addition, electrospun carbon fibers have potential applications in energy storage devices, such as battery and supercapacitors, due to their high surface area and conductivity. The structural stability, mechanical strength, and flexibility of these materials make it possible to use them as freestanding and binder-free electrodes.

Lignin, as a renewable precursor for carbon fiber, has been studied for making carbon fibers. In this study, softwood kraft lignin, from the LignoBoost process, was fractionated to isolate the high molecular weight fraction. The high molecular weight lignin performs better during both electrospinning and conversion process. Chemical and thermal properties of lignin sample were determined. Electrospinning solutions were prepared by dissolving different lignin concentrations in DMF or mixture of DMF/methanol. A simple electrospinning apparatus was used to produce electrospun mats. The electrospun mats were subsequently thermostabilized and carbonized to produce electrospun carbon fiber mats. The morphologies of the electrospun lignin fiber mats were studied by scanning electron microscopy (SEM). The performance of the electrospun mats in both lithium-ion battery and supercapacitor were evaluated by using the mats as electrodes in both devices.

Microwave-assisted conversion of pulp industry waste stream into levulinic acid

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Fiber sludge is cellulose-rich by-product generated ca. 750000 tons per year in Finland by pulp and paper industry. At the moment fiber sludge has mainly been incinerated or placed in the landfills. However, new applications are actively sought for its utilization. In this work fiber sludge was converted into levulinic acid (LA), which is one of the most important platform chemicals. LA can be converted into various other important chemicals and hence be used as a raw material for e.g. resins, plasticizers, textiles, coatings and fuel additives.

The conversion reactions were performed in mild H_2SO_4 solutions with microwave (MW) heating. In the first part of the study the reaction conditions i.e. reaction time (15-60 min), temperature (140-180 °C), H_2SO_4 (0.1-0.5 M) as well as additional Lewis acid ($CrCl_3$, 0.0019-0.0075 M) concentration were first studied with full 2^4 factorial design and then the reaction time (48-132 min) and the additional Lewis acid ($CrCl_3$, 0-0.022 M) concentration in more detail with central composite circumscribed design. According to the results the reaction temperature and the H_2SO_4 concentration had the most significant effect on the LA yield. The highest yield, 34%, was achieved at 180 °C in 60 min with H_2SO_4 concentration of 0.3 M and $CrCl_3$ concentration of 0.019 M.

In the second part of the work the effect of various Lewis acid catalysts on the LA yield was studied. Previously determined optimal reaction conditions, i.e. 180 °C for reaction temperature and 0.3 M for H_2SO_4 concentration, were used in the reactions. The studied catalysts were $FeCl_3$, $ZnCl_2$, $CuCl_2$ and $NiCl_2$ and the concentration of the catalyst was 0.0075 M or 0.019 M. The reaction time was 60 or 120 min. Based on the results, all the studied Lewis acids had a similar effect on the LA yield as $CrCl_3$. The highest LA yield (34%) was achieved with $ZnCl_2$ (0.0075 M) in 60 min.

To conclude, the results achieved in this study indicate that fiber sludge can be used as the raw material for LA production. Studies regarding the further optimization of the reaction conditions in order to improve the LA yield are on going.

Preparation of cellulose - based conductive materials

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With the development of printed electronics technology, electronic products tend to be personalized and intelligent. As a special functional ink, conductive inks rely on the market of various electronic products, and become thinner and more flexible. In the increasingly tense global energy demand, cellulose was favored by people as a natural material.

In this paper, carboxymethyl cellulose was used as matrix and graphene was used as conductive filler, compounding graphene with carboxymethyl cellulose. To prepare graphene/cellulose composite conductive film, the composite effect of it was discussed.

Firstly, with ascorbic acid as reducing agent, the graphene was prepared by the chemical reduction graphene oxide method. The optimal conditions for the reduction: the reaction temperature was 40 °C, the reaction time was 36 h, and the amount of reducing agent ascorbic acid was GO:L-AA=1:10. The prepared reduced graphene oxide has a conductivity of 110.2 S/cm. Secondly, graphene was composited with carboxymethyl cellulose by physical mixing，and the experiment explored the effect of different composite ratios on the composite result. When the mass ratio of graphene oxide to carboxymethyl cellulose was GO:CMC=1:6, the conductivity of the composite film was 8.5×10-2 S/cm. Due to the presence of physical interactions, graphene can be uniformly dispersed in the cellulose matrix.

Finally, the graphene/cellulose composite system was coated on a polytetrafluoroethylene substrate to prepare graphene/cellulose composite conductive films whose conductivity was regulated.

Influence of solvent on microwave - assisted cellulose activation

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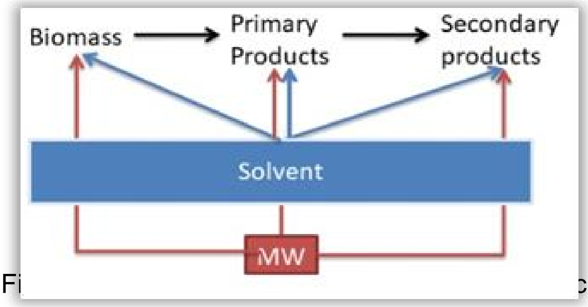
In this study, the influence of organic liquids on microwave (MW) pyrolysis of cellulose was investigated. MW-related solvent parameters were separated into three main groups which could be characterise as i) MW-solvent, ii) solvent-cellulose and iii) solvent-product interactions. The characterisation of MW-solvent interaction was performed by measuring the dielectric loss factor (ε'') of selected solvents using the resonant cavity perturbation (RCP) technique. The solvent-cellulose interaction was measured by the degree of cellulose swelling. The solvent-product interaction was evaluated with Abraham solvation parameters by using Multilinear regression (MLR) and PCA analysis. The MW heating rate was analysed with nonlinear regression and the efficiency of solvent-cellulose interaction in MW was found to correlate with the mass balance of products. MLR of cellulose swelling and solvation parameter was found to be independent of each other. A relation between McGowan volume of solvent with pyrolysis rate of cellulose was revealed.

Introduction

Although the intensive use of fossil resources causes environmental concerns, 95% of world chemical production is reliant on such aforementioned reserved[1]. Only 3% of biomass produced on the planet is used for both food and non-food purposes[1]. About 10% of the world's total biomass is forest waste and it may be converted into high-value chemicals using the biorefinery concept. Cellulose, the significant part of woody biomass, is a source of platform molecules. The activation of cellulose by microwave (MW) pyrolysis has already proven effective. However, product selectivity remains a challenge due to the polymerisation of primary products[2]. In conventional biomass pyrolysis, the use of selective solvent system has been shown to be a promising method of improving product selectivity[3]. In this project, solvent-assisted MW pyrolysis was investigated in a systematic way (as depicted in Figure 1).



Fi cess

The selection of organic liquid prove molecules was based on the COSMO-RS (COnductor like Screening Model for Real Solvents). The interactions of MW-solvent, solvent-cellulose and solvent-product were studied according to the scheme highlighted in Figure 2.

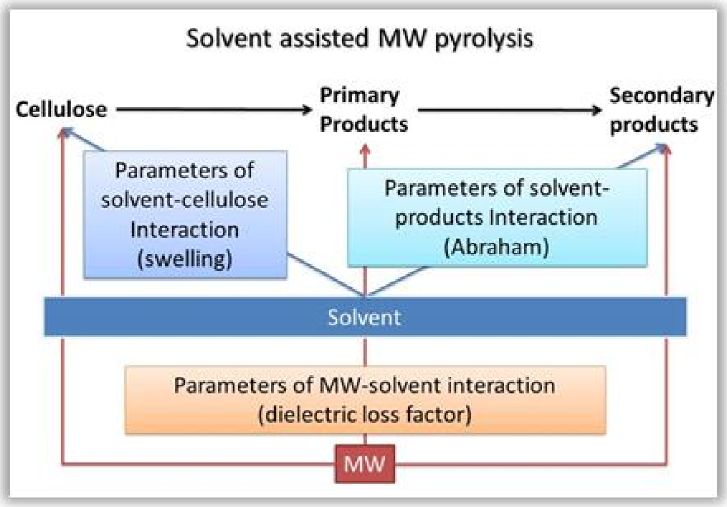

Solvent assisted MW pyrolysis
Cellulose
Primary Products
Secondary products
Parameters of solvent-cellulose Interaction (swelling)
Parameters of solvent-products Interaction (Abraham)
Solvent
Parameters of MW-solvent interaction (dielectric loss factor)
MW

Figure 2. Investigative steps involved in the solvent-assisted MW pyrolysis process

Understanding the mechanistic interactions of a solvent during MW pyrolysis would be beneficial in guiding the selection of the correct solvent required to control the pyrolysis process to gain a desired product/s

Experimental

Solvent-product interaction (MW liquefaction ability, MW pyrolysis kinetics and product identification) were studied according to the scheme drawn in Figure 3.

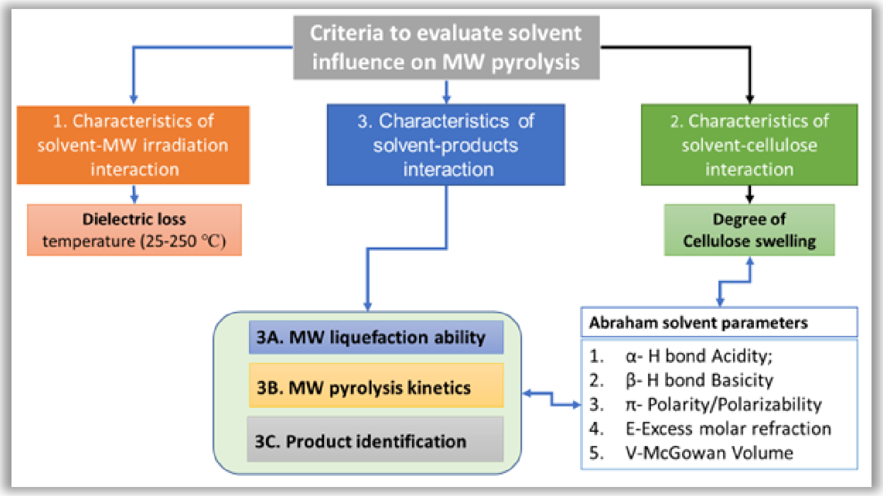
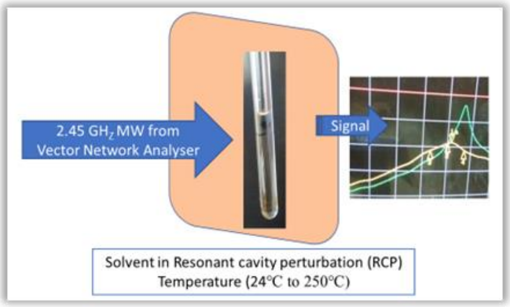

Criteria to evaluate solvent influence on MW pyrolysis
1. Characteristics of solvent-MW irradiation interaction
3. Characteristics of solvent-products interaction
2. Characteristics of solvent-cellulose interaction
Dielectric loss temperature (25-250 ℃)
Degree of Cellulose swelling
3A. MW liquefaction ability
3B. MW pyrolysis kinetics
3C. Product identification
Abraham solvent parameters
1. α- H bond Acidity;
2. β- H bond Basicity
3. π- Polarity/Polarizability
4. E-Excess molar refraction
5. V-McGowan Volume

Figure 3. Criteria used to evaluate the influence of solvent on MW pyrolysis.

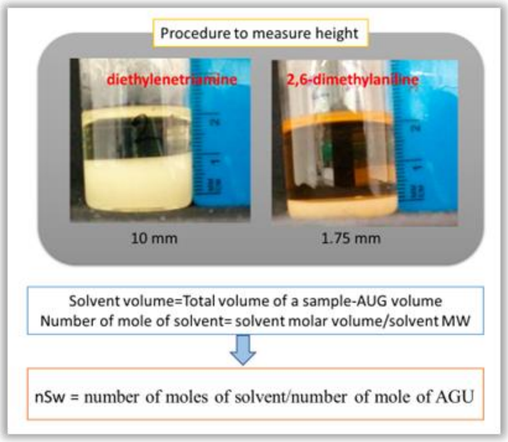
It is known that cellulose interacts with Microwave irradiation at a temperature near 180℃[4]. The interaction parameters were evaluated taking this temperature into account. To characterise solvent-MW interaction, an in-house instrument based on the resonance cavity perturbation technique (Figure 4) was constructed.


2.45 GH$_z$ MW from
Vector Network Analyser
Signal

Solvent in Resonant cavity perturbation (RCP)
Temperature (24°C to 250°C)

Figure 4. Graphical representation of a solvent in the resonant cavity (at a temperature of 24 ℃ to 200 ℃)

The solvent-cellulose interactions were evaluated according to the degree of cellulose swelling. The molar ratio of solvents (nSw) with the anhydroglucose unit (AGU) is shown in Figure 5.


Procedure to measure height
diethylenetriamine
2,6-dimethylaniline
10 mm
1.75 mm

Solvent volume=Total volume of a sample-AUG volume
Number of mole of solvent= solvent molar volume/solvent MW

nSw = number of moles of solvent/number of mole of AGU

Figure 5. Method of measuring solvent-cellulose swelling

Results and discussion

The comparison of the dielectric loss factor at high temperature (Figure 6) suggests that the choice of solvents for MW pyrolysis should be prioritised for product selectivity rather than its initial thermal energy conversion efficiency.

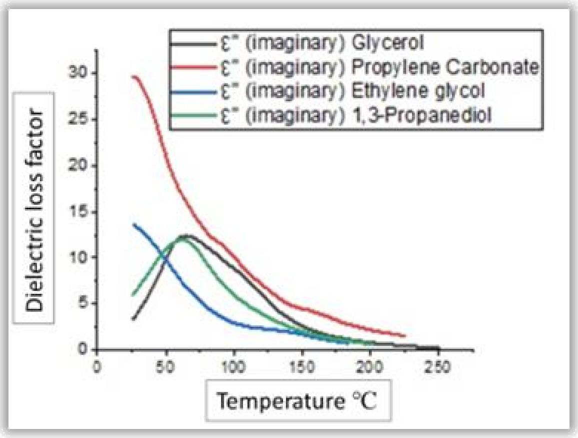


Figure 6. Comparison of dielectric loss factor at a high temperature

The degree of swelling and Abraham solvochromatic parameters was compared. The global p-value of MLR is significant but except for the McGowan Volume, the other four predictors appeared to be insignificant. Therefore, the model is non-significant, and the swelling effect does not have any correlation with solvation property (Figure 7).

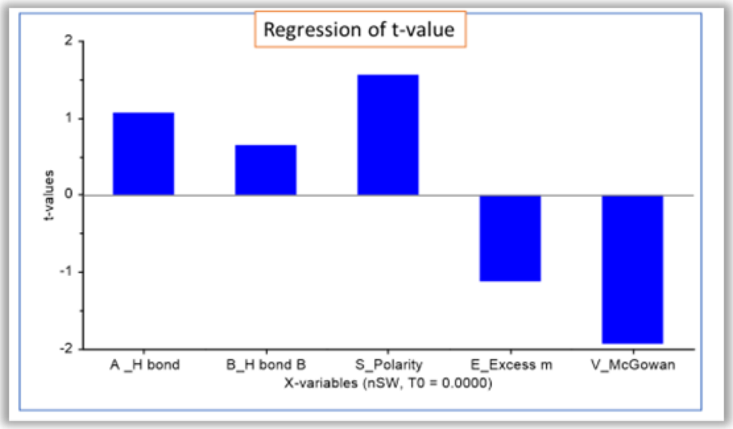


Figure 7. Analysis of solvent-cellulose interaction with multilinear regression.

Comparing MW pyrolysis residue with solvents solvation property in loadings of PCA (Figure 8) it was demonstrated that the MW activation process of cellulose is independent of the solvation parameters of the solvent used in the process.

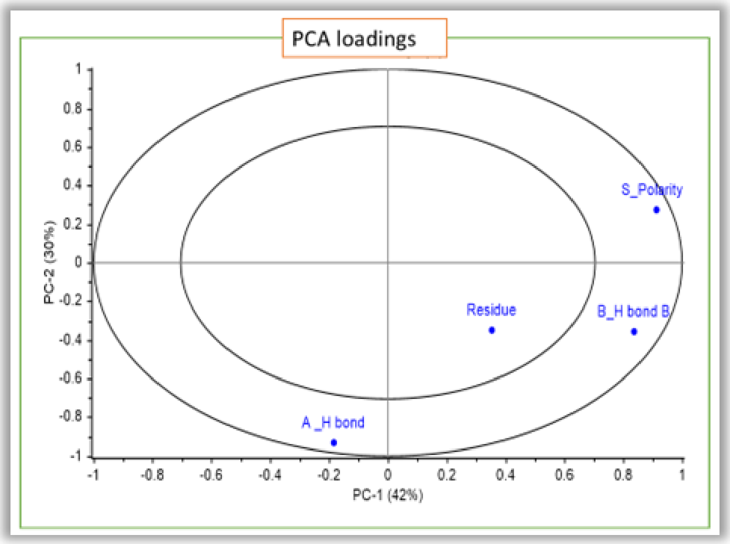


Figure 8. PCA loadings plot of solvent residue.

The MW heating rate was analysed with nonlinear regression (Figure 9) and the efficiency of solvent-cellulose interaction under MW irradiation was found to be correlated with the mass balance of products.

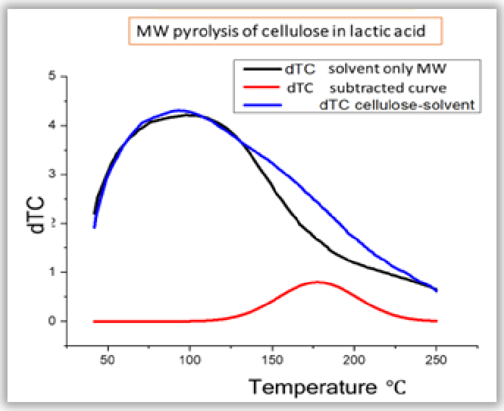


Figure 9. MW pyrolysis kinetics of cellulose in Lactic acid.

It was found that there was no significant linear correlation between all tested parameters of solvents and the solid residue yields of MW pyrolyzed cellulose. Therefore, all experimental dependencies were investigated in further detail. As a result of this analysis, it was found that the McGowan volume of the solvent and the correspondent solid residue yield were separated as three main cluster (Figure 10). The group 1 (coloured in black) and group 2 (coloured in orange) are corresponded to the low McGowan volumes and loosely related to this parameter. However, group 3 of the solid residues (coloured in green) demonstrate a reverse linear relation. Most of the molecules included in the group three cluster have a significant molecular volume. This means, there is a specific McGowan volume (c.a. 1.25) which separates two types of mechanism of influence of solvent nature on MW pyrolysis of cellulose. Above of this point, the degree of pyrolysis increases as McGowan volume increases which is independent of their chemical functionality. Below this point, other parameters have a more significant influence over the McGowan volume. It could be proposed that the molecules with high volume have limited ability to penetrate inside of the amorphous region of the cellulose. However, the highly volatile solvents help to retain the generated MW dielectric heat and prevent primary pyrolysis products from undergoing secondary reactions. On the other hand, a small molecule can penetrate inside of the amorphous cellulose region and is able to influence cellulose decomposition with their functional group.

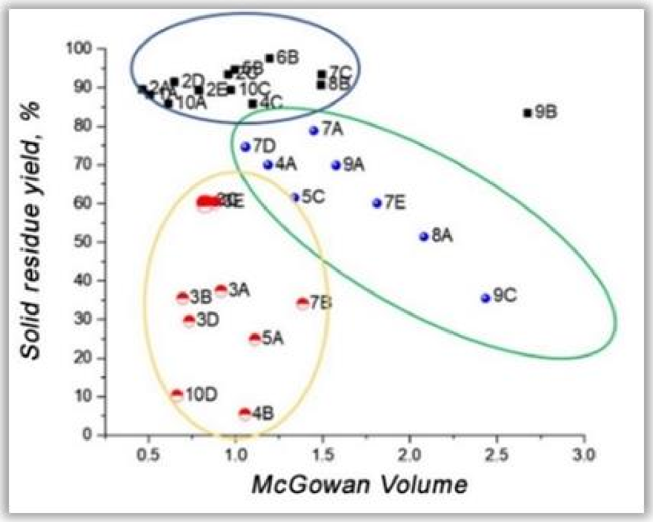


Figure 10. Relationship between cellulose pyrolysis residue and McGowan Volume.

Conclusions

This current work presents the first systematic study of solvent-cellulose interaction under the influence of MW. A high-temperature RCP instrumental technique was designed, developed and calibrated. The degree of cellulose swelling was proven to be independent of solvation parameters. The efficiency of MW treatment on solvent-cellulose interaction was calculated from the heating rate. The solvent-product interaction was evaluated by using MLR and PCA and a mechanism which explains the influence of solvent nature on MW pyrolysis of cellulose was proposed.

Acknowledgements

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Alkaline pre-treatment for the production of bioethanol and xylan from eucalyptus pinchips

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Pinchips are a residue generated at the pulp mills during the screening of the chips. Nowadays, pinchips are normally used in the power boiler to generate steam and energy. The big pulp mills existing in South America are energy self-sufficient and the surplus energy generated at the mills are converted in electricity and sell to the national grid. However, the introduction of other renewable energy like wind-power or solar goes down the price of the energy paid by the Electricity companies and the generation of electricity with biomass is being not profitable.

In this work, the aim is to obtain other products capable of added value to this residue. For this an alkaline pretreatment was tested with the objective of deconstructed the lignocellulosic biomass in order to obtain a liquor with high molecular weight xylans and a less recalcitrance lignocellulosic solid. In the solids obtained, enzymatic hydrolysis is done as a first step to produce bioethanol.

To study the alkaline treatment, pinchips from a local pulp mill were used. It was defined a 33 experimental design. The process´s parameters used were: temperature (105 - 155 °C), alkali charge (5 – 20 % NaOH) and time (45 - 135 minutes) with a fix L/W ratio of 5. The enzymatic hydrolysis took place on Erlenmeyer flasks, the ratio between solid and liquid was 1:7,5 and pH is adjusted to 4.85. The enzyme complex used were Cellic CTec2 (provide by Novozymes) and the concentration 25 FPU/gglucan. Temperature and stirrer speed were 48°C and 150 rpm.

The xylan content in the liquor is near the 20% of the original xylan in the wood, the molecular weight and polydispersity was determinated. The enzymatic hydrolysis yield for the best conditions are greater than the 85% at 48 hours.

Influence of lignosulfonate impurities on hemicellulose hydrogel properties

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Hydrogels are hydrophilic networks of polymers that are natural or synthetic. Applications of hydrogels are many in the biomedical field, many because of the high water absorption (10 to 200 grams of water per gram of hydrogel), that give the gels a high degree of flexibility similar to natural human tissue. Human cells can be incorporated into the hydrogel, which in turn can be used to repair damaged tissues. An option is to incorporate drugs in the hydrogels to treat a damaged area by a sustained-release drug-delivery system. Other uses have been in the production of bio-sensors, as absorbent in, e.g. diapers or in the production of contact lenses.

Hemicelluloses are a promising renewable raw material for the production of hydrogels. Given their high abundance (constituting up to 25% of the wood cell walls) and current lack of use (incinerated together with other biopolymers in the pulp and paper industry), makes this work valuable from an economical and industrial point-of-view.

In this work, we examine the possibility of producing hydrogels from hemicelluloses originating from sodium-based spent-sulfite-liquor. A combination of membrane filtration and anti-solvent precipitation was used for the extraction and purification of the different components. The influence of hemicellulose purity or the addition of lignosulfonates (emulated impurities in the downstream processing) to the cross-linking reaction mixture on the mechanical, thermal and chemical properties of the hydrogel have been studied.

Enforced tannin-furanic based heterogeneous catalysts support materials

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It is a fact, that fossil fuels are depleting fast and efforts are already been taken to overcome this issue (Chakraborty et al., 2016). Development of new greener ways to produce biofuels using biomass based heterogeneous catalyst has grown tremendously in the 21st century. In the past, various biomass-based catalyst has been created and already tested in some applications. Carbon supported catalysts based on carbons produced from nutshells (Liu et al., 2013), lignin (Kang et al., 2013) and sucralose (Hu et al., 2014) have been successfully tested previously with high conversion rates (55-65 %) in bioethanol production. From the green chemistry point of view, catalyst must be stable have a high specific surface area, well-defined porosity, made out of renewable resources and have high mechanical strength. Moreover, support materials must be resistant to the operating conditions used in the specific processes. For these reasons, tannin-furanic foams have gained a lot of interest among researchers.

The aim of this study was to demonstrate that tannin furanic based foams enforced with H_3BO_3 and $ZnCl_2$ are suitable to be used as support materials for heterogeneous catalysts. This study shows that mechanical strength of enforced tannin-furanic foams are better than the matured tannin-furanic foams, and these enforced carbon foams can be thermally stabilized for further higher mechanical strength. According to the results, up to four times stronger materials can be achieved by carbonizing the foams. Specific surface area, pore volume and pore size distribution play a key role in catalyst materials. Due to this, tannin-furanic foams, without additives, are thermally carbonized and converted to highly porous activated carbons with physical activation. In addition, comparison between physically and chemically activated tannin-furanic foams is made in order to see the difference in the pore size development. According to the results, there is hardly any differences in the pore size distribution between chemically and physically activated tannin-furanic foams. Most of the pores are microporous, which makes these foams more suitable and selective to be used as catalyst support materials in the catalytic conversion of small molecules.

Aknowledgements

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Totally bio-based, high-performance wood fibre biocomposites

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VTT has developed totally bio-based and compostable PLA – wood fibre composite material to be utilised in industrial applications. The usability of the material has been demonstrated in several processing methods and products. A large-scale injection moulding chair demo was carried out together with a design company KO-HO to demonstrate the usability of the material in industrial scale. Adhesion between PLA and wood-based fibres was improved with bio-based additives and chemo-mechanical treatments providing improved ductility, tensile strength and stiffness. Especially epoxy functional polyunsaturated vegetable oils was shown to act as a combined reactive plasticiser-coupling agent in bleached softwood kraft pulp reinforced PLA composites. The material was also shown to be applicable for novel light-weight structures, contributing towards decreased ecological footprint with savings in materials, energy and costs. In thermoplastic extrusion foaming process, wood fibre reinforced PLA was demonstrated to provide a promising alternative in formation of a closed-cell structure with low density. Furthermore, the material was shown to be suitable for production of thermoformable sheets produced by film extrusion. The extruded sheets can be utilised e.g. in light-weight honeycomb structures. The developments can open new business opportunities together with contribution to more sustainable world.

Introduction

In recent years, novel wood-based solutions have entered the markets due to renewing forest industry as well as requirements for more sustainable products. One of the solutions are biocomposite materials made with wood-based fibres from papermaking processes. Wood fibres offer sustainable reinforcement for thermoplastic polymers with low cost and easy availability. At present, commercial wood fibre based biocomposites are mostly based on crude-oil derived, non-biodegradable polyolefins[1]. While improving the mechanical properties and decreasing the use of fossil-based plastics with wood fibres, the ultimate aim should be totally renewable-based, recyclable or compostable materials in line with climate change protocol. For meeting this target, compostable but durable material solution could be one of the solutions. Poly(lactic acid) (PLA) offers a totally bio-based, industrially compostable polymer option for pulp fibre reinforced composites. PLA is commercially available in large scale with competitive price, sold in various polymer grades for several conventional thermoplastic processing methods[2]. Due to its more hydrophilic nature compared to polyolefins, PLA is naturally more compatible with cellulosic fibres[3]. Alternatively, adhesion promoters have also been introduced for applications with need for highly uniform fibre dispersion and improved mechanical performance[4-8]. Within the various adhesion promoting methods, modified vegetable oils offer simple, affordable and sustainable additive options[9,10]. In this paper, the potential of totally bio-based, wood fibre reinforced biocomposite material for industrial applications has been demonstrated by utilising various production methods and applications.

Experimental

Materials

All the materials have been produced in VTT polymer pilot facilities. Bleached kraft pulp fibres were utilised as wood fibres, and the PLA grades and additives were selected depending on the used processing method.

Injection moulding

Bleached softwood kraft pulp (BSKP) from Stora Enso were used as fibres and Ingeo PLA 3052D from NatureWorks as polymer matrix in injection moulded materials. Fibres were pre-treated with epoxy functional linseed oil Vikoflex 7190 according to procedure presented elsewhere[10]. The additive amount used was 5% in proportional to dry fibre. Compounds were prepared with fibre content of 40 wt% using co-rotating twin-screw extruder (Berstorff ZE25x33D). The extruder zone temperature ranged from 60 to 195°C. After compounding materials were injection moulded to dog bone shaped test specimens according to ISO 527 using Engel ES 200/50 and chair using injection moulding equipment in Plastec Finland Oy.

Foam extrusion

BHKP fibres were obtained from UPM Kymmene Oy. As matrix polymer, foam grade Ingeo PLA 8052D from NatureWorks was used. BASF Joncryl chain extender was added to increase the melt strength of the PLA (dosage 0,7 wt%). After vacuum oven drying, materials were compounded with Berstorff ZE25x48D co-rotating twin-screw extruder to fibre contents of 0-20 wt% using temperature profile from 195ºC in zone 1 to 175ºC in the die. Extrusion foaming was performed with laboratory-scale extrusion foaming line Brabender Plastograph EC plus equipped with single-screw extruder, melt pump and round die with L/D of 2/20 (mm), using 5% of carbon dioxide (CO_2) or isobutane (IB) as physical blowing agent. Blowing agents were acquired from AGA/Linde group.

Film extrusion and thermoforming

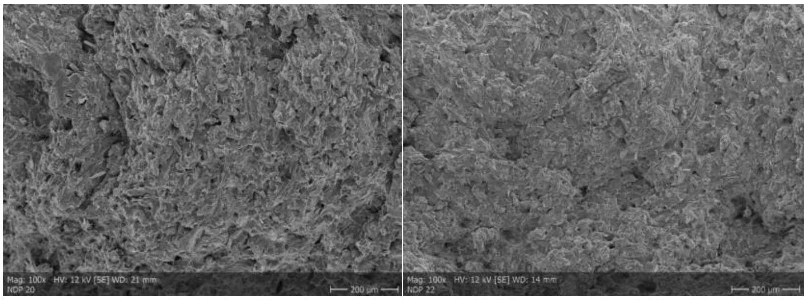
Micro-scale cellulose fibres were compounded with PLA with Berstorff ZE25x48D co-rotating twin-screw extruder. The fibre content was 10, 20 and 30 wt%. The compounds were extruder into 10 cm wide sheets by Brabender Plastograph EC with single-screw extruder and 120 mm film nozzle. The sheets were thermoformed.

Results and discussion

By intensive material and process development, VTT developed totally bio-based and compostable PLA - wood fibre composite material. The material properties can be tuned depending on the end-application and production process. The functionality of the material has been successfully demonstrated in several processing methods and products introduced below.

Injection moulded biocomposites

Biocomposite materials with BSKP modified with 5% epoxidised linseed oil showed 7% tensile strength, 5% tensile modulus and 37% Charpy impact strength increase compared to materials without additive. The impact strength value is in the same level (16.5 kJ/m^2) as neat PLA. The fibre dispersion in PLA matrix was improved due to additive and the coupling between fibre and PLA was proved using FTIR and visually in SEM-pictures (Figure 1).


Mag: 100x HV: 12 kV [SE] WD: 21 mm
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Mag: 100x HV: 12 kV [SE] WD: 14 mm
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Figure 1. SEM-pictures of cross-cut injection moulded BSKP-PLA composites without additive (left) and with additive (right)

The same material was used in a chair designed by designer company KO-HO and injection moulded by Plastec Finland Oy. A totally bio-based chair (Figure 2) was produced to demonstrate the usability of the material in large-scale injection moulding process. This project showed the importance of close connection with designer, manufacturer and mould development together with material development to achieve novel sustainable products on market.

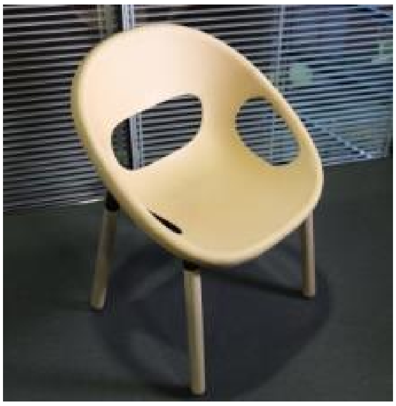

Figure 2. Injection moulded, totally bio-based and compostable design chair

Extrusion foamed biocomposites

Wood fibre reinforced PLA materials were shown to be applicable for novel light-weight structures, contributing towards decreased ecological footprint with savings in materials, energy and costs. Even without absolute process optimisation, the resulting extrusion foamed pulp fibre reinforced PLA biocomposite materials show potential in several application areas. Both physical blowing agents were found to be suitable for foaming of the material. With 0 and 10 wt% of fibre content, the obtained foam densities were 50-60 kg/m^3 and 72-73 kg/m^3, respectively. When fibre content was increased to 20 wt%, the foam density increased to 126-135 kg/m^3. In general, it was noticed that fibre addition reduces the overall foamability of PLA, since the amount of foamable polymer is reduced. However, low density (< 200 kg/m^3 (11)) foam were still generated even with 20 wt% fibre content. Additionally, much finer cell structure was achieved with composite material compared to pure PLA since the addition of fibres restricts the growth of cells in the foam (Figure 3). Finer cell structure is associated with enhanced mechanical properties[12]. The use of chain extender was crucial in achieving low density foam from PLA based biocomposite.

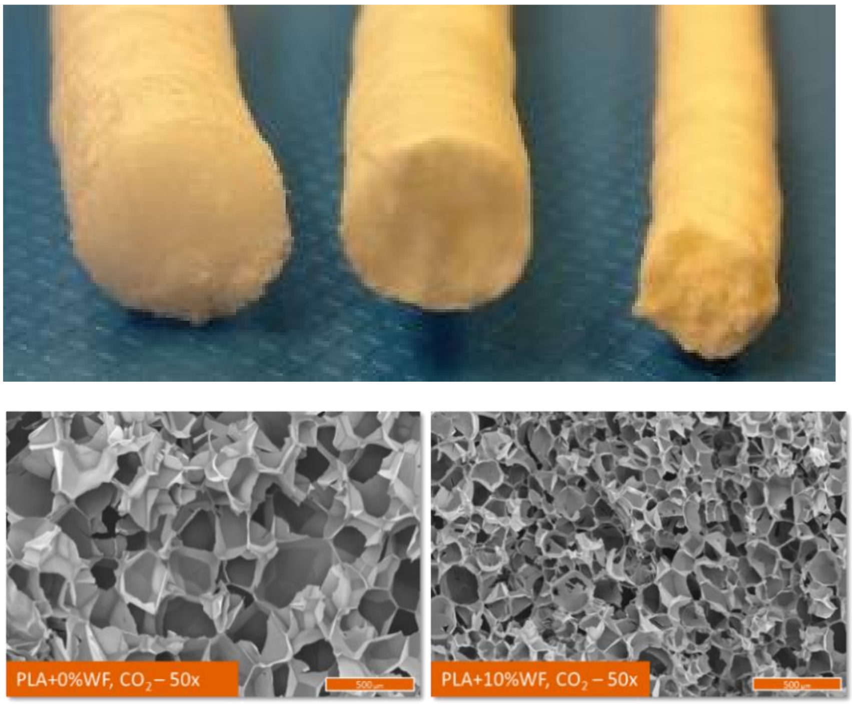

Figure 3. Extrusion foamed PLA-wood fibre biocomposites

Thermoformed solutions

In addition, cellulose fibre reinforced PLA material has shown to be suitable for production of film extruded, thermoformable sheets, which can be utilised e.g. in light-weight honeycomb structures or packaging. Cellulose fibres provide an opportunity to improve the stiffness of the thermoformable sheets ecologically without increasing the weight, and at the same time decreasing the use of oil-based polymers. EconCore and VTT developed cellulose fibre reinforced thermoplastic film for honeycomb structures in EU-INCOM project. PLA and petroleum-based polypropylene (PP) sheets were reinforced with 10, 20 and 30 wt-% microcellulose. PLA film with up to 30% was thermoformable (Figure 4). Thermoformed bio-based and biodegradable films could be an option for example for future packaging materials.

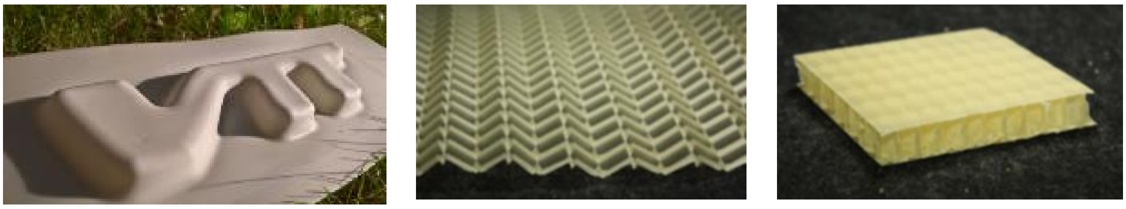

Figure 4. Thermoformed PLA-wood fibre sheet (left). Thermoformed web and (laminated) honeycomb structures were demonstrated with PP-based core including 20% cellulose.

Conclusions

VTT has demonstrated that totally bio-based and compostable materials can be tailored according to the industrial need for various polymer processing methods and applications. With proper process and recipe development, PLA-based biocomposites can be used in injection moulding process with good end-product properties also in large items. The material is also suitable for light-weight foams produced by extrusion foaming for applications such as packaging or insulation. The developed bio-based materials can also be utilised in structural or packaging applications through film extrusion and thermoforming processes.

Totally bio-based materials are competitive and sustainable alternatives to traditional oil-based plastics both functionally and economically. Close collaboration between products designers, manufacturers and materials researchers can open new business opportunities together with contribution to more sustainable world.

Acknowledgements

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Novel processing technologies for cellulose-based electrical insulation components

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NOVUM project addresses the challenges in the state-of-the art production of electrical insulation components from cellulose. It aims to develop more efficient and agile manufacturing processes with the help of three versatile manufacturing processes, namely 3D printing, foam forming and thermoforming, together with development of cellulose-based materials. At the end of the project, the new processing concept will be demonstrated as a pilot line with significant efficiency improvement and higher productivity and flexibility as compared with the state-of-the-art process. Manual production will be replaced by an automated manufacturing concept with increased resource efficiency, targeting at 40% reduction in labour time and 60% reduction in waste generation, 20% lower energy consumption and 40% decrease in operating costs.

Introduction

Electrical insulation components are used in oil-cooled power and distribution transformers. The components are made to different three-dimensional shapes, and cellulose is a common raw material for these components due to its high purity, excellent dielectric strength, good mechanical strength, ability to be permeated with oil, and long lifetime at operating temperature.

The production of electrical insulation components using cellulose as the raw material is based on an established technology. However, in the increasing global competition, there is a growing need to develop more efficient and agile manufacturing processes as the current manufacturing is complex, consisting of multiple stages, consuming a lot of time and energy, and being labour-intensive. In addition, utilization of raw materials and energy are not optimal.

The challenges mentioned above will be addressed in a recently started EU-funded NOVUM project, aiming at development of a pilot line based on novel manufacturing technologies for cellulose-based electrical insulation components. The new pilot line will target at rapid, automated and design-driven production of the components as well as significant improvement in operational efficiency, higher productivity and flexibility, while achieving lower operational costs compared to the current technology. In addition, increased resource efficiency is expected, including reduction in labour time, waste generation and energy consumption. Besides technical feasibility, the end user requirements as well as economic, social and environmental impacts, including circular economy considerations will be taken into account.

NOVUM focuses on three technologies for processing of cellulose-based materials: 3D printing, also known as additive manufacturing, foam forming and thermoforming. Cellulose material development will take place simultaneously to the process development in order to take into account the requirements of the different processing technologies, such as the thermoplastic features needed for 3D printing, as well as the operational requirements for electrical insulation components.

In this presentation, the idea behind NOVUM will be discussed. Progress to-date will also be outlined, the first actions focusing on cellulose material and process development and finding out the end user requirements.

The idea behind NOVUM

Cellulose as a raw material

Cellulose, as a renewable, non-toxic, non-allergic, and abundant forest material, has several benefits to be utilized in a wide range of applications. Currently, it is, however, mostly used in large scale applications: paper, packaging, and textile[1]. The current industrial technologies have limitations in forming three dimensional structures from cellulose, which could be beneficial in complex shaped soft or hard objects.

The introduction of feasible on-demand and customer-oriented manufacturing could increase the market competitiveness of cellulose-based materials. An additional benefit with the introduction of novel processing for cellulose-based materials is promoting the utilisation of renewable and abundant bio-based raw material for the current application and beyond.

Versatile processing technologies

The technologies selected for NOVUM, 3D printing, foam forming and thermoforming, have been demonstrated for cellulose-based materials in different industrial sectors such as pulp & paper, food packaging, construction (as insulation materials) and medical materials/scaffolds. They are however new to the electrical insulation application sector in focus of NOVUM, but upon success, will facilitate the electrical insulation part design and provide flexibility and resource efficiency for their manufacturing. Furthermore, the process technology advances in the NOVUM can also be transferred to other industrial sectors interested in applying cellulose-based materials in novel manufacturing processes.

3D printing

Each power transformer unit usually has a very specific and individual design, which influences also the design of the insulation components (Figure 1). Consequently, for each insulation component an individual metal mould has to be fabricated resulting in hundreds or even thousands of moulds being organised and stored. Finally, the process results in significant material waste. It would be beneficial if the dependency of the process on moulds, especially metal moulds, could be reduced. By introduction of 3D printing into the process these goals are expected to be accomplished. Implementation of 3D printing will enable easier production of components with complicated design and/or smaller production series. In addition, it will potentially make exploitation of the full potential of design in generating shape and form possible. Furthermore, it is also possibly that the moulds used in the forming technologies are produced by 3D printing.

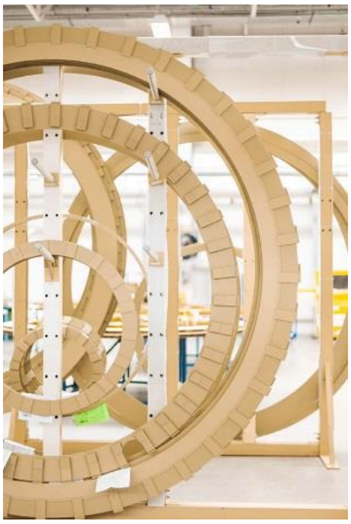

Figure 1. Power transformer unit. Photo: Urszula Czapla/ABB.

Foam forming

The use of liquid foam as a material carrier phase for production of 3D shapes and structures from cellulose fibres enables the production of lightweight cellulose structures, potentially leading to significant resource savings in conventional products, such as paper products[2]. In addition, it may lead to novel product opportunities for cellulose fibres, for example in medical and hygienic applications, filtration and as sound-absorbing and insulation materials[3,4]. The structural properties of wet foams enable tailoring of the formed cellulose structure. As an example, the pore size distribution of the structure can be tuned with the bubble size of the foam, having an impact on various transport properties, such as gas and liquid permeability. In addition, water removal in wet-pressing is much better for foam-laid structures as compared to water-laid, with dryness improvements between 2-8%-units after press section, which indicates more than 20% savings in the drying energy.

Thermoforming

In thermoforming, the cellulose pulp is sucked though a net, depositing the fibres on the net structure, which is roughly in the shape of the final product. The deposited pulp is transferred from the net section, to a set of heated moulds. The heated moulds consist of male and female moulds that fit together with the rough paper moulding in between. In the moulds there are steam channels that allow for steam evacuation. The final product, 3D shaped cellulose structure, has excellent mechanical properties and a high quality surface finish[5].

The biggest benefit in thermoformed fibre technology is gained by utilising the Impulse Drying Technology (IDT), with the potential to reduce the required energy by at least 75%, compared to the conventional thermoformed fibre process and reduce the process times from minutes to seconds.

Progress to-date

The NOVUM project started on October 1st 2017 and is approaching the end of its first period (M12). Progress so far has been made in formulating cellulose-based materials for the different processing technologies and in development of the processing technologies.

Material formulation

The first task in material formulation was to screen the potential cellulose-based raw materials on the market that could fulfil the requirements of both the processing technologies and of end-use. For 3D printing, the suitable raw materials were sought among cellulose derivatives, composites and powders. For the forming technologies, market pulps as such or with some property adjustments were assessed.

Raw materials evaluated suitable were obtained from the consortium partners and ordered also from other suppliers. Material processing was tested with the NOVUM processing technologies and if the material was found suitable for processing, the component is then send for testing for their applicability as electrical insulation components performed according to the industry standards. The work in this task is still on-going, with the first deliverable and milestone expected in M18.

Process development

Some selected cellulose-based materials, such as thermoplastic cellulose developed at VTT[6] and commercial wood polymer composites, have been tested for their 3D printability using for example Fused Deposited Modelling (FDM). So far, all of the tested materials have been found to be processable by 3D printing using commercial equipment. However, at later stages in the project, further development of the equipment might be needed, in order to suit the material needs and end-user requirements.

Foam forming technology has been applied for the production of first test pieces at different density levels. The next steps will involve adjustment of solids content of the components after forming and wet-pressing to an optimal level.

In the thermoforming process, the progress to-date has focused on the development of SMART Tool, which is a reconfigurable tooling system. The concept development for this tool is still on-going. The next steps will be evaluation of most interesting and promising concepts, followed by prototype preparation and testing.

Acknowledgements

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Biohydrogen from wood hemicellulose hydrolysate

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The aim of the present study was to evaluate the possibility to produce hydrogen from wood hemicellulose by performing reactive extraction experiments for soft-wood (Pinus sylvestris) particles and aqueous phase reforming (APR) experiments with synthetic water solutions of pure xylitol and mixtures of xylitol and xylose. In the reactive extraction experiments, it was observed that a high monosaccharide concentration can be reached while forming relatively low concentrations of soluble oligomers and furanics. In the APR experiments, it was found that hydrogen can be produced with high selectivity from synthetic water solutions containing xylitol, but mixing xylitol with xylose results in the caramelization of the reacting mixture.

Introduction

Currently, one of the key processing operations in the production of advanced bio¬fuels in Finland is hydrotreatment. Correspondingly, the stabilization and refining of bio-oils originating from biomass pyrolysis and liquefaction lead typically to different hydrotreatments[1,2]. One potential source for the hydrogen used in the hydrotreatments is biohydrogen produced from wood and wood hydrolysates. Basically, biohydrogen can be produced from biomass with a number of different routes as re¬viewed by Tanksale et al[3]. In this study we investigate biohydrogen production applying first selective reactive extraction of hemicellulose from wood to monosaccharides. Earlier, we reported results for the pressurized hot water extraction of spruce hemicelluloses[4]. Recently, we reported results for the reactive extraction of hemicellulose from European silver birch (*Betula pendula*), which showed that a high extraction selectivity of hemicellulose can be reached by using formic acid water solutions[5].

After the reactive extraction we evaluate if the monosaccharides can be used directly, or first after hydrogenation to sugar alcohols, as a raw material to produce hydrogen using aqueous phase reforming (APR) over a solid catalyst. Aqueous phase reforming of sugar alcohols, and more generally polyols, to hydrogen and light alkanes can be performed over various supported metal catalysts at rela¬tively mild operating conditions (ca. 225 °C, 30-50 bar)[6,7].

Experimental

The reactive extraction experiments were performed using ground softwood (*Pinus sylvestris*) particles. Extraction solvent was a mixture of water and formic acid, which acted as the catalyst. The effects of operation conditions (reaction time, temperature and acid concentration) and particle size to the quality of the hydrolysate were in¬vestigated. The reactive extraction experiments were carried in the zirconium alloy extraction cells of an Accelerated Solvent Extraction equipment (Dionex ASE350, Thermo Fisher Scientific). The composition of the liquid fraction of the hydrolysates were analysed by HPLC (Agilent 1200).

To enable initial evaluation of the characteristics and feasibility of the selected biohydrogen production route from wood hemicellulose, the following APR experi¬ments were performed using synthetic water solutions of either pure xylitol or mixtures of xylitol and xylose (Sigma-Aldrich). A commercially (Sigma-Aldrich) available 1 wt % Pt/Al2O3 catalyst was employed in the experi¬ments. The effects of temperature and gas flow through the reactor on the conversion of xylitol and selectivity to hydrogen and CO_2 were investigated. Additionally, experiments were performed with mixtures of xylose and xylitol to test the viability of treating xylose in the APR system. A schematic of the set-up is displayed below in Figure 1.

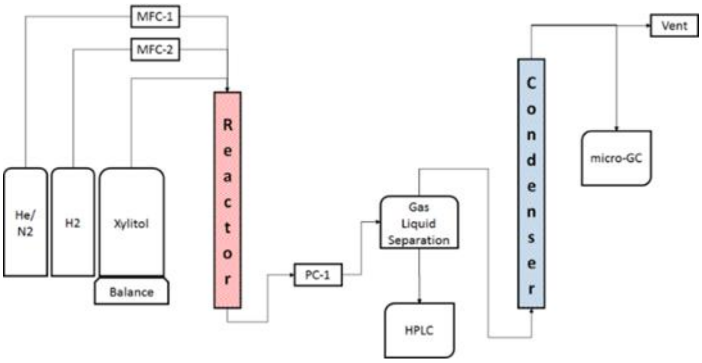

Figure 1. APR reactor set-up.

The APR reactor set-up consisted of a fixed bed tubular reactor heated by an electrical oven, mass flow controllers for inert (1 % He in N2) and catalyst reduction (hydrogen) gases, membrane pressure controller (Equilibar). A gas-liquid separator was utilized downstream of the pressure controller. Liquid samples were withdrawn from the separator and analysed by HPLC (Agilent 1100) in order to obtain the xylitol conversion. The column used in the HPLC was a Aminex HPX-87H and the eluent 5 mmol/L H_2SO_4. The product gas was led through a condenser prior to being ana¬lysed by a micro-GC (Aglient 3000A), 1 % helium in the inert gas flow was used as an internal standard to calculate the molar flows of gaseous products and the se¬lectivities to hydrogen and CO_2. The xylitol solution was fed with an HPLC pump (Eldex). The reactor was operated in co-current trickle flow.

Different reaction conditions were tested in the aqueous phase reforming of xylitol. The xylitol conversion was calculated based on the peak areas obtained from the HPLC. The selectivity to hydrogen was calculated with the equation below:

$$S_{\mathrm{H}_2} = \frac{\dot{n}_{\mathrm{H}_2}}{\dot{n}_{\mathrm{carbon}}} \frac{1}{RR}, \qquad (1)$$

where $\dot{n}_{\mathrm{H}_2}$ is molar flow of hydrogen in the product gas, $\dot{n}_{\mathrm{carbon}}$ is the total molar flow of carbon and RR is the reforming ratio, which has a value of 11/5 for xylitol.

Results and discussion

Based on the reactive extraction experiment results, formic acid catalyzed hemicellulose extraction results in the recovery of hemicellulose as monosaccharides with the efficiency ranging from 60% to 75% at the optimal extraction time. Maximum recovery is relatively independent on the reaction temperature or formic acid con¬centration, when temperature is over 140 °C and formic acid concentration is over 4 wt-% as shown in the case of 7 wt-% in Figure 2.

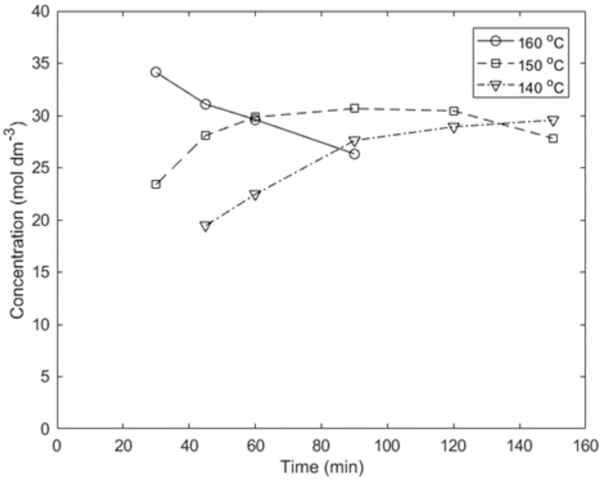

Figure 2. Concentration of monosaccharides in the hydrolysate after reactive ex-traction at different temperatures using formic acid water mixture solvent. Formic acid concentration was 7 wt-%.

On the other hand, higher solid to solvent ratio decreases the maximum monosac¬charide recovery. Moreover, a trade-off between forming furaldehydes (furfural and 5-HMF) and soluble oligosaccha¬rides (mostly di- and trisaccharides) occurs in the investigated conditions as illustrated in Figure 3.

As can be seen in Figure 3, at high temperature and longer reaction time the for-mation of furaldehydes through dehydration of monosaccharides is fa¬vored whereas at lower temperature and shorter time the hemicellulose is only partially hydrolyzed to form different length soluble oligosaccharides.

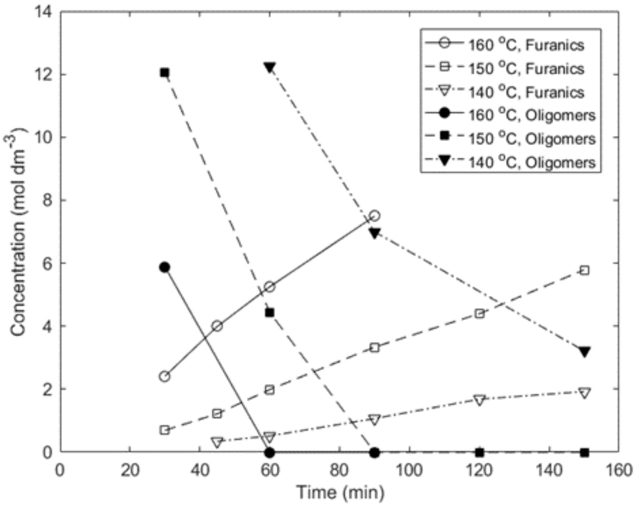

Figure 3. Concentrations of furaldehydes (furfural and 5-HMF) and soluble oligo¬mers in the hydrolysate after reactive extraction at different temperatures, marked as ’Furanics’ and ’Oligomers’, respectively.

Low formic acid concentration favors oligosaccharide formation, and as an extreme, extraction with pure water results mainly in the formation of oligomers instead of monosaccharides, e.g. at 160 °C after a 4 hours reaction time only 5 g/dm3 mono¬saccharides was formed while simultaneously 20 g/dm3 oligosaccharides was formed. Furthermore, use of a higher temperature does not in¬crease the monosac¬charide content significantly. Thus, the acid catalyst is crucial when producing monosaccharides from hemicelluloses by reactive extraction.

In the APR experiments, it was observed that in order to achieve high con-version of xylitol the temperature should be preferably above 225°C. Additionally a three phase system with a flow of inert gas is very beneficial for increasing the conversion. No significant changes in selectivity to hydrogen was observed at different xylitol conversions obtained at varying experimental condition, as displayed in Figure 4.

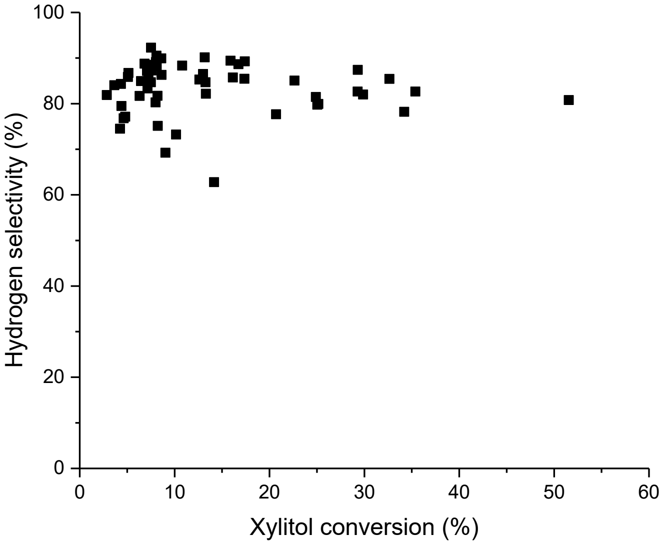

Figure 4. Selectivity of xylitol to hydrogen at different xylitol conversion levels in the APR experiments.

Mixtures with different ratios of xylose and xylitol were tested in the same experi-mental conditions with the idea that the hydrogen produced from the xylitol could in situ hydrogenate the xylose and initiate the further APR reaction. All of the experi¬ments resulted in the same conclusion; the mixture caramelized rapidly and blocked the reactor. This strongly indicates that it is necessary to hydrogenate the xylose to xylitol in a separate step prior to performing the APR.

Conclusions

In the extraction experiments, it was found that with controlled combinations of tem¬perature and time a hydrolysate can be produced that has a high monosaccharide yield while the amount of furanics, 5-HMF and furfural remain relatively low. In the APR experiments, it was observed that xylitol can be converted to hydrogen with high selectivity in a wide range of operating conditions. Instead, having xylose in the solution results in caramelization, which suggests that xylose should be hydrogen¬ated to xylitol before performing APR. As a whole it can be concluded that the pro¬duction of biohydrogen from wood hem¬icellulose hydrolysate via APR is a potential method for hydrogen production.

Acknowledgements

The authors wish to thank Business Finland for the financial support to the HEMIH2 project.

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Bioactive compounds extraction from forestry residues using ionic liquids with emphasis on solvents recycling

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Carried out the (polyphenol nature) investigations regarding to characterization of the plant biomass processing by-products, using fractionation, namely, treatment with ionic liquids (ILs), using conventional and microwave assisted extraction (MAE). The suitability of ionic liquids (different imidazolium based ILs) for the fractionation of grey alder bark (Alnus incana) in comparison with organic solvents has been evaluated and the potential of the obtained fractions as antioxidants has been determined. The results of the study have shown that, using the select “antisolvents”, it is possible to separate the carbohydrate fraction of the polyphenol fraction with a fairly high selectivity. The work shows the whole chain of analytical process performed, from sampling to full analysis, emphasizing the evaluation of the effect of the extraction process on the target polyphenol compounds, their composition and antioxidant activity. The solid phase extraction allows an effective increase in the compounds’ recoverability from the IL dissolved part, which cannot be re-extracted with “antisolvents”, and allows the recovery of ionic liquid, which is a problematic issue in biomass processing with ionic liquids in the world. In addition, the analytical process integrates sustainable development, which reduces the use of toxic and hazardous substances in extraction processes, replacing them with more environmentally friendly ones.

Introduction

Forestry residues and wood mechanical processing waste represent an abundant and potentially sustainable source of biomass which could be used as a raw material for value added products obtaining. These wastes are underexploited now or found application that is not in conformity with their potential. First of all, it is concern of a large variety of polyphenolic substances having multifactorial biological activity connected with antioxidant and antimicrobial properties. Extraction is regarded as a key for obtaining value added products in general, and valorizing of lignocellulosic biomass as a source of such chemicals in particular. However, the conventional extraction of phenolic compounds most commonly used volatile, toxic and flammable organic solvents, is not correspond to global integrated sustainable development that envisages reducing the application of such solvents and, replacing them with more environmentally friendly solvents. Ionic liquids (ILs) consisting of organic cations paired with organic or inorganic anions are one of the prospective candidate for this purposes. The aim of the work was to test different imidazolium based ILs and IL mixtures with water for extraction of grey alder bark using conventional and microwave assisted extraction (MAE), determine chemical composition of extracts obtained and to characterize their antioxidant properties.

Experimental

Dried (vacuum, 40 ◦C) grey alder bark was treated with different ILs at a solid : liquid ratio (w/w) of 1 : 20 at 100 ◦C for 6 h under an inert (N2) atmosphere. As was found by our previous experiments, at the lower solid : liquid ratios (e.g. 1 : 10) dissolved in ILs only partly but at the ratio = 1 : 20 the extraction yield increased significantly varying the treatment time from 1 to 5 h and after 6 h reaches the maximum solution then filtered to remove the dissolved part from the undissolved part. After filtration, was gradually added firstly to the excess of the acetone-water (1 : 1) mixture (antisolvent 1) in order to obtain rich-in carbohydrates fraction (Fraction 1). Water (pH = 2) was used in the same manner as the second antisolvent (antisolvent 2) to obtain rich-in lignin fraction (Fraction 2), respectively). After the solution was centrifuged (5500 rpm for 15 min), the recovered fractions were separated, washed and vacuum dried. Three parallel fractionation experiments were conducted. Extraction with organic solvents were made according[1]. Dissolved part in ionic liquids after antisolvent uses which can’t recover with anti-solvents put on pre-swelled and washed out columns. Continue extraction with 5 column volumes of water. Collect fraction obtained and continue extraction with 2 column volumes of ethanol. Fractions was collected and freeze dried. Radical scavenging activity against DPPH●, ABTS●+ radicals was measured spectrophotometrically as described in[2]. Total phenolic content in the extracts was determined using Folin–Ciocalteu method and expressed as milligrams (mg) of gallic acid equivalents (GAE) per g of oven dry, ash free sample. Analysis of individual compounds was performed on ACQUITY UPLC H-Class system coupled to SYNAPT G2-Si High Definition Mass Spectrometer. Column: Waters Acquity UPLC BEH C18, 2.1 x 50 mm, 1.7μm, flow 0,35 mL/min, The eluents: 0.1% formic acid in water (A) and acetonitrile (B), gradient from 10% A to 100% B, injection 2μL. Mass range (50-1200 Da), ESI negative mode, cone voltage 40 V, scan time 0.1s, desolvation gas Nitrogen (600 L/h), source temp. 120ºC.

Results and discussion

It was shown that the ILs structure, their concentration, biomass/IL ratio, time, temperature strongly influenced the results obtained. Solubility in ILs of biomass used varies from 30 % using 1-butyl-3-methyl-1H-imidazolium 4-methylbenzenesulfonate [C4C1im]OTs up to 60 % using 1-butyl-3-methylimidazolium dimethylphosphate [C4C1im] DMP (Figure 1) and up to 75 % using [C4C1im] DMP when MAE of original construction was used. IL anion has been shown to play a leading role in lignocellulosic solubilization. Based on the literature data[3,4]. As “antisolvents” different organic solvents (ethanol, acetone, ethyl acetate), as well as their mixtures with water were tested. To obtain carbohydrate containing fractions, “antisolvent” - acetone : water (1 : 1) was used (1 fraction), but for obtaining the polyphenol containing fractions, acidified water (pH = 2) was used (2 fraction). The amounts of the obtained fractions, treating the IL soluble fractions with the corresponding ”antisolvents”, are summarized in Table 1.

Table 1. Yields of fractions (%) obtained from alder bark IL solubles as a result of processing with “antisolvents” 1 and 2

IL + fractionation conditions	**1. fraction mass, % from bark**	**2. fraction mass, % from bark**
Grey alder bark (various solubility in different IL)		
[C_4C_1im]DMP, 6h/100 ºC	8.3 ± 0.8	2.43 ± 0.11
[C_4C_1im]Cl, 6h/100 ºC	8.8 ± 0.3	0.8 ± 0.02
[C_4C_1im]OTs, 6h/100 ºC	10.2 ± 0.3	0.9 ± 0.04
[C_4C_1im]OAc, 6h/100 ºC	9.5 ± 0.3	1.12 ± 0.08
[C_4C_1im]DMP, microwave 30min/100 ºC	14.6 ± 0.4	1.38 ± 0.09
[C_4C_1im]DMP, microwave 30min/150 ºC	10.2 ± 0.3	0.9 ± 0.04

Since it is not possible to recover all the lignocellulosic material dissolved in ionic liquids with the “antisolvents” used in the work, then a solid phase extraction method was developed for more effective separation of individual compounds, compound groups and IL regeneration (Figure 1.). The scheme for the ionic liquid recovery and valuable polyphenols obtaining from the lignocellulosic feedstock see in Figure 3. The solid phase extraction allows an effective increase in the compounds’ recoverability from the IL dissolved part, which cannot be re-extracted with “antisolvents”, and allows the recovery of the ionic liquids.

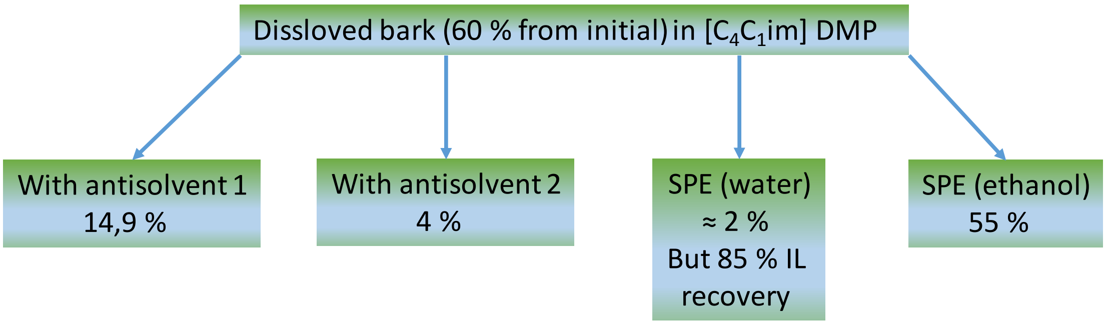

Figure1. Yields of fractions (%) obtained from alder bark, IL solubles combine antisolvent use with SPE

Fractionating alder bark with ILs, the valuable polyphenolic compounds with a wide range of practical application were obtained, for example, ferulic acid derivatives 1 (m/z 193, m/z 178) (esters with fatty alcohols). Ferulic acid and its derivatives possess a biological activities; in addition, ferulic acid is widely used as a food additive. In parallel to proanthocyanidins, also prodelphinidins and gallocatechin formed tannin compounds 2, and flavonoids were obtained using [C_4C_1im]. Fractions of grey alder bark obtained using [C_4C_1im]DMP contained mainly diarylheptanoid compounds 3 and tannin compounds 2. Low molecular weight polyphenols as flavonoids, tannins and ferulic acid derivatives’ (see Figure 2.) compounds, obtained with ionic liquids, have the possibility of extensive practical uses. They can be used as food additives, cosmetic products’ ingredients and even as potential active substances in homeopathic pharmaceutical preparations. Results obtained confirm the opportunity to modify the chemical composition of fractions using different ILs respectively with improved targeted properties according to application.

In the case of grey alder bark sequential fractionation with organic solvents of different polarity, three soluble fractions were obtained (Table 2). The obtained extraction results have shown that, using pure solvents, the highest yield of extraction for obtaining polyphenol containing extracts is obtained by using ethyl acetate - mainly diarylheptanoids and ethanol - mainly proanthocianidins. On the average, the polyphenol compounds (ethyl acetate and ethanol extracts obtained) content in alder bark growing Latvia is within the range of 0.50 – 0.65 GAE g·g^{-1}, depending on the extraction method and solvent used. The fractions obtained with ionic liquids after the SPE using ethanol as a eluent showed slightly higher amounts of polyphenol up to 0.70 GAE g·g^{-1}.

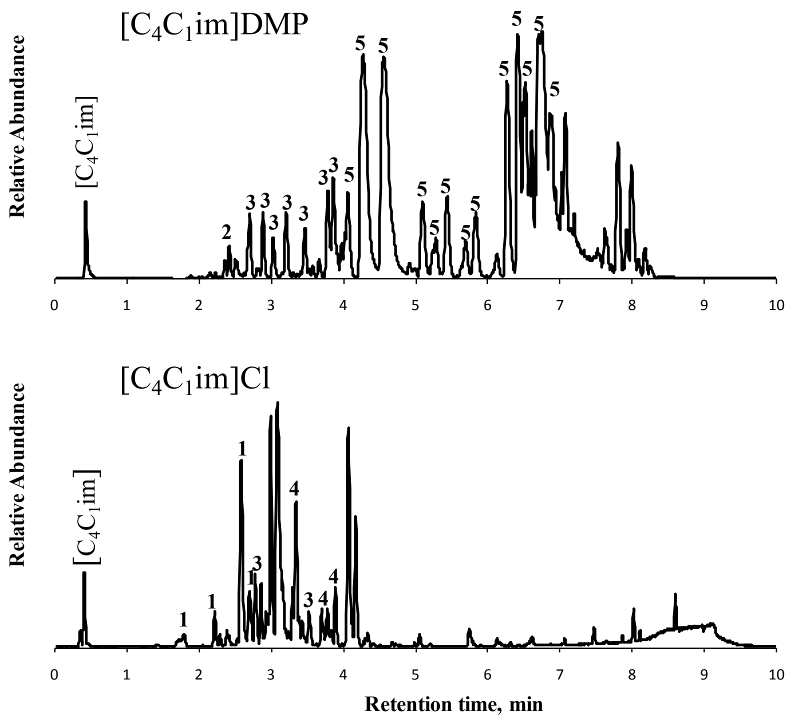

Figure 2. Total ion chromatogram for the grey alder bark ILs fractions after purification with the C18 column using ethanol as an eluent. 1-ferulic acid derivatives; 2-other organic acids; 3- tannin derivatives, 4- flavonoids, 5 – diarylheptanoids

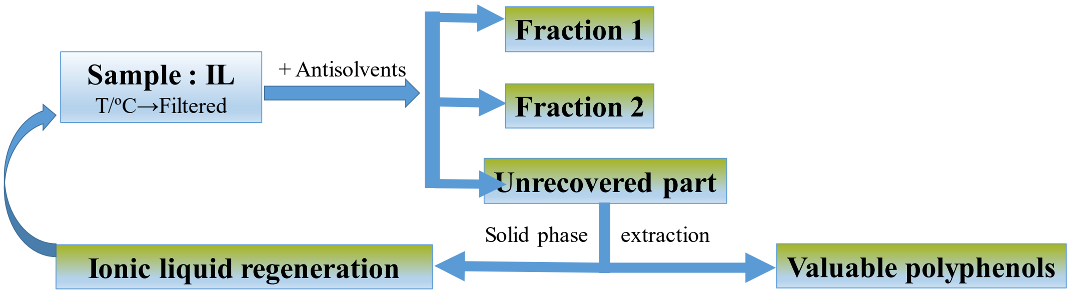

Figure 3. Scheme of the full use for the ionic liquid recovery and obtaining valuable polyphenols from the lignocellulosic biomass part dissolved in ionic liquids, non-recovered with “antisolvents”

Table 2. The yield % of extractives obtained from bark by sequential extraction

Solvent	**Yield, %**	**Polyphenol compounds’ content, GAE g·g^{-1}**
Hexane	4.5	not detected
Ethyl acetate	16.7	0.57
Ethanol	17.2	0.49

The results of the ABTS$^{\bullet+}$ and DPPH$^{\bullet}$ test are presented (Table 3) in terms of the IC$_{50}$(mg·L^{-1}) value. A lower IC$_{50}$ value is associated with higher radical scavenging activity of the compounds, as the IC$_{50}$ displays the concentration of the tested antioxidant compound required for a 50% inhibition of the radical species. All tested fractions demonstrated better or close antioxidant activity than the reference antioxidant Trolox (water soluble E vitamin analogue). Among the samples obtained after treatment with ILs, the [C_4C_1im] DMP fraction showed the good test results. The IC$_{50}$ values obtained for the fractions extracted with organic solvents were slightly lower than those for the IL fractions.

Table 3. The yield % of extractives obtained from bark by sequential extraction

Sample	**IC$_{50}$, mg·L^{-1}**	
	ABTS$^{\bullet+}$	**DPPH$^{\bullet}$**
Grey alder ethyl acetate extract	3,14 ± 0,13	5,52 ± 0,16
Grey alder ethanol extract	4.73 ± 0,16	9.4 ± 0,14
[C_4C_1im] DMP after SPE (ethanol)	4.91 ± 0,16	5,26± 0,15
Trolox	4,01 ± 0,12	4,72 ± 0,12

Conclusion

The present work has allowed highlighting powerful antioxidants isolated from the bark of Boreal trees. They are more active or close than the reference antioxidant Trolox. It is shown that lignocellulosic dissolution in different ionic liquids solute different. It is directly related with IL structure. Using [C_4C_1im]DMP it is possible to achieve up to 60 % bark solubility. SPE allows an effective increase in the compounds' recoverability from the IL dissolved part, which cannot be re-extracted with "antisolvents", and allows the recovery of ionic liquid. Results obtained shows the opportunity to modify the chemical composition of fractions using different ILs respectively with improved targeted properties according to application.

Acknowledgements

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A comparable study on analytical pyrolysis of silver birch (*Betula pendula*) and Norway spruce (*Picea abies*) sawdust

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Biomass pretreatment processes prior to pyrolysis can improve the quality of pyrolysis products. In this study, the thermochemical behavior of silver birch (Betula pendula) and Norway spruce (Picea abies) sawdust as such and after hot-water extraction were investigated by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). In each case, the yields of major GC-amenable condensable products were measured semi-quantitatively, and the individual compounds were classified into furans (mainly furfural and 5-(hydroxy-methyl)furfural), anhydrosugars (mainly levoglucosan), ketones (hydroxyacetone, furanones, pyranones, cyclopentanones, and cyclopentenones), and phenols. The formation of these groups from feedstock samples with varying mass portions of their structural constituents (carbohydrates and lignin) was determined at 500 °C and 700 oC with a residence time of 5 s and 20 s. The formation of pyrolysis products was shown to be characteristically dependent on feedstock composition as well as on pyrolysis conditions. This kind of approach was of practical importance with respect to efforts not only to develop rapid characterization tools for lignocellulosics, but also to uncover new biorefinery possibilities to produce bio-oils, for example, enriched either with aliphatic or aromatic constituents.

Introduction

All hardwood- and softwood-derived feedstocks are made up of cellulose, hemicelluloses, and lignin with minor amounts of extractives and inorganics. The percentage of each constituent varies significantly among biomass feedstock depending on species (genetic differences), growing conditions, and presence of specialized tissues within individual plants[1,2]. It has been described that hardwoods and softwoods are dissimilar due to their cell types, the content of total hemicelluloses, the percentages of individual hemicellulose constituents, as well as the lignin[3,4]. Hardwoods have a higher proportion of hemicelluloses than softwoods, but softwoods have a higher proportion of lignin. In hardwoods there is mainly xylan (containing xylose units) and in softwoods mainly glucomannan (containing mannose and glucose units). Lignin can be classified based on the type of its precursors into two major groups, such as guaiacyl-syringyl lignins (almost equal amounts in hardwood lignins) and guaiacyl lignins (in softwood lignins)[4,5].

Wood pyrolysis is the primary stage in various thermochemical conversion processes and is performed in the complete or near complete absence of an oxidizing agent (air or oxygen) typically at 500-700 °C. It produces complex fractions of gases, condensable liquids (tars), and char (solid residue). It has been reported that during pyrolysis, thermochemical behavior of each constituent is unique[6,7].

One of the integrated biorefinery concepts, mainly for recovering valuable carbohydrates-derived material, is to apply hot-water extraction (“autohydrolysis”) to wood raw materials prior to further processing, such as pulping[8-10]. In addition, this type of fractionation possibility generates, for example, a wide range of potential feedstocks for thermochemical conversion. The aim of this study was to conduct fast pyrolysis to untreated and hot-water-extracted (HWE) silver birch (*Betula pendula*) and Norway spruce (*Picea abies*) sawdust by analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). In each case, the selective formation of specific condensable product groups was also compared. Furthermore, the suitability of this rapid analytical method for detecting chemical changes during the different chemical treatments was primarily evaluated.

Materials and their analyses

The untreated (ref) and HWE birch and spruce feedstocks were investigated. The hot-water extraction was applied in the case of birch at 170 °C for 38 min, and for spruce in three separate stages (at 160 °C for 40 min, at 170 °C for 60 min, and at 180 °C for 180 min). The chemical analyses were performed based on the methods shown in Ref[11]. Pyrolysis experiments were conducted in a quartz tube (3.0 cm x 1.0 mm i.d., between quartz wool) at a heating rate of 20 °C/ms using a CDS Pyroprobe 1000 resistively heated coil filament pyrolyzer coupled to an HP 5890 II gas chromatograph (Py-GC, Hewlett Packard Company, Wilmington, NC, USA). The column was a ZB-35HT (Inferno) capillary GC column (30 m x 0.25 mm with a film thickness of 0.25 µm). Detection was carried out with an HP 5970 mass spectrometric detector under electron ionization (70 eV) with 2.92 scan/s in the 30-550 m/z interval. For the identification of chromatogram peaks, the mass spectra (based on the National Institute of Standards and Technology (NIST) mass spectral library) were used. Quantitative analysis was conducted according to[12].

Results and discussion

Chemical compositions of the reference initial and HWE birch and spruce feedstocks are presented in Table 1.

Table 1. Chemical composition of the initial and HWE birch and spruce sawdust (% of the sample[a] dry solids)

Components	**B_{ref}**	**B_{HWE}**	**S_{ref}**	**S_{HWE}**
Carbohydrates	67.5	72.7	60.6	59.2
Arabinose	0.4	0.1	1.4	-
Galactose	1.0	0.6	1.4	-
Glucose	43.4	60.8	40.0	55.9
Mannose	1.4	1.0	11.9	1.0
Xylose	21.3	10.2	5.9	2.3
Lignin	22.1	20.7	29.8	36.8
Klason	17.6	18.2	29.4	36.6
Acid-soluble	4.5	2.5	0.4	0.2
Extractives	2.9	2.8	1.2	4.0
Others[b]	7.5	3.8	8.4	0.0
Total	100.0	100.0	100.0	100.0

[a] B_{ref}, S_{ref}, B_{HWE}, and S_{HWE} refer to untreated and hot-water-extracted birch and spruce feedstock, respectively.
[b] Includes acetyl groups of xylan, pectins, and inorganics.

The results indicated that the cellulose is rather stable during hot-water treatment. In contrast, 20-25 % of hemicelluloses (mono-, oligo, and polysaccharides) and 30-35 % of the initial lignin were removed during the treatment in birch feedstocks while in spruce feedstocks these removals were

90 % and 10 %, respectively. Due to the hot-water extraction, there was an increase in the mass ratio of carbohydrates to lignin in the hardwood matrix from 3.1 to 3.5 and a decrease in the softwood matrix from 2.0 to 1.6. The corresponding mass ratio of aldohexose units (galactose, glucose, and mannose) to aldopentose units (arabinose and xylose) in the fraction of carbohydrates raised both in hardwood and softwood matrix from 2.1 to 6.1 and 6.1 to 24.7, respectively.

In practice, the results also suggested that the hydrolyzate primarily contained xylose moieties and mannose moieties from the principal hardwood hemicellulose component, xylan, and softwood hemicellulose component, glucomannan, respectively. This soluble carbohydrates fraction as such or after further enzymatic hydrolysis can be highly used for the production of a wide range of platform chemicals, for example, by fermentation. Additionally, the main monosaccharide moiety, mannose, can also be converted into many potential chemicals (e.g., mannitol and mannonic acid) by conventional chemical methods.

Pyrolysis conditions indicated a high impact on the pyrolysis products. In the case of B_{ref}, a pyrolysis time of 5 s at 500 °C and 700 °C led to the highest pyrolysis yields similar to those obtained from B_{HWE} at 500 °C for 5 s. In the case of S_{ref} and S_{HWE}, pyrolysis times of 5 s and 20 s at 500 °C yielded more pyrolysis products. Typically, the yield was found to decrease or remain almost similar when the pyrolysis temperature increased from 500 °C to 700 °C.

Based on the classification of pyrolysis products[12,13], The GC-amenable condensable liquid pyrolysis products could be characteristically classified into about ten compound groups (Figure 1). The main compound groups were aliphatic compounds, such as lactone, furan, cyclopentenone, and anhydrosugar derivatives from carbohydrates (mainly hemicelluloses) and aromatic compounds, such as guaiacol, phenol, and syringol derivatives from lignin. The ratio carbohydrates to lignin at 500 °C/20 s for birch- and spruce-derived samples was B_{ref}/B_{HWE} 0.7 and S_{ref}/S_{HWE} 1.2 (estimated value from Table 1 are 0.9 and 1.3, respectively). On the other hand, the ratio xylan to lignin was B_{ref}/B_{HWE} 0.5 (estimated value from Table 1 are 0.5). Additionally, the ratio xylan to lignin could be ignorable due to less portion of xylan in spruce backbone.

Typically, among the prominent pyrolysis products, three times higher amounts of 3-hydroxy-2-penteno-1,5-lactone (a xylan-derived compound) was formed from hardwood than softwood; the percentual amount of xylose in birch sawdust (i.e., in B_{ref}) was 21.3 and 5.9 in S_{ref} (Table 1). Furthermore, anhydrosugars (e.g., levoglucosan) detected only in the pyrolysis of hexoses (i.e., D-glucose, D-mannose, and D-galactose) were formed 1.2 times more from S_{ref} than from B_{ref} at 500 °C for 5 s (the hexose portions are 53.3 % and 45.9 %, respectively). Additionally, the softwood lignins were principally formed from *trans*-coniferyl alcohol-type units (i.e., guaiacyl lignin), whereas hardwood lignins were mainly originated from almost the equal amounts of *trans*-coniferyl alcohol-type and *trans*-sinapyl alcohol-type moieties (i.e., guaiacyl-syringyl lignin). Hence, for example, no syringols could be obtained from softwood pyrolysis.

The feedstock composition and pyrolysis conditions had a major impact on the ratio aliphatic pyrolysis compounds to aromatic pyrolysis compounds. The formation of aromatics was detected from lignin-containing materials (untreated and HWE materials) under harsher pyrolysis conditions, whereas aliphatic products could be principally obtained under milder pyrolysis conditions from carbohydrates-containing materials. For example, at a temperature of 500 °C (for 5 s and 20 s) more primary products were formed without further degradation, whereas at 700 °C more aromatics were obtained.

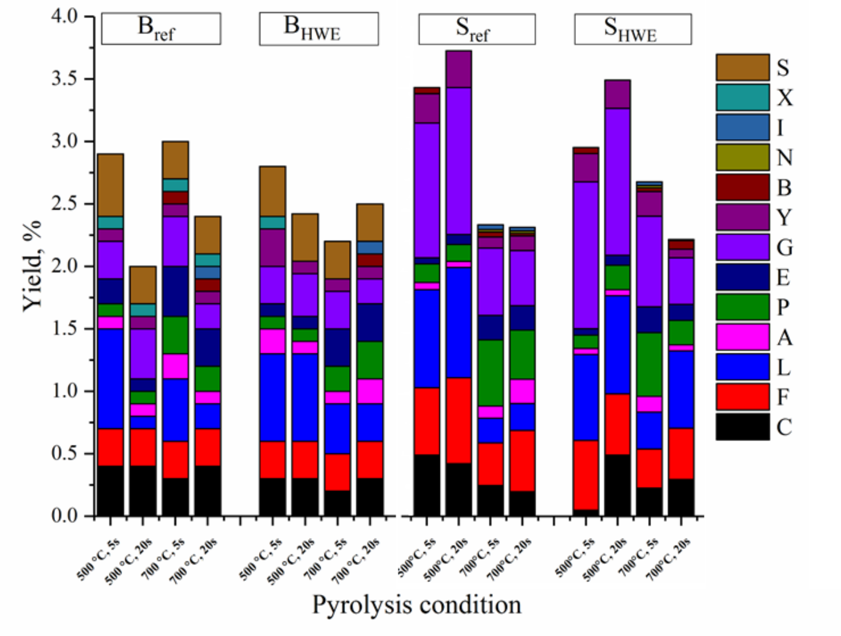

Figure 1. Effect of temperature and residence time on yields of various product groups of wood feedstocks. Letters indicate A (anhydrosugar derivatives), B (benzene derivatives), C (cyclopentenone derivatives), E (catechol and benzenediol derivatives), F (furan derivatives), G (guaiacol derivatives), I (indene derivatives), L (lactone derivatives), N (naphthalene derivatives), P (phenol derivatives), S (syringol derivatives), X (fatty acids derivatives), and Y (pyrone derivatives).

Conclusions

Fast pyrolysis has been applied to the initial and solid residues from hot-water extraction of birch and spruce sawdust from the integrated biorefinery concept. It is generally well-known that the total amount of pyrolysis products recovered from laboratory-scale pyrolyzers is low, but this fraction is still representative for all condensable products. On the other hand, a simultaneous gas-chromatographic determination of the main compound groups and the selected fingerprint pyrolysis products provides rapid and useful information about the chemical composition of different samples.

Acknowledgements

Financial support from the Academy of Finland, within the framework of the project IMUSTBC (Maryam Ghalibaf) and from the Maj and Tor Nessling Foundation and the Finnish Cultural Foundation (within the framework of Foundations' Postdoc Pool) (Joni Lehto) is gratefully acknowledged.

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Lignin purification from poplar hydrolysis rest: a sub-product from a bioethanol pilot plant

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Within the European H2020 project REHAP, lignin has been purified from a solid poplar hydrolysis rest obtained from BIOCHEMTEX after their improved pilot production of bioethanol. The aim in the project is to develop an industrial scalable process, to obtain lignin for further transformation into a high value product, such as cement superplasticizer. As the main sub-product is the solid residue enriched in cellulose, that will be hydrolyzed to glucose and tested for the fermentability. The optimized simple and mild lignin extraction method used 1M NaOH at 90ºC for three hours to solubilize most of the lignin content in the hydrolysis rest. Thereafter, sulfuric acid was added to acidify the solution to pH 1.5, then the reaction was heated to 70ºC and kept at that temperature for 1h. During all the procedure the stirring was maintained giving a flocculated lignin product, easy to filter and wash with water. After drying in a ventilated oven at 80ºC a free flowable light brown powder was obtained. The dry weight yield of purified lignin was 54.5% when starting with 69.3% initial Klason lignin content and 30% yield was obtained when the starting material Klason lignin was 53%. The purified lignin was characterized by GPC, ATR-FTIR and 31P-NMR. Further upscaling of the method is planned at the project partner`s site Bio Based Europe Pilot Plant in Belgium.

Introduction

Within the European H2020 project REHAP, Tecnalia has been working on a lignin purification method from a solid poplar hydrolysis rest obtained from Biochemtex after their improved pilot production of bioethanol. The aim in the project has been to develop an industrial scalable process, to obtain lignin for further transformation into a high value product, such as cement superplasticizer. As the main sub-product was obtained a solid residue enriched in cellulose, that has been hydrolysed to glucose and tested for the fermentability.

Experimental

Chemicals: Sodium hydroxide (Reagent grade) and Sulfuric acid (Synthesis grade) both from Scharlau. Poplar hydrolysis lignin: Samples came from Biochemtex bioethanol pilot plant in Italy, as a sub-product from their Proesa process.

31P-NMR measurement is based on the method developed by Granata and Argyropoulos (1995)[1], analysing phosphitylated samples using a Bruker 500 MHz NMR spectrometer. GPC analysis of acetylated lignin fractions was done using an Agilent GPC/SEC system (PL-GPC50) with an RI-detector, column ResiPore (300mm x 7,5mm inner diameter, 3 µm particles multi pore). Mobile phase: THF stabilized with 0,025% BHT, Temperature: 40 ºC, Flow: 1 ml/min, Injection vol.: 20 µl. For calibration, polystyrene references were used. The general procedures were based on Tolbert et.al. (2014)[2]. ATR-FTIR on vacuum-oven dried powder samples was done using a Nicolet iS5 apparatus from Thermo Scientific.

Results and discussion

Alkaline lignin extraction

A simple and mild lignin extraction method was tested using 1M NaOH at 75, 90 and 120ºC for three hours to solubilize most of the lignin content in the hydrolysis rest from poplar wood-shavings. Thereafter, sulfuric acid was added to acidify the solution to pH 1.5 and then heated to 70ºC and kept at that temperature for 1h. During all the procedure the stirring was maintained giving a flocculated lignin product, easy to filter and wash with water. The best yield and filterability obtained extracting at 90ºC. After drying in a ventilated oven at 80ºC a free flowable light brown powder was obtained. The dry weight yield of purified lignin was 54.5% when starting with 69.3% initial Klason lignin content and 30% yield was obtained when the starting material Klason lignin was 53%, see table 1. The purified lignin was characterized by GPC, ATR-FTIR and 31P-NMR.

Table1. Starting materials composition, obtained from Biochemtex bioethanol pilot plant.

Starting material	**Hemicellulose**	**α-Cellulose**	**Lignin**	**Lignin**
Poplar hydrolysis lignin: 1st Batch	16,3	10,1	73,6	69,3
Poplar hydrolysis lignin: 2nd Batch	10,1	23,4	66,5	53

Residual cellulose hydrolysis

The cellulose rest then obtained was successfully hydrolysed with Cellic Ctec2 enzyme cocktail (Novozymes) to mainly glucose and some xylose and successfully used for fermentation into 2,3-butanediol with a proprietary Lactococcus strain. Further upscaling of the method is ongoing at the project partner`s site Bio Based Europe Pilot Plant in Belgium.

Characterization of purified lignin

The purity of the purified poplar (hardwood) lignin was confirmed by a well-defined FTIR spectra (Figure 1), showing less guaicyl and more syringyl unit bands compared to Indulin AT lignin, that is a pure lignin from softwood. A relatively high phenolic hydroxyl content was detected with 31P-NMR methodology, see Table 2. Using GPC, the Mw was determined to 5697 g/mole and PD=3.8 on sample RE-WP2-18b obtained with optimised conditions.

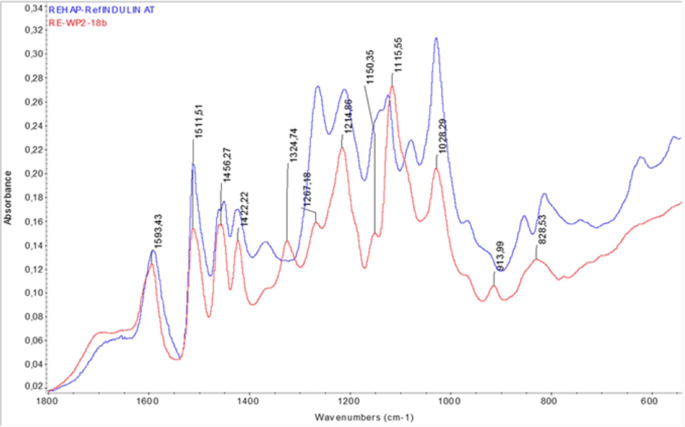

Figure 1. ATR-FTIR spectra of purified lignin RE-WP2-18b (in blue) and Indulin AT Kraft lignin (in red) for comparison

Table 2. 31P-NMR of phosphitylated lignin samples, amounts of -OH species in mmol/g lignin

Sample	**Alifatic OH**	**Carboxylic acid**	**Condensed + Syringyl**	**Guaiacyl**	**P-OH-phenyl**	**Phenolic OH**	**Total OH**
RE-WP2-3b (extraction at 75ºC)	3,00	0,24	1,42	0,72	0,08	2,22	5,46
RE-WP2-5b (extraction at 90ºC)	0,72	0,38	2,33	0,87	0,17	3,38	4,48
RE-WP2-18b (extraction at 90ºC)	2,5	0,48	1,77	0,87	0,15	2,79	5,77
RE-WP2-6b (extraction at 120ºC)	1,55	0,44	2,29	1,02	0,16	3,46	5,46

Conclusions

- The method used, based on alkaline extraction followed by acid precipitation, was found to yield lignin with high purity, starting with a poplar residue from a bioethanol pilot plant.
- The acidification to pH 1.5 followed by heating to 70ºC for 1h were crucial to have a lignin easy to filter and wash with water.
- The cellulose rest obtained was possible to saccharify by enzymes and further to ferment to 2,3-butanediol.

Acknowledgements

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Enzymatic technology for lignin valorisation

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Main hurdles of lignin valorization are its diverse chemical composition, recalcitrance, and poor solubility due to high-molecular weight and branched structure. Controlled depolymerisation and activation of lignin could lead to its use in higher value products such as binders, coatings, fillers, etc. Oxidative enzymes (i.e., laccases and peroxidases) have long been proposed as a potentially promising tool in lignin depolymerization. However, their application was limited to ambient pH, where lignin is poorly soluble in water. A Finnish biotechnology company, MetGen Oy, that designs and supplies industrial enzymes, has developed and brought to market several lignin oxidizing enzymes, including an extremely alkaline lignin oxidase MetZyme® PURECO™, a genetically engineered laccase of bacterial origin. This enzyme can function at pH values as high as 10–11 and at elevated temperatures (up to 85 °C), addressing lignin at its soluble state. In this study, main characteristics of this enzyme as well as its action on bulk lignin coming from an industrial process are demonstrated. Lignin modification by MetZyme® PURECO™ was characterized by size exclusion chromatography, UV spectroscopy, and dynamic light scattering for monitoring particle size of solubilized lignin. Under highly alkaline conditions, laccase treatment not only shifts the molecular weight distribution of lignin towards smaller values but also activates the lignin through strong demethylation and increase of hydroxyl groups (both aliphatic and phenolic). Importantly, organic solvent-free soluble lignin fragmentation allowed for robust industrially relevant membrane separation technologies to be applicable for product fractionation. These enzyme-based solutions open new opportunities for biorefinery lignin valorization, thus paving the way for economically viable biorefinery business.

Valuable furfural side stream from large scale pellet production - "Steam explosion of lignocellulosic biomass"

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Large-scale steam explosion is today performed by Arbaflame AS to produce black ArbacoreTM pellets. Coal is substituted with ArbacoreTM pellets in multiple coal-fired power plants by only minor alterations to the plant itself for the plant to remain its power generation capacity. Increased pellet-production due to demand has resulted in a large-volume liquid side stream containing organic components of interesting character. The five main components of highest concentration in the liquid side-stream (effluent) is furfural, methanol, acetic acid, formic acid and acetone, in descending order. As furfural is a high-value chemical, recovery of the side-stream organics is of considerable interest[1].

Identification of the side-stream components was performed by 850 MHz NMR, and dimethyl sulfone as internal standard was used for quantification studies. The steam explosion parameters were studied in order to achieve maximum performance in furfural generation, while still maintaining the production of high-quality pellets. A fractional factorial design on important steam explosion parameters such as cooking time, -temperature, -pressure etc. has been used in order to screen optimal furfural generation potential.

In addition, the development of a large-scale separation process of i.a. furfural and methanol from the production side-stream will be suggested together with the production potential studies, as well as purification and regeneration of the production-water.

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New Bulk - Modified wood powder

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Light paper has been applied to print and print production more and more. At present, the main way to produce light paper is to add high yield pulp, and some manufacturers even use 100% chemical mechanical pulp. For the current situation of shortage of wood resources, it is necessary to improve the bulk of paper under the condition of minimizing the use of chemical mechanical wood pulp. A method of improving the bulk of light paper was studied in this paper. Silane coupling agent modified wood powder is added to the paper to improve the thickness of paper. The process conditions of silane coupling agent modified wood powder were studied. The influence of different silane coupling agent modified wood powder on the thickness of paper making pine was analyzed, and the mechanism of silane coupling agent modification was discussed. The process conditions of silane coupling agent modified wood powder were studied. The experimental results showed that the silane coupling agent was more efficient by spraying. When the reaction temperature was 70 ℃, the reaction time was 30 min and the dosage of silane coupling agent was 2%, the thickness of the finished paper pine was the largest. The best of silane coupling agent KH-570 is obtained by comparing the bulk and paper-forming properties of different types of silane coupling agent modified wood powder.

Introduction

With the improvement of living standards and the increase of population, the demand for pulp and paper is increasing. However, in recent years, with the increasing awareness of natural ecological protection and the increasing concept of environmental protection, the paper industry is also deeply affected. How to reduce the use of pulp raw materials has become one of the current research directions. If the same quality of the case can make the thickness of paper increased, that is, paper bulking, then in a certain volume of fiber raw materials can be reduced, so as to achieve lightweight paper and reduce the amount of fiber raw materials. Therefore, the bulk of paper has been paid more and more attention by the industry. How to maintain the high bulk of paper under the condition of meeting the use requirements is a very important issue. Paper thickness is often affected by fiber morphology, packing, beating, wet pressing and calender, *etc*[1]. By improving the process parameters such as raw material, beating degree, filler type and dosage, press and press line pressure, or adding loose chemical additives, the paper bulk can be improved to a certain extent[2].

Paper tightness refers to the quality of paper per unit volume. It can be calculated by dividing the weight (g) of paper by the thickness (δ) and expressed by g/cm^3 or kg/m^3. It is one of the important performance indexes of paper. The tightness is related to the type of pulp, beating degree, filler, sizing degree, wet press and pressing pressure.

Bulk (v) refers to the volume of a certain quality of paper, that is, the reciprocal of compactness, expressed in cm^3/g or m^3/kg. It is also commonly used instead of tightness to indicate the performance of paper or paperboard.

$$v = \frac{\delta \times 1000}{g}$$

One of the hotspots in the research of increasing the paper bulk thickness is to add coupling agent to modify wood powder to realize the change of biomass fiber.Among these commonly used coupling agents, silane coupling agents are the most widely studied and applied coupling agents, which can be divided into amino, vinyl, epoxy, acrylate, mercapto and so on according to the different functional groups[3]. Silane coupling agent is a kind of to R-Si (OR ’)[3] represented by the coupling agent, its function is through one of the alkoxy OR its hydrolysis of alcohol and biomass fiber hydrogen bond OR ether key links, while at the other end of the chain hydrocarbon R base connected to the plastic[4], resulting in the improvement of the interfacial compatibility and the anticorrosion properties of the compound material mechanics performance and purpose[5].Thus, the interface compatibility, the mechanical properties, and corrosion resistance of composite materials were improved. The structure of functional group R has significant influence on the modification performance. Silane coupling agents are one of the most widely used coupling agents nowadays. Many organosilicon components have been proved to improve the dimensional stability, durability, water resistance and aging resistance of biomass fibers[6].

Experimental

Materials

Silane coupling agent KH-570, 3-(methacryloxy) propyl trimethoxysilane,was obtained from Chenguang company, Jiangsu Province; Wood powder was obtained from a factory in Shandong Province; glacial acetic acid; ethanol (concentration of 95 wt%); NBKP was obtained from a paper mill in Shandong Province.

Modification of wood powder

1. Screening of wood powder

Wood powder was milled by planetary ball mill for 6 hours, then coarse wood fibers were removed by 120-mesh standard sieve. Subsequentlywood fibers were screened by 200-mesh standard sieve to remove shorter wood fibersto ensure the uniformity of wood fibers. The uniform wood power were dried at an 90°C oven for 4 hours[7].

2. Treatment of wood powder with silane coupling agent

(a) Preparationof silane coupling agent solution

The 95% ethanol water solution was prepared by mixing ethanol and water. The pH value of the solution was adjusted to about 3 with acetic acid. Silane coupling agent was added to the solution while stirring (the weight percentage of fiber weight) to reach a certain concentration and hydrolyze for several hours.

(b)Treatment of wood powder

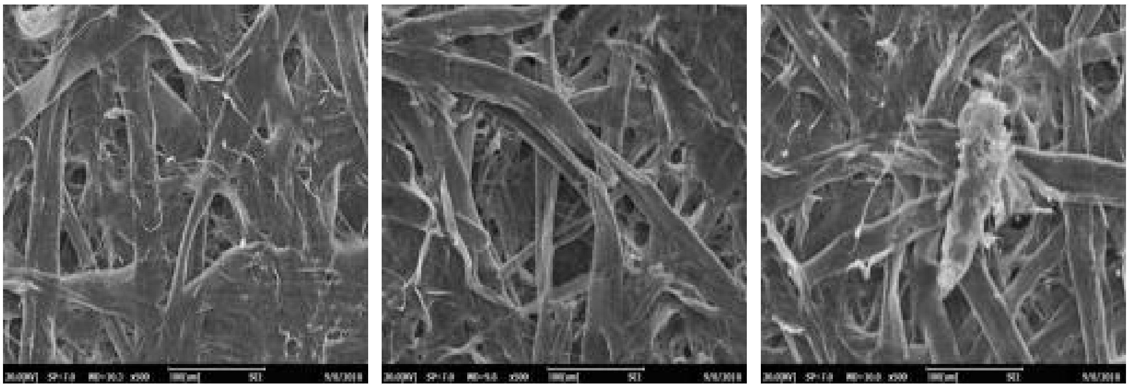
The weighed wood powder was put into a high-speed mixer, and the wood powder was sprayed with a silane solution at different temperatures. After spraying, the wood powder was stirred for 30 minutes. Remove wood powder and leave it at room temperature for at least 12h to ethanol and acetic acid to evaporate completely.

3. Drying of wood powder after treatment

Wood fiber contains a large number of warp-based, easy to adsorb water molecules and agglomerate, so that wood fiber can not be well dispersed in the processing process, resulting in a weak interfacial layer between wood fiber and polymer, but also the formation of pores in the composite material, seriously deteriorating the mechanical properties of the composite. Therefore, before silane coupling agent treatment and extrusion processing, wood powder needs to be fully dried to reduce the production of water vapor and other small molecular volatile substances during processing. The treated wood powder was placed in an electrothermal constant temperature drying box and dried at 105 ℃ for about 24 hours to ensure that the moisture content of wood fiber was below 1%.

Results and discussion

Scanning electron microscopy (SEM) of raw paper without wood powder in Figure 1 (a) shows clearly that the fibers without wood powder interweave with each other, forming a dense three-dimensional network structure. There are pores in the paper, but the porosity is small. Figure 1 (b) is a raw paper with unmodified wood powder. It can be seen that the porosity of the paper with wood powder is obviously larger than that without wood powder, indicatingthat wood powder is an effective thickening agent. The fiber network structure becomes loose and porous, as shown from the SEM image of the paper with modified wood powder (Figure 1c), It can be attributed to the decreasing bonding between the fibers after adding the modified wood powder



(a) (b) (c)

Figure 1 a: Original paper;b:Paper with Unmodified wood powder;c: Paper with modified wood powder

As shown in Figure 2, the FTIR spectra of wood powder and modified wood powder show that a new peak appears at 700cm^{-1}, which is the characteristic absorption peak of Si-O-Si bond. This should be the effect of self-polymerization of silanesol. It can be seen from the diagram that wood powder has been successfully modified by silane coupling agent[8].

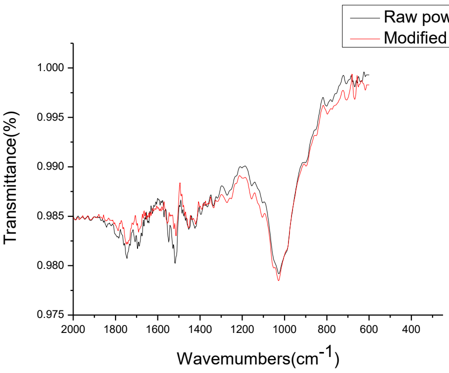


Figure 2 FT-IR of raw powder and modified powder

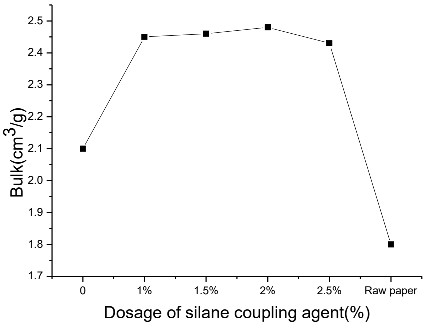


Figure 3 Effect of silane coupling agent dosage on bulk

Effect of silane coupling agent dosage on paper making

Table 1 shows the experimental scheme of different wood powder content (relative to absolute dry pulp) and silane coupling agent dosage.

Table 1 Papers modified withdifferent silane coupling agents

Paper number	**1**	**2**	**3**	**4**	**5**	**6**
Wood powder content (%)	10	10	10	10	10	0
Dosage of silane coupling agent (%)	0	1	1.5	2	2.5	0
Modified temperature	50 ℃					

From the effect of silane coupling agent dosage on the paper bulk in Figure 3, it can be seen that the paper bulk without wood powder is the smallest, only 1.80 cm^3/g. The paper bulk with unmodified wood powder is higher than that without wood powder, because the space between fibers increases and the porosity increases with the addition of wood powder. With the increase of silane coupling agent, the bulk of paper increases, reaching the maximum when the silane coupling agent dosage is 2%, but when the silane coupling agent dosage is 2.5%, the bulk of paper decreases. This is mainly due to the hydrolysis of silane coupling agent to form silanediol, and the dehydration and condensation between silane hydroxyl groups to synthesize oligomeric siloxane; at the same time, the hydroxyl groups in oligomers form hydrogen bonds with the hydroxyl groups on the surface of wood fibers. Wood fibers modified by covalent silane coupling agent dehydrated under heated conditions interact with macromolecular free radicals to reduce hydrogen bonding between fibers. With the increase of silane coupling agent dosage, the more silanediols loaded on wood powder and the more hydrogen bonds formed between wood powder and pulp fiber, the thicker the pine is. The thickness did not significantly increase, however, the overall quality increased, resulting in a decrease in the bulk of paper.

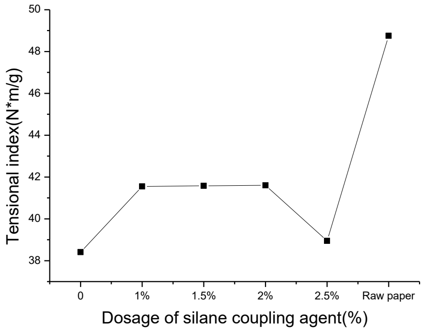


Figure 4 Effect of silane coupling agent on tensile index

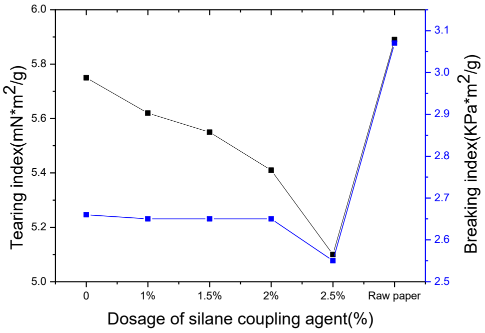


Figure 5 Effect of silane coupling agent dosage on tearing index and breaking index

As shown in Figure 4, the addition of wood powder will reduce the tensile index of paper. It is only because the addition of wood powder will fill in between the wood powder, affecting the binding between fibers, thereby reducing the tensile index. However, the modified wood powder by silane coupling agent will form hydrogen bonding, which makes the tensile index ratio of modified wood powder higher.

As can be seen from Figure 5, the addition of wood powder has some effect on tearing index and breaking index of base paper, but the effect is very small. The amount of silane coupling agent had no significant effect on the tear index and bursting index of paper, but it reached the minimum when the amount of silane coupling agent was 2.5%. This is because wood powder has little effect on the physical properties of paper, but with the increase of silane coupling agent dosage, the paper quality increases, so tear index and bursting index are relatively small.

According to the analysis above, the silane coupling agent dosage is 2%. It has little influence on the physical properties of paper, and the bulk is the best.

Effect of modified temperature on paper making

Modification temperature is also a very important condition when silane coupling agent is used to modify wood powder. Table 2 shows the experimental scheme for different modification temperatures.

Table 2 Paper number of different modified temperature

Paper number	**1**	**2**	**3**	**4**	**5**
Modified temperature (℃)	40 ℃	50 ℃	60 ℃	70 ℃	80 ℃
Wood powder content (%)	10				
Dosage of silane coupling agent (%)	2				

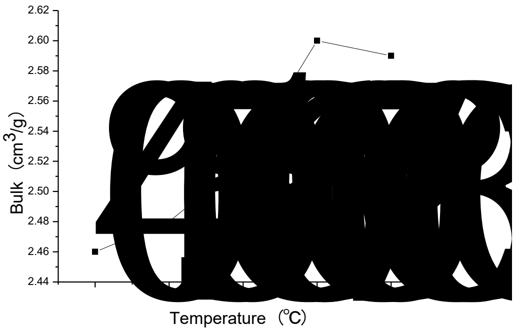


Figure 6 Effect of modified temperature on bulk

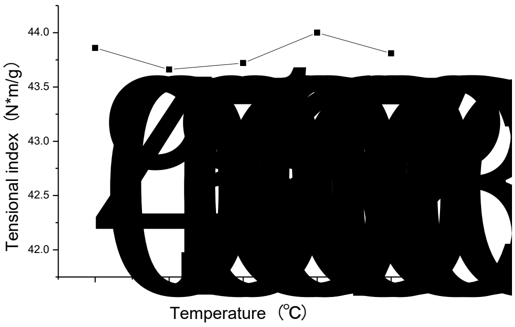


Figure 7. Effect of modified temperature on tensile index

It can be seen from Figure 6 that with the increase of modified temperature, the bulk of paper also increases. This is due to the hydrolysis of silane coupling agent to form silanediol. With the increase of temperature, the dehydration and condensation of silane hydroxyl groups lead to the formation of hydrogen bonds between the hydroxyl groups in the oligomers and the hydroxyl groups on the surface of wood fibers, thus reducing the hydrogen bonding between fibers. However, the dehydration between the hydroxyl groups of silicon at about 70 °C has little effect on the binding between the fibers. At 80 °C, the bulk of the fibers has little change.

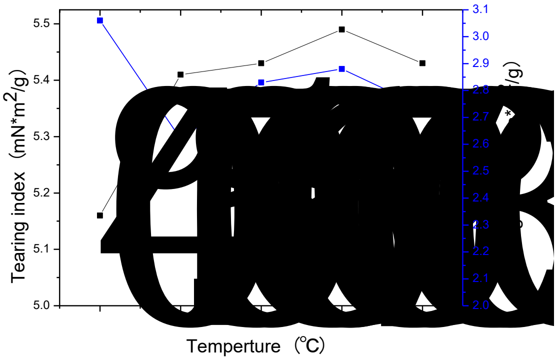


Figure 8 Effect of modified temperature on tearing index and breaking index

From the influence of temperature on tensile index in Figure 7 and the influence of modified temperature on tear index and burst index in Figure 8, it can be seen that the change of modified temperature has little effect on the physical properties of paper, and the overall change trend is very small. This is because silane coupling agents have little effect on the physical properties of paper.

Conclusions

In recent years, the demand for y paper is growing. Bulky paper is light but keeps the quality and thickness of the original paper. It can reduce the use of pulp, reduce the environmental pollution load and save energy. In addition, because of its light weight, it also has the advantage of saving transportation cost. In this paper, the bulk, tensile index, tear index and bursting index of the paper were considered comprehensively. When the silane coupling agent dosage was 2%, the physical index was lower than the original paper, but the bulk was the best. When the modification temperature was 70 °C, the silane coupling agent had little effect on the physical index of paper, and the bulk was the best.

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Use of novel biomass based carbon catalysts in production of valuable chemicals from pine sawdust

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Lignocellulosic biomass such as forestry residues can be converted into various chemicals or biofuels and hence utilized as a replacement of the fossil-based feedstocks. For example 5-hydroxymethylfurfural (HMF) and furfural, are valuable aromatic aldehydes, which have a very versatile structure to form multiple biomass based chemicals. HMF can be synthetized by acid catalyzed dehydration from C6 carbohydrates. It can be produced either by one-step process from biomass or from monosaccharides prepared first by biomass hydrolysis. Furfural on the other hand, is formed trough C5 sugar dehydration. Woody biomass like pine sawdust contains C6 and C5 sugars in the form of cellulose and hemicellulose, having the C6 monosaccharide (glucose, mannose and galactose) content of 63 wt-% and C5 monosaccharide (xylose and arabinose) content of 8 wt-%. Rest of the biomass is lignin, extractives and ash.

Typically, biomass dehydration to chemicals is catalyzed by mineral acids or metal salts. However, these homogenous catalysts are not environmentally friendly and are difficult to recycle. In this study pine sawdust was converted into HMF and furfural using solid biomass based carbon catalysts. Carbon catalysts were prepared from birch sawdust, which was carbonized and steam activated in a one-step process. The produced activated carbon was then refluxed with sulfuric acid and/or impregnated with zinc chloride in order to create Brønsted and/or Lewis acid sites on catalysts surface. Catalysts were characterized by ICP-OES, SEM-EDS and XPS. Conversion reactions were carried out in a microwave reactor using biphasic system (water and THF or MIBK). Purpose of the work was to select the best catalyst for conversion reaction, and also to optimize the reaction conditions for maximal HMF and furfural production. Studied reaction parameters were temperature, time, liquid to solid ratio and amount of the catalyst. Organic phase of reaction mixture was characterized with GC-MS and water phase was analyzed with HPLC. In addition to furfural and HMF, isoeugenol from lignin was identified from the organic phase.

The degradation of bark extractives - derived phenolics during storage

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As the social demand for ecological sustainability and raw material efficiency increase, the valorization of wood bark and other related forestry sidestreams becomes one of the key issues. The logistic problem of getting the right kind of material to the right place at the right time imposes demands to the quality of feedstock materials. Choosing a correct way of storing and handling raw materials can multiply its worth as potential source for value-added chemicals. Especially, important hydrophilic phenolic compounds which are abundantly present in many tree barks are chemically unstable during the supply chain.

In our studies, various experimental setups were developed, which allowed for a more comprehensive understanding of all the different variables affecting the chemical changes during storage. Chromatographic methods, such as GC-FID and LC-MS-QQQ were used for qualification and quantification of extractives-derived substance groups and individual compounds. Stilbenes were highlighted as an example of how different storage conditions affect their degradation. Stilbenes and their oligomers are known for their anti-inflammatory, antioxidant, antifungal, and chemoprotective activity. They are present in a wide range of plants and are currently being used, for example, as dietary supplements.

Based on the total amount of dissolved solids, the bark intact on sawlogs within a storage period of 24 weeks contained about 40 % more extractives than that removed from logs and stored separately in a pile. The amount of stilbene glucoside monomers (piceid, astringin, and isorhapontin) decreased from 16.9 mg/g of dry matter to undetectable levels already within four weeks, while in the bark of sawlogs the same stilbene derivatives could still be observed after a storage period of 24 weeks. This demonstrated that both the quantity and quality of the total hydrophilic extractives in spruce bark are significantly affected by storage.

Introduction

Forest biomass is being consumed in boreal-countries like Finland and Sweden in substantial amounts. As a result of this utilization the accumulation of by-products, such as bark is significant. The bark of spruce (*Picea abies*) is one of the major contributors in this class of secondary forest resources. The amount of spruce bark generated at mills in Finland is 0.8-1.2 Mt/a (d.m.) calculated with an estimated average dry density of 380 kg/m^3[1]. Bark is currently used mainly for producing heat and power, or landscaping[2]. However, spruce bark is a rich source of important polyphenolic extractives and natural antioxidants, such as stilbenes and tannins[3,4].

The popular trends for green bio-sustainable and economical solutions are influencing the thinking about forestry sidestreams. This has led to the re-imagination of what was commonly utilized as burnable waste as now raw-material with untold amount of latent potential. Tapping into a deeper understanding of both the chemical and physical nature of a given substance can open the doors for new applications. Biorefining industries with a focus on new extractives-based products will have feedstock requirements different from the existing forest and power industries. The new applications set demands both for the chemical composition and microbiological quality of the feedstock. These aspects need to be considered when planning on the logistics of feedstock to biorefineries.

Many initial extractives suitable for potential raw material applications are either rather volatile or chemically unstable. The extractives content starts to decrease immediately after tree felling and this degradation continues during storage[5,6,7,8]. This also means that the chemical composition of the extractives-based fraction changes gradually. It has to be pointed out that not only storage, but also other phases of the wood handling process affect the extractives content of the biomass material, as well as the composition of the extractives fraction. The duration of each of the phases in procurement chain, as well as environmental conditions, are important with respect to changes in extractives content and composition.

Utilization of valuable extractives and antioxidants from spruce bark is not possible if the raw material is chemically barren by the time it reaches the end user. Knowledge of the rate and the way of degradation of specific compounds of interest, such as the stilbene glucosides: piceid, astringin, and isorhapontin, can be useful in making the logistical decisions about raw materials as well as planning of the storage of raw materials in such a way that would help to minimize the loss of any such compounds.

The aim of our study was to investigate the degradation of both lipophilic and hydrophilic spruce bark extractives. In order to provide a clear contrast in the way that different storage conditions affect the preservation of bark extractives, two different experimental setups were established: a single stem setup and a bark pile setup.

Experimental

The single stem setup

Freshly felled spruce saw log (*Picea abies*) stems were cut to approximately 4.5 m length and placed on top of tree trunks so that they would not touch the ground. The logs were stored in this manner for 24 weeks during winter time. In addition to the zero-sample, the bark for the samples was collected from sample discs cut from the logs after 4, 12, and 24 weeks. The bark samples at each sampling point were collected from two stems. The height, diameter, and age of the trees were determined. Weather station which measured temperature, precipitation, wind, and UV radiation, was also placed in the location of the storage study.

The bark pile setup

Freshly debarked (less than 48 h old) spruce bark (*Picea abies*) from saw mill was compiled into a 450 m^3 storage pile. The pile was divided into three sectors out of which one was opened for sampling at a time. Thermocouples were placed in specific locations (to the top, middle, and side of the pile) to keep track of the temperature profile in the pile. In addition to the zero-sample, bark samples were taken from three different locations after 4, 12, and 24 weeks. The sampling locations were chosen based on the data offered by prior storage studies, with the intention of representing areas in the pile where the temperature and moisture contents are expected to show significant variation[9].

Sample pretreatment

Samples were stored in frozen state (< -20 ºC). Samples were freeze-dried and ground to a particle size of 1 mm in a mill of Wiley type. The moisture content of the powders was determined by drying 1 g of bark powder at 105 °C in oven overnight.

Extraction

The extraction of bark samples was done with a Dionex ASE 100 equipment using 120 °C extraction temperature, 10 min static extraction time, at a pressure of 1500 psi. 2 g of bark powder was used for each extraction. All samples were first extracted with hexane and then with water for the collection of lipophilic and hydrophilic extractives, respectively. The extractions were performed in duplicate.

Total dissolved solids (TDS) and preparation of stock solutions

The TDS of bark extracts was determined gravimetrically. TDS of hexane extract was determined by evaporation and weighing of the extract. The TDS of water extract was calculated based on the weight of lyophilized 10 mL aliquot of water extract stock solution, which was prepared by diluting the raw extract to 100 mL with UHQ water. Hexane extract stock solution was prepared by dissolving the dried extract into acetone (100 mL).

Bark extract analysis with gas-chromatography

The bark extracts were analyzed qualitatively and quantitatively with GC-MS and GC-FID, respectively using a HP-5 column, injecting the sample at 290 °C, and detecting the compounds with MS or FID at 300 °C. The method used was: 1,.5 min at 100 °C, 6 °C/min to180 °C, 4 °C/min to 290 °C, 13 min at 290 °C, 4 °C/min to 300 °C, and 20 min at 300 °C. For the preparation of a single bark sample 3 mg of bark extract and, with quantitative analysis, 100 µg of internal standards (heneicosanic acid and betulinol) were dried. The dried mixture was then dissolved in 500 µL of pyridine, silylated by adding 300 µL of silylation reagent (BSTFA/TMCS, 99/1, v/v) and keeping the mixture in 70 °C oven for 1 hour, and finally, transferred to GC vial.

Stilbene analysis with LC-DAD/ESI-MS/MS

The stilbenes from the water extract were analyzed with an Agilent 6460 LC-DAD/ESI-MS/MS modifying a method described by Gabaston et al. 2017 [10] with an Agilent Zorbax SB-C18 column, using water and acetonitrile as the solvents (with 0.1 % formic acid).

Results and discussion

TDS

The TDS of the samples from the single stem and bark pile setups are summarized in Table 1. While the lipophilic hexane fractions remained quite stable within the storage period, the hydrophilic water extract fractions showed a clear decline over time. There was a big difference between the different storage setups in the rate of degradation of the hydrophilic fractions. While the hydrophilic fraction of the single stem samples remained stable for 12 weeks the hydrophilic fraction of the bark pile samples showed significant deterioration just after 4 weeks. The different sampling locations in the pile also depicted clear trends: the rate of decrease in extractives content was the fastest in the top of the pile, the slowest in the middle of the pile, and somewhere in between them in the side of the pile. These results make sense considering the different level of exposure to UV light, oxygenation, and weather in each of the sampling locations. The bark samples removed from the saw logs had experienced the least amount of these harmful effects because the bark was still mostly in its native state where the dead outer bark could fulfill its natural function of protecting the inner bark from external attacks. This functionality of the outer bark was lost when the bark was removed and chipped. This was evidenced by the fact that the overall difference in TDS between the storage experiments was about 40 %.

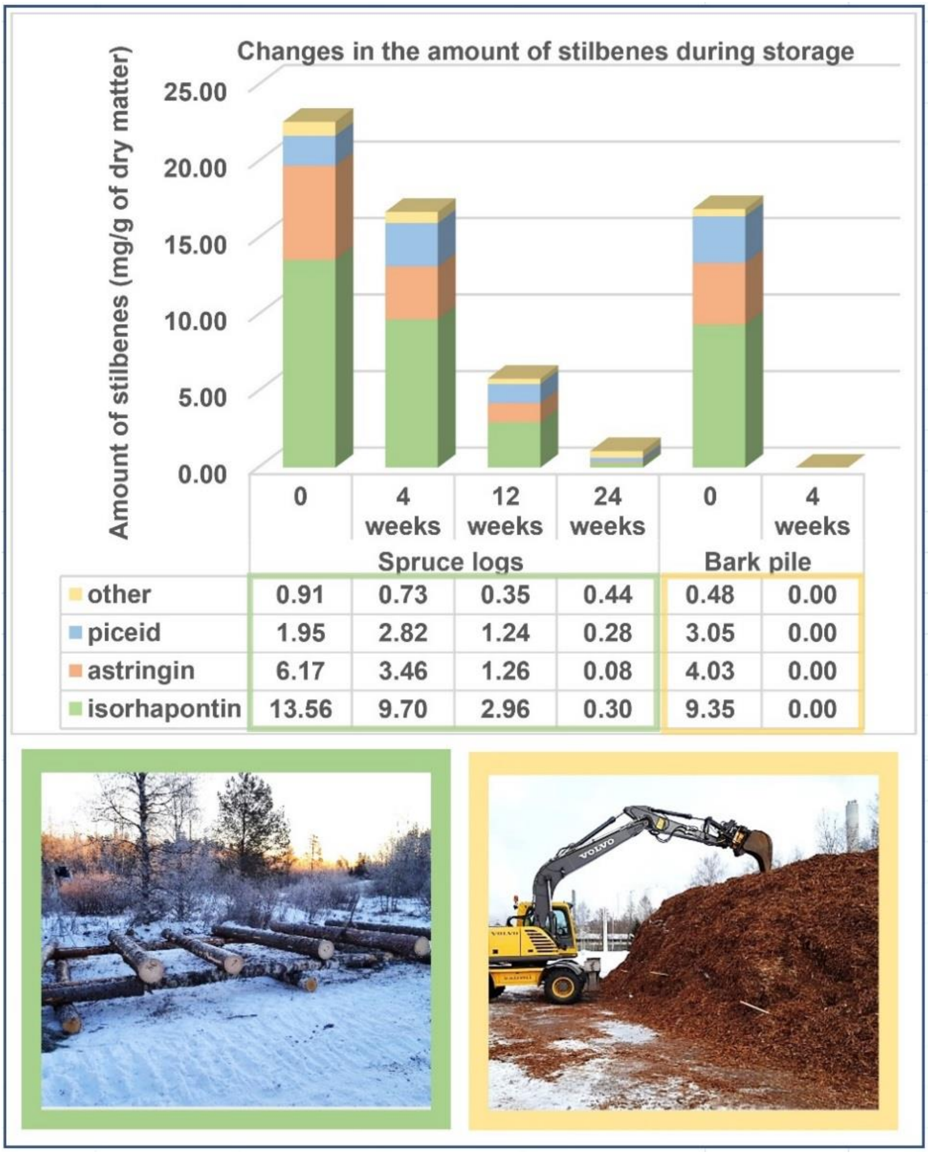
Table 1 TDS of bark extracts

SS = single stem setup; BP = bark pile setup;
A = top, B = side, C = middle; values are reported as % of dry matter.

Sample	**Hexane extract**	**Water extract**	**TDS**
SS 0-weeks	4,81	29,87	34,68
SS 4-weeks	3,16	31,00	34,17
SS 12-weeks	5,70	30,85	36,55
SS 24-weeks	3,58	17,61	21,19
BP 0-weeks	4,11	33,46	37,57
BP (A) 4-weeks	3,84	14,56	18,40
BP (B) 4-weeks	4,12	17,42	21,54
BP (C) 4-weeks	4,35	20,31	24,66
BP (A) 12-weeks	3,62	8,90	12,51
BP (B) 12-weeks	3,97	11,48	15,45
BP (C) 12-weeks	3,83	16,39	20,22
BP (A) 24-weeks	3,02	7,25	10,28
BP (B) 24-weeks	3,43	9,17	12,60
BP (C) 24-weeks	4,09	14,33	18,41

Stilbene concentration

The abundance of data from the experiments referred to in this paper was too vast for us to give even a simple overview regarding all the different extractive groups and individual compounds found in spruce bark. Thus, we focused on stilbenes, as they are one of the most interesting phenolic extractives in spruce bark and can provide a good illustration of how different storage conditions affect their concentration. The concentration of the major stilbene glucosides (piceid, astringin, and isorhapontin) in the spruce bark samples from the single stem and bark pile experimental settings are illustrated in Figure 1. The difference in the amounts of stilbenes is great and could already been seen in the zero samples. The freshly debarked spruce bark from saw mill seemed to correspond to the bark that was stored intact on saw logs for 4 weeks in terms of stilbene concentration. Most significantly, at four weeks the stilbene concentration in the bark pile reached undetectable levels, while the stilbenes in log bark could still be found after 24 weeks. This can be very important and practical issue, e.g., if one wishes to extract stilbenes from spruce bark, it needs to be done within days after debarking, not weeks. Isorhapontin is the most abundant stilbene glucoside in spruce, following with astringin and finally, piceid. However, based on the gas chromatography and LC-MS-QQQ results it seemed that astringin is the most unstable of the three stilbene glucosides. If left at room temperature, the astringin peak will disappeared from the MS spectrum first. The spruce logs results for the weeks 12 and 24 showed this trend as well. At week 12 astringin was already at the same concentration as piceid, while at week 24 piceid was at least three times more abundant than astringin. The reactivity of stilbenes has been studied since the 1980s[11]. According to these earlier studies, stilbenes naturally undergo *cis-trans* conformation changes which can in the presence of UV light and oxidant eventually lead the *cis*-conFigured stilbenes to undergo photocylization reactions forming dihydrophenathrenes and other aromatic hydrocarbons. Reactions like these may be used explain the degradation of at least some of the stilbenes present in spruce bark.



	Spruce logs 0	Spruce logs 4 weeks	Spruce logs 12 weeks	Spruce logs 24 weeks	Bark pile 0	Bark pile 4 weeks
🟨 other	0.91	0.73	0.35	0.44	0.48	0.00
🟦 piceid	1.95	2.82	1.24	0.28	3.05	0.00
🟧 astringin	6.17	3.46	1.26	0.08	4.03	0.00
🟩 isorhapontin	13.56	9.70	2.96	0.30	9.35	0.00

Figure 1 The changes in the concentration of stilbenes in spruce bark during the storage of bark in logs and bark pile.

Conclusion

Different methods of storing raw materials like spruce bark can have huge impact on the composition of its extractives-fractions. The valuable stilbenes in spruce bark are quickly lost if the bark is stored in a pile, whereas storing the bark in logs shelters the stilbenes from oxidation and UV light induced reactions. If wood-extractives-based products are to be produced in the future, this has to be taken into consideration when planning on the logistics of feedstock.

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Bioethanol from untreated waste lignocellulose materials - Transcriptomics of Phlebia radiata under fermentative conditions

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Renewable lignocellulose waste materials such as straw and sawdust are abundant, underused and sustainable sources for production of different biocompounds to replace the thinning fossil fuels resources. We have previously stated that several untreated lignocelluloses can be bioconverted into bioethanol in a simultaneous saccharification and fermentation (SSF) process by a wood-degrading white-rot fungus *Phlebia radiata*. To better understand the SSF process, *P. radiata* was cultivated either under aerobic or fermentative conditions and the transcriptomes and ethanol fermentation related metabolite profiles were compared.

P. radiata is capable of producing ethanol from untreated wood-waste in microaerophilic conditions while only trace quantities of side products such as acetate and glycerol are detected. The P. radiata transcriptome is very different during fermentation in comparison to aerobic conditions especially concerning cellulose, hemicellulose and pectin degradation and catabolism. A comparison to other *P. radiata* transcriptomes has also revealed several co-regulated gene clusters within the wood degradation genes and core metabolic pathways.

Simultaneous bioconversion of high - inhibitor xylose - glucose media using diffusion - based reverse membrane bioreactor

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Industrial production of lignocellulosic bioethanol is hindered by the presence of sequentially fermented saccharides and high content of inhibitory compounds. The newly-introduced cell retention technique of reverse membrane bioreactor (rMBR) used in this study, was a promising approach for tackling issues involved in the fermentation of high-inhibitory xylose-glucose media simulating a lignocellulosic hydrolysate. The concentration-driven mass transfer in rMBR, enhanced co-utilization of prioritized sugars and boosted cell furfural detoxification capacity in the target highly inhibitory media. In this regard, the fluxes of all compounds over the membrane in rMBR and diffusion cell were determined and compared. It was observed that in rMBR set-up cells could readily convert up to 10 g/l of furfural, which is extremely toxic to freely suspended cell. Moreover, in the presence of 2.5 g/l of furfural cells had the same exceptional performance as in medium with no inhibitor and could simultaneously convert glucose, xylose, and furfural with the latter two at the same rate with no lag phase. The performance of rMBR in remediating issues revolving around lignocellulosic bioethanol production covers the shortcomings of the conventional encapsulation technique and introduces new areas of application for diffusion-based bioconversion systems.

Introduction

In recent decades, great attention has been given to the production of 2nd generation bioethanol from processing lignocellulosic materials (agricultural residues etc.). However, 2nd generation bioethanol fermentation faces limitation in production technology and processing costs[1]. Lignocellulosic materials have a recalcitrant structure of cellulose, hemicellulose and lignin. In order to makes structural sugars available for fermentation, this structure has to be pretreated and enzymatic hydrolyzed[2]. During pretreatment, different hexose and pentose monosaccharides, such as glucose and xylose, respectively, and cell-inhibitory by-products such as furfural and 5-hydroxymethylfurfural are produced that deteriorate the cell's metabolic and physiologic condition[3]. In addition, wild-type yeasts cannot consume pentoses and xylose-consuming recombinant yeasts have a preferential sugar consuming behavior[4]. In inhibitory fermentation systems with freely suspended cells, all cells experience the same toxicity levels. However, it has been reported that enhanced inhibitor tolerance and co-utilization of different sugars can be achieved by providing microenvironments with high local cell concentration[5]. These conditions can be obtained in the new membrane cell confinement technique of rMBR[6]. In rMBRs cells are retained between membrane layers and diffusional mass transfer of compounds occurs over the membrane due to a concentration gradient[6]. In this research, by the application of an rMBR set-up, we tried to remediate some issues with simultaneous sugar consumption along with detoxification of inhibitory compounds commonly face during lignocellulosic bioethanol production. In this regard, the diffusion behavior of different chemical compounds involved in fermentation were first measured using a diffusion cell and then compared to that of compounds during rMBR fermentations.

Materials and methods

Diffusion rate measurement

A Side-Bi-Side diffusion cell (PermeGear Inc., Hellertown, PA, USA) was used to measure the diffusion rate and flux of different compounds through the membrane used in rMBR. A single membrane layer was cut from a 2nd generation IPC (Integrated Permeate Channel) dual layer membranes and used to separate donor and receptor cells. The concentration of compounds in the diffusion cell was chosen to be comparable to that of acid pretreated and enzymatically hydrolyzed wheat straw hydrolysate. The cumulative amount compounds released per unit area of membrane (Q) was calculated[7]. Graphs of Q versus time with the slope of the regression line representing flux (J) of a component per unit area of membrane surface were plotted[8].

Preparation of pre-culture and reactor medium

In this study, a recombinant xylose-utilizing *Saccharomyces cerevisiae* was used. Yeast extract, peptone, glucose and xylose broth was inoculated with yeast and kept in a shaking water bath at 30°C for 48 h. Then the total culture medium was concentrated 16-times by centrifugation and a total of 25 ml of the inoculum was injected in between membrane layers representing a cell concentration of 0.82±0.09 g/l in the overall rMBR reactor volume (3 l). After cell inoculation, the glucose-xylose (24 and 12 g/l, respectively) semi-synthetic medium containing different levels of furfural (0, 2.5, 5, 10 g/l) were added to the bioreactor's shell-side.

Membrane panels and analytical methods

In this rMBR set-up, 2 membrane panels of 2nd generation Integrated Permeate Channel (IPC) (Flemish Institute of Technological Research (VITO NV), Belgium) were used for cell confinement[9] . The detection and quantification of the changes in the concentration of substrates and metabolites in the rMBR and the diffusion cell was analyzed using high-performance liquid chromatography (HPLC) (Waters 2695, Waters Corporation, Milford, USA). The software package MINITAB® 17 was used for statistical analysis of the obtained data.

Results and discussion

Firstly, the diffusion rates of different compounds involved in fermentation with the same initial concentrations as the medium used in the rMBR were measured using a diffusion cell and these were further compared with the flux and conversion rates of compounds during rMBR fermentation Figure 1.

A surprisingly comparable performance was observed for media with 0 and 2.5 g/l initial furfural when considering the changes in diffusion and utilization rates of glucose during rMBR fermentation (Figure 1). The most significant change in the concentration of glucose (5 g/l) was recorded for the aforementioned cultivations with no considerable difference (p-value=0.465) in flux (0.0017±0.0004 g/cm^2.h). Ishola *et al*[10]. reported that the flux of glucose in an rMBR containing wheat straw hydrolysate and xylose-glucose semi-synthetic media with about 50 and 6 g/l of initial glucose was 0.0025 and 0.0006 g/cm^2 h, respectively. By increase in the initial furfural concentration to 5 and 10 g/l, 70% and 92% drop in glucose concentration was observed compared to that of the diffusion cell, respectively (Figure 1). As the in all preparations glucose has the same diffusion rate, cell metabolic and physiologic condition in the absence or presence of furfural is responsible for changes in the glucose concentration. Considering the two-folded glucose diffusion rate in the diffusion cell compared to the rMBR, the rate-limiting factor in the consumption of glucose, even in the non-inhibitory condition, may be either bioconversion kinetics or diffusion hindrance in cell aggregate. Similar to the trend was observed for xylose in the case of non-inhibitory and 2.5 g/l furfural media. Xylose diffusion rates in the abovementioned preparations (p-value=0.095), are more or less the same although five-times less than that measured in the diffusion cell (Figure 1). However, drop in xylose content with the increase in the inhibitor content can be due to glucose suppression and the direct effect of furfural on cell activity. A reason can be that there is less ATP production (lower metabolic energy flux) for xylose than glucose and that inhibitor-exposed cells have lower energy levels to spend on cell maintenance[11]. Moreover, co-factors (NADH and NADPH) play an important role in xylose conversion by yeast and when furfural (a reactive aldehyde) acts as an electron sink the amount of intercellular co-factors plunge. Furthermore, conversion of furfural by the enzyme alcohol dehydrogenase (ADH) utilization of the same co-factors, leading to even less xylose conversion[12]. Xylose utilization can drop as high as 95% if 1% furfural is present in the rMBR cultivation medium (Figure 1). Nearly similar trend was observed in in ethanol production and release rate during rMBR fermentation.

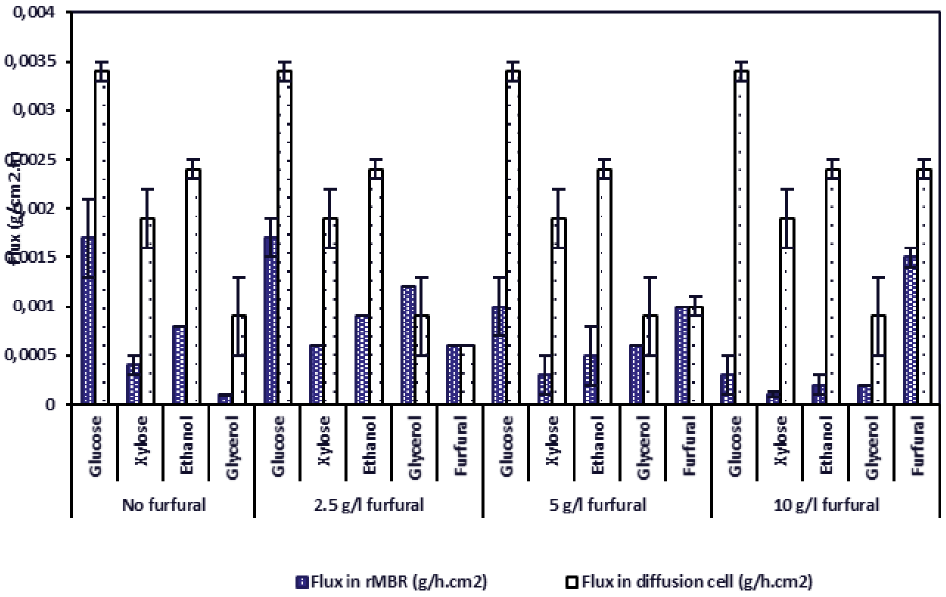

Figure 1. The comparison of the flux of different compounds in the diffusion cell with their conversion/release rate in rMBR at different furfural concentrations.

In order to prevent cell damage and long lag phases during fermentation [3], cells should be able to readily convert the toxic inhibitor at exposure. Surprisingly, due to diffusion mass transfer conditions built by rMBR application, the diffusion rate of furfural for feed media with 2.5 and 5 g/l of furfural was nearly equal to the detoxification rate by yeast cells. Having the same conversion (rMBR) to diffusion rate (diffusion cell) ratio of about 1:1 and having about the same (0.82±0.04 g/l) starting inoculum concentration, shows that the conversion rate is not the limiting factor for furfural detoxification. Comparing to the specific rate of furfural detoxification (0.0051 g/g cells.h) reported previously for an rMBR system[10], in this rMBR set-up, the specific rate of detoxification for initial furfural of 5 g/l was considerably higher. Doubling the furfural content to 10 g/l was only accompanied with 50% increase in the conversion rate (Figure 1). This low detoxification rate to diffusion rate ratio describes that the cell redox imbalance and cell metabolic and physiologic disturbance is the reason for the dramatic drop in the consumption of substrates and production of metabolites. However, inhibitor tolerance levels are considerably higher in rMBR compared to freely suspended cells cultures that experience this noticeable shift in metabolic performance even at furfural content of less than 2 g/l[13]. Glycerol concentration during anaerobic fermentation is an indicator for the alternations in yeast cell's redox balance. Glycerol production experienced a12-fold jump by the addition of 2.5 g/l of furfural. However, high concentrations of furfural can act as electron sink by oxidizing the excess co-factors, the amount of glycerol released drops at 5 and 10 g/l of furfural and all other conversions including glycolysis chain reactions are affected[14] [14]. According to the results acquired during rMBR fermentation, four scenarios are visualized in Figure 2. As illustrated in Figure 2a, the cells in the outer layers of the cell aggregate get involved in preferred glucose utilization, while cells in the inner layers closer to cell cluster core that are glucose-starved tend to consume the xylose. The condition built based on glucose and xylose diffusion and conversion rates assist simultaneous sugar consumption. At 2.5 g/l of initial furfural, furfural is converted at the same rate as xylose is consumed. As shown in Figure 2b, this exposure to the inhibitory compound can hypothetically separate the cell aggregate into three distinct regions: high-inhibitor/detoxification region, low-inhibitor/glucose consumption region and low-inhibitor and glucose/xylose consumption region. By increasing the furfural, content to 5 and 10 g/l the metabolic balance is dramatically disturbed (Figure 1). Measurement in the diffusion cell show that the diffusion rate of furfural through the membrane jumped 1.7 and 4-times when having 5 and 10 g/l furfural, respectively, compared with the condition with 2.5 g/l furfural. This increase in flux of furfural through the membrane layers leads to deeper infiltration of furfural at the early stages of fermentation and causes cell toxicity in the cell aggregate confined to membrane layers (Figure 2c and d).

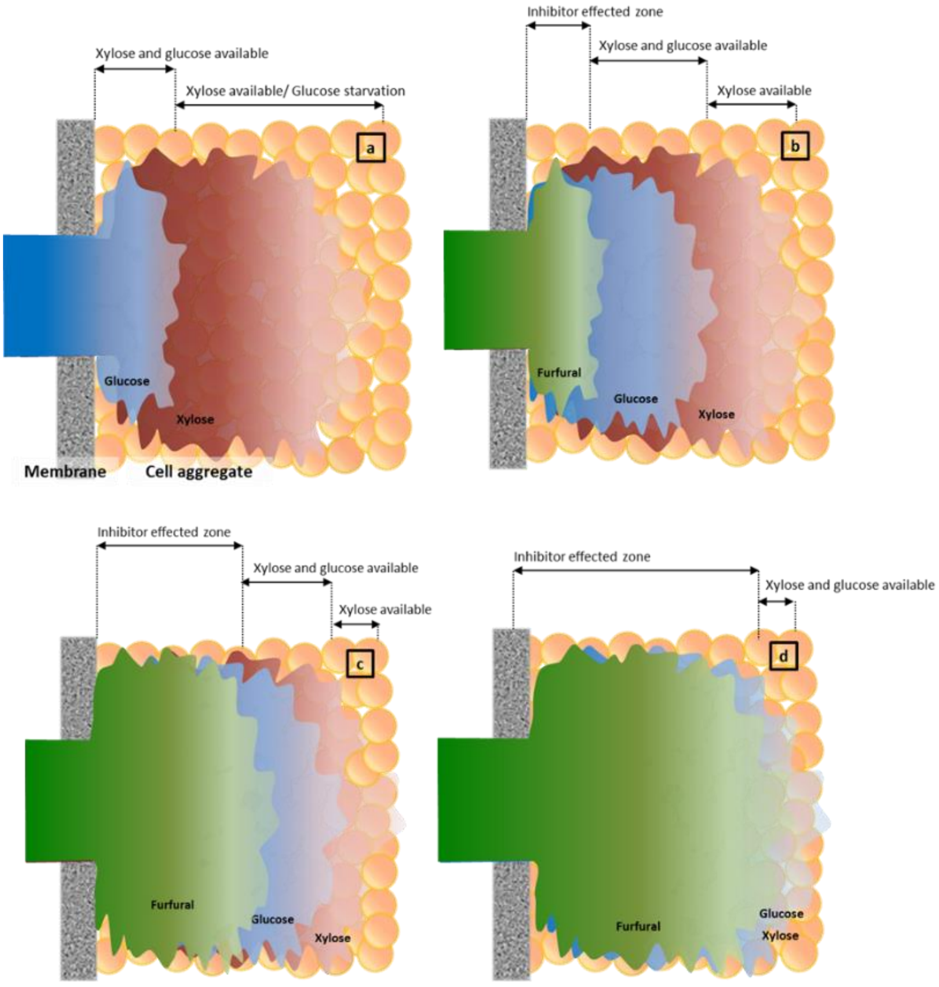
Xylose and glucose available
Xylose available/ Glucose starvation
a
Glucose
Xylose
Membrane
Cell aggregate
Inhibitor effected zone
Xylose and glucose available
Xylose available
b
Furfural
Glucose
Xylose
Inhibitor effected zone
Xylose and glucose available
Xylose available
c
Furfural
Glucose
Xylose
Inhibitor effected zone
Xylose and glucose available
d
Glucose
Xylose
Furfural

Figure 2. Conditions built up in the cell aggregate due to concentration gradient of different medium components in rMBR fermentation: (a) zero, (b) 2.5 g/l, (c) 5 g/l and (d) 10 g/l furfural.

Conclusions

The rMBR set up builds a desirable diffusion-based mass transfer conditions over the membrane layers and cell-aggregate that lead to enhanced co-utilization of xylose and glucose. In addition, the concentration gradient built over the high local concentration of cells boosted furfural tolerance and in situ detoxification capability of the cell aggregate in highly inhibitory media.

Acknowledgements

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Modification of natural fibres and preparation of cellulose - based mixed – matrix - membranes

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We demonstrate the modification of cellulose filters by polymer resin nanoparticles, i.e. amino resins. Highly porous (specific surface areas up to 160 m^2g^{-1} as determined by cryogenic N_2 adsorption/desorption) mixed-matrix-membranes can be obtained using colloidal destabilization techniques. The membranes can combine filtration processes with adsorption techniques.

The obtained membranes are characterized with regard to their morphology using electron microscopy. Their permeability will be analysed using dead-end filtration. Application of the membranes in separation tasks, e.g. the adsorption of organic molecules or micropollutants from water will be demonstrated.

The presented work is part of the joint research task: “Lusatian Alliance on Natural Fibre Reinforced Composites: Decentral Energy, Raw Materials, Resources and Recycling (LaNDER^3)”.

Introduction

Membrane technology is an old, yet very vivid field of separation science. Usually, membranes are used for separation by filtration. The sizes of rejected particles range from less than 1 nm (reverse osmosis) up to several hundreds of µm, spanning all dimensions form molecules up to macroscopic objects. Rejection of very small solutes does usually require very small pore sizes, which in turn results in high pressures that are needed to force the fluids to flow through such small pores, resulting in high energy demand. This is especially the case, when only minor amounts of solutes need to be removed, as it is the case for so-called micropollutants (e.g. heavy metal ions, organic contaminants such as pesticides, etc.).

One possibility to target this issue could be the use of so called mixed-matrix-membranes (MMM) that combine, simply speaking, filtration and adsorption within one membrane. Schiestel and co-workers demonstrated for instance MMM based on polyether sulfone as base material with incorporated polymeric nanoadsorber particles for selective heavy metal binding[1]. Another kind of polymeric adsorbers are nanoporous melamine resins. Their use for adsorption applications was investigated throughout the last years by various researchers, including us[2-7].

However, the shaping of these nanoporous materials into a macroscopic useful form (monolith, spheres, membranes) remained an unsolved issue so far. We got aware of the fact that the modification of cellulose by amino resins, including melamine-formaldehyde resins, has however been well-known already for decades and was used e.g. for improvement of the wet-strength of paper[8]. Hence, it seems reasonable to combine these two strategies.

Within this contribution, the modification of cellulose filters by porous melamine resins is demonstrated. The resulting membranes feature high specific surface areas and combine filtration and adsorption into a single membrane. The modification is based on the destabilization of a colloidal aqueous suspension of melamine resin and silica nanoparticles.

Experimental

The **colloidal suspension of melamine resin (PMF) and silica nanoparticles** was prepared using a slightly modified protocol that was reported earlier[9]. The reaction was performed using an IKA laboratory reactor (IKA LR 1000) that allowed an upscaling of the earlier reported protocol by a factor of 10. The resulting opaque suspension was stable against sedimentation and had the following characteristics: $C_{PMF} \approx 20$ g/l; $C_{SiO2} \approx 15$ g/L; $C_{H3PO4} = 0{,}07$ M.

Xerogels were prepared using the resulting suspension for comparative reasons according to the known protocol[9].

Preparation of the MMMs was done using following procedure

A cellulose filter paper (Whatman Nr 3, 70 mm diameter, 6 µm pore size) was placed in the bottom of a solvent-resistant stirred filtration cell (Merck, borosilicate glass and stainless steel, outer diameter 76 mm). The cell was filled with 40 mL of the colloidal suspension and 50 mL ethanol were added. Impregnation of the filter was achieved by applying a pressure of 2-6 bar. The gelling solution was pressed through the filter three times. The exact amount of PMF/SiO2 deposited on the membrane depends on the applied pressure. The filter paper was taken out of the stirred cell and immediately transferred to a hot press (transfer press). A second filter paper, which was just impregnated by simple addition of 2 mL of the colloidal suspension was placed on top of the first filter paper. Curing was achieved by applying gentle pressure at 120°C for 16-17 min followed by post-curing at 120°C for 24 h in a dry oven. Silica was eventually etched by passing a 1 M NaOH solution through the membrane for 2 hours (using the stirred filtration cell) followed by thorough washing of the membrane with deionized water.

Instrumental analytics

ATR-FTIR spectra were collected using a Bruker Tensor 27. Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were collected using a JEOL JSM-6510Q. Nitrogen adsorption/desorption isotherms at 77.4 K were recorded using an Autosorb 1 MP machine of Quantachrome instruments. High-purity gases were used for analysis. Data analysis was performed using the AS1Win software of Quantachrome Instruments. UV/Vis-Spectra were measured using a Specord 50 (Analytik Jena).

Results and Discussion

We developed recently a technique that allowed us to synthesize mesoporous (that is: pore diameters between 2 and 50 nm) melamine resin xerogels starting from a stable suspension of PMF nanoparticles that does also contain silica nanoparticles[9]. The aqueous dispersion can be electrostatically destabilized by addition of ethanol, resulting in a gelation. It has been recognised that the gel needs to be compacted before the final curing step in order to achieve a highly porous xerogel. This step was usually done using centrifugation of the gel.

In order to transfer the concept to the preparation of membranes, we decided to perform the colloidal destabilization within a stirred cell (usually used for (ultra)filtration), which allowed us to perform the necessary compaction step by applying pressures from 2-6 bar.

Membrane Characterization

Initial experiments were conducted using a single filter paper impregnated by the melamine resin, which led to problems of partially not sufficient adhesion. This resulted in a loss of the adsorber particles. To overcome this problem, a second filter paper, that was only impregnated by a very small amount (2 mL) of PMF/silica dispersion was added as a cover cap on the filter carrying the major amount of PMF/silica.

After hot pressing and curing a very good adhesion between the two filters (double-membrane) was achieved. The membranes showed increased stiffness but were not brittle. Figure 1 shows exemplary SEM micrographs of the hybrid MMMs that contain PMF and silica. It appears that the fibres are coated rather homogenously, however, cracks are visible within the coating. The total amount of PMF/silica that could be introduced within the membrane can be varied from 20-55 wt.-%, depending on the exact conditions of the impregnation step. The presence of both species was verified by ATR-FTIR spectroscopy (data not shown) and EDX (see Figure 2).

The thickness of the overall MMM is within a range of 900-1000 µm. The cover plate has a thickness of roughly 200-250 µm. The lower part, i.e. the PMF/silica coated filter has a thickness of roughly 700-750 µm. Elemental mapping by means of EDX does show that the melamine resin (which contains a lot of nitrogen) and the silica particles are homogenously distributed with the coated filter, but almost absent within the cover plate filter.

The porosity of the hybrid membranes was investigated by means of nitrogen adsorption/desorption at 77.4 K. Exemplary isotherms are depicted within Figure 3.

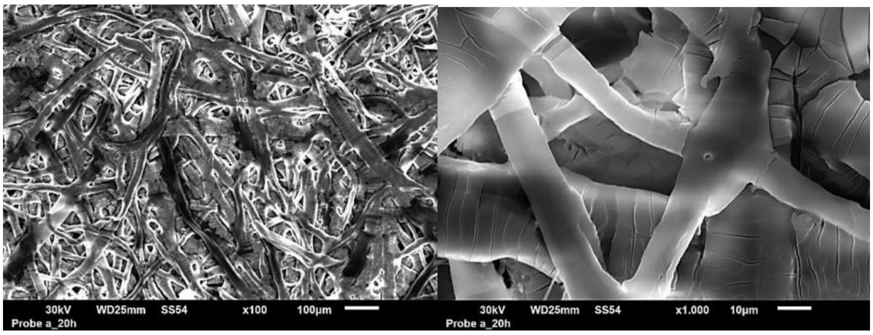

Figure 1. exemplary SEM micrographs of the single cellulose filter (no cover-plate) coated/modified with the PMF/silica mixture (curing time 12 h, curing temperature: 90°C).

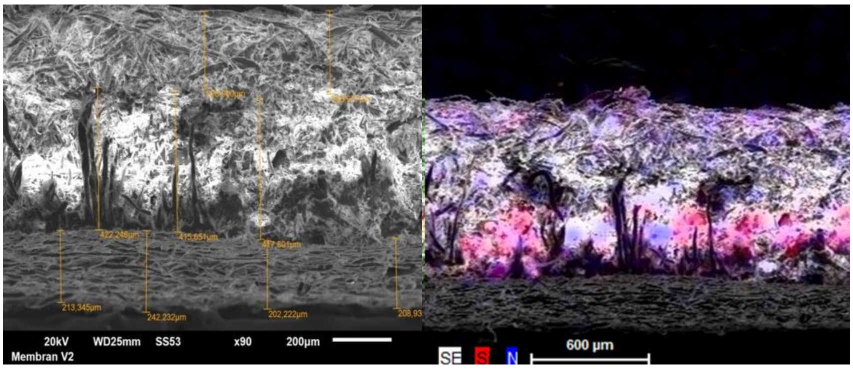

Figure 2. left-hand side: cross-section of a hybrid MMM, the bottom part is the cover-plate, the upper part is the filter modified by the PMF/silica gel within the filtration cell. right-hand side. SEM micrograph with EDX elemental mapping (nitrogen: blue colour, silicium: blue colour) of the cross-section of a hybrid MMM

The hybrid MMMs show pronounced mesoporosity with specific surface areas ranging from 140-160 m^{2}g^{-1} and pore volumes between 0.12 to 0.15 cm^{3}g^{-1}. Again, the finer details depend on the exact preparation conditions and will be part of a more detailed study. The silica particles can be removed by treatment with 1 M sodium hydroxide. However, contrary to Xerogels reported before, we did not observe an increase in porosity upon silica removal. This observation does also require further investigation.

Finally, we were interested if the permeability of the membranes does change upon modification. Permeability was determined by pressing water through the membranes in a dead-end-filtration setup at constant applied pressure. Data was collected by recording the mass of filtrate vs. time (not shown). Interestingly, we found that the permeability increased upon modification, when compared to the permeability non-modified filters (two filters were used at the same time for better comparability, i.e. quasi-constant cellulose content). This effect might be attributed to the fact that the coating is rather homogenous (cf. Figure 1 and 2) and does smoothen the fibrous structure. Additionally, PMF is a hydrophobic material, which might increase the water flow rate as less pronounced interactions between the material and the fluid are expected. We modified the filter paper also by a silica gel coating, which indeed decreased the permeability, which is would be expected as silica gel is a quite hydrophilic structure.

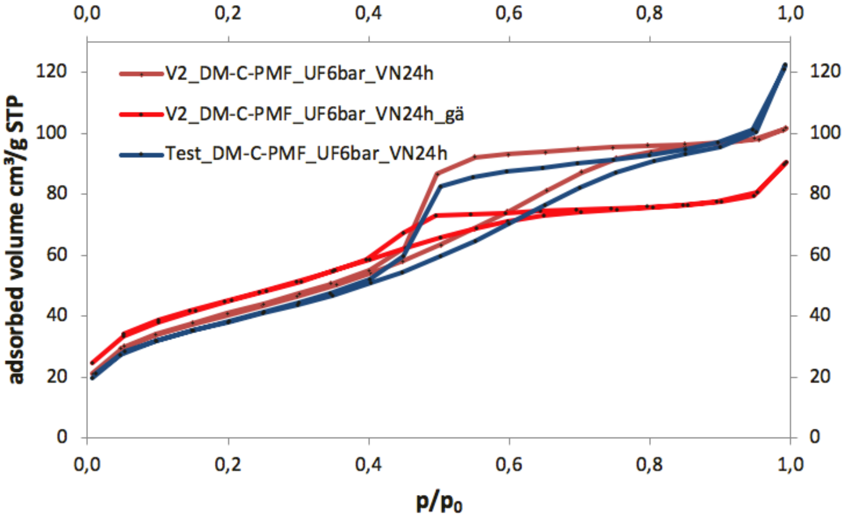

Figure 3. N2 adsorption/desorption isotherms (77.4 K) of two hybrid MMMs and one MMM that was prepared upon etching of the silica particles (ID: V2_DM-C-PMF_UF6bar_VN24h_gä)

Application as Adsorber

To demonstrate the applicability of the MMMs, we tested them for the removal of a model substance (fluorescent dye) dissolved in water (c = 34.1 mg·L^{-1}). The solution was pumped through the MMM filter for 5 times to simulate (in a crude manner) a cascade of MMMs. Figure 4 shows photographs of the solution before and after filtration (under UV illumination at 366 nm) and the hybrid MMM after filtration. It becomes clear that the process is very effective. However, the dye is distributed on the hybrid MMM inhomogeneously, which indicates that the modification is not as evenly as expected from SEM analysis. Again, this leaves space for a more detailed investigation in future experiments. Furthermore, analysis of the filtrate by UV/Vis-spectroscopy could not only prove that the dye was effectively removed, but gave also the hint, that the MMM might release other organic substances in a small amount. This effect is well-known from e.g. ion-exchange resins (so called leachables). Those can however be removed by extraction as first experiments indicate.

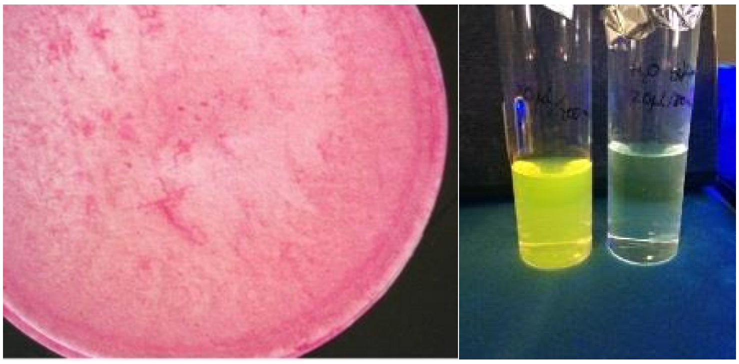

Figure 4. left-hand side: hybrid MMM after filtration, right-hand-side: fluorescence of the original solution and the filtrate under UV light illumination

In summary, the hybrid MMMs that are formed from PMF and silica particles fixed on cellulose filters show good adsorption properties for organic substances. Future experiments will focus on a more detailed characterisation, but also on the application of the MMMs for separation tasks related to biorefinery processes. For instance, the separation of 5-hydroxy methyl furfural (HMF) from aqueous solutions can be achieved by adsorption on nanoporous polymers particles10, and it will be interesting to see, whether this task might profit from the use of the here shown MMMs.

Acknowledgements

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Life cycle assessment of lignocellulosic biomass valorisation into high - added value products

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A life cycle assessment (LCA) of novel pilot-scale hemicellulose and lignin valorisation processes into high-added value products has been developed. Hemicellulose and lignin waste from biomass have been valorised into different high-added value products including: Chemicals (acetone, butanol, ethanol, acetic acid and butyric acid), Single Cell Proteins (SCP) and xylitol (from hemicellulose) and PHA bioplastics (from lignin). Results show that, in the hemicellulose value chain, enzymatic hydrolysis has the higher impact in the chemicals and xylitol production, while in the case of SCP production, aerobic fermentation has most relevant impact. Regarding lignin valorisation, chloroform extraction represents the major contribution to climate change environmental impact of the whole lignin value chain. LCA results have pointed out the life cycle stages which require further optimisation from the environmental point of view. Therefore, LCA is suitable methodology for the development of bio-based processes.

Introduction

Over the last decade, sustainability has become in one of industry's most overused buzzwords. The goal of sustainability is to "create and maintain conditions, under which humans and nature can exist in productive harmony, that permit fulfilling the social, economic, and other requirements of present and future generations[1]." A sustainable approach is a systems-based approach that seeks to understand the interactions which exist among environmental, social, and economic pillars to better understand the consequences of our actions. The environmental pillar often gets the most attention. Companies are focusing on reducing their carbon footprints, packaging waste, water usage and their overall effect on the environment. Companies have found that have a beneficial impact on the planet can also have a positive financial impact.

The life cycle assessment (LCA) method, following ISO standards[2,3], has been conducted to estimate the overall net environmental impact associated with hemicellulose and lignin pilot-scale valorisation processes from biomass into high-added value products including: Chemicals (acetone, butanol, ethanol, acetic acid and butyric acid), Single Cell Proteins (SCP) and xylitol (from hemicellulose) and PHA bioplastics (from lignin).

Hemicellulose is the second most abundant biopolymer found in nature, depending on wood species, constitute about 20-30%[4]. They are heterogeneous polymer of pentoses, hexoses and sugar acids. The two main hemicelluloses in wood are xylans and glucomannans. In recent years, hemicellulose has received attention because of its potential applications in various agro-industrial processes[5].

Lignin is an amorphous polymer that is primarily found in the cell wall of plant cells. Lignin presents a 3D random structure disordered and branched, insoluble in water and in most common solvents and with a molecular mass ≈10 kDa. Currently, lignin is produced mainly as a by-product of the paper industry, separated from trees by a chemical pulping process and classified as a waste which is storage or used for combustion. In bio-refineries, lignin must be degraded and effectively removed, in order to avoid problems in fermentation processes related to the production of biofuels[6]. In the extraction of lignin, several physical and chemical processes are involved, including for example the boiling in acid or alkaline environment in presence of sulphur compounds. Catalytic and enzymatic depolymerisation are environmentally friendly alternatives to the degradation of lignin[7]. This would allow the use of lignin degradation products as starters within synthetic chemistry, as well as the development of new products.

Experimental

LCA involves four steps: (i) Goal and Scope, (ii) Life Cycle Inventory, (iii) Impact Assessment and (iv) Interpretation of results.

Goal and Scope

The main goal of this LCA is the assessment of the potential environmental impacts related to the valorisation of hemicellulose and lignin waste.

An LCA is usually made in a cradle-to-grave perspective. However, because of the wide range of uses of the chemicals produced from valorisation procedures (e.g.: ethanol, xylitol, butanol, lactic acid, phenolics, etc.) it would be difficult to assess the real picture of the different usages (end markets). Consequently, it was decided to focus the LCA in a cradle-to-gate approach. This means to assess the potential environmental impacts from raw material extraction to the production of the different chemicals.

In all the stages considered, the inputs of materials, energy and water were considered, while the outputs in form of products, co-products, waste and emissions to air, water and soil were considered as well. Avoided impacts (i.e.: those credits because of the avoidance of the use of other conventional sources of energy and materials) were considered too.

The selection of the functional unit is one of the key aspects in every LCA. Although EN 16760:2015 [8]recommends using functional units able to represent with a reference flow of 1 kg of product, due to the large number of final products and co-products obtained from the valorisation processes, it has been decided to fix the functional unit as 1 ton of feedstock (dry basis).

When processes have several products or by-products, mass allocation has been performed for the distribution of the impacts.

Figure 1 shows the hemicellulose valorisation value chain. It is based on two different flow charts. On the one hand, the production of high added-value oligosaccharides via enzymatic hydrolysis. Such oligosaccharides are used to produce pre-biotics. And on the other hand, monosaccharides are also obtained through enzyme hydrolysis, and then fermented to obtain the desired high-added value products. Figure 1 also includes the system boundaries considered for the hemicellulose value chain. As it can be seen, the use of the final products is excluded due to the cradle-to-gate LCA perspective selected. In addition, the previous stages of separation/distillation, have not been included as well within system boundaries because of the difficulty of scaling-up such type of processes.

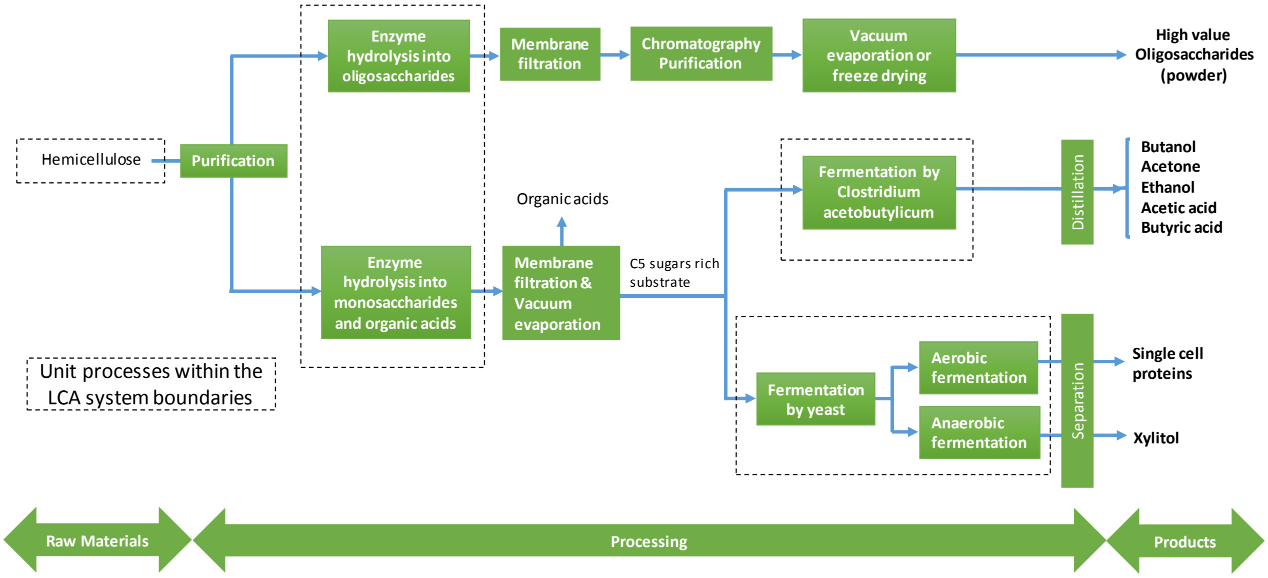
Hemicellulose
Purification
Enzyme hydrolysis into oligosaccharides
Membrane filtration
Chromatography Purification
Vacuum evaporation or freeze drying
High value Oligosaccharides (powder)
Organic acids
Enzyme hydrolysis into monosaccharides and organic acids
Membrane filtration & Vacuum evaporation
C5 sugars rich substrate
Fermentation by Clostridium acetobutylicum
Distillation
Butanol
Acetone
Ethanol
Acetic acid
Butyric acid
Unit processes within the LCA system boundaries
Fermentation by yeast
Aerobic fermentation
Anaerobic fermentation
Separation
Single cell proteins
Xylitol
Raw Materials
Processing
Products

Figure 1. Hemicellulose valorisation value chain flow chart.

In the case of lignin waste, the process involved in the value chain consists first in a degradation via chemical depolymerisation and its subsequent conversion into polyhydroxyalkanoates (PHA) bio-polymers as it is shown in Figure.

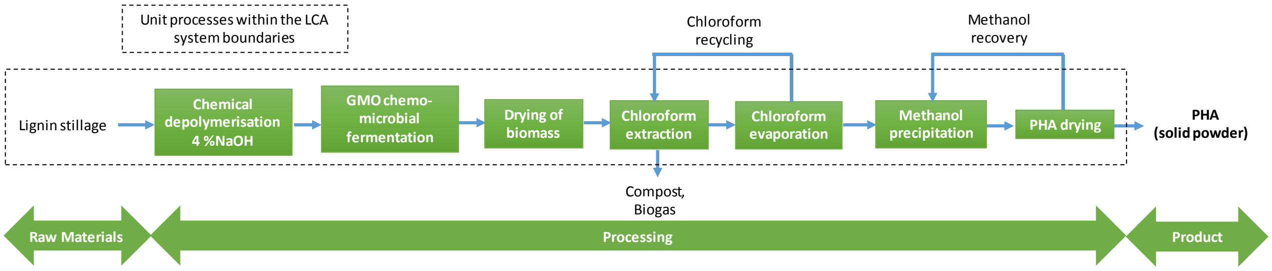
Unit processes within the LCA system boundaries
Chloroform recycling
Methanol recovery
Lignin stillage
Chemical depolymerisation 4 %NaOH
GMO chemo-microbial fermentation
Drying of biomass
Chloroform extraction
Chloroform evaporation
Methanol precipitation
PHA drying
PHA (solid powder)
Compost, Biogas
Raw Materials
Processing
Product

Figure 2. Lignin valorisation value chain flow chart.

Life cycle inventory

The Life Cycle Inventory (LCI) Analysis includes the collection of data for the processes and sub-processes for each value chain considered (inputs and outputs). Then, the collected data are treated with SimaPro software in order to obtain the main results from the LCA assessment, which are the environmental impacts of the whole process.

LCI is an analytical tool used to comprehensively quantify (within the limits of available data) and estimate the flows to and from the environment. These include the use of raw and ancillary materials, the air emissions (e.g. CO_2, NOx, SOx, etc.), water effluents (e.g. ammonium, nitrate), solid waste (e.g. heavy metals) produced, as well as the consumption/depletion of energy and other resources, over the entire life cycle of a product or process. According to the ISO standards, all those environmental parameters mentioned are analysed in a first balancing step for each single process. These are then added up over the whole life cycle to obtain the LCI.

In this study, the life cycle inventory analysis was built mainly on primary data collected from the processes as well as on secondary data from Ecoinvent 3 Database[9].

Results and discussion

Life cycle impact assessment and interpretation of results

A total of 16 several impact categories have been selected in this LCA, each of them representing a specific impact to the environment: Climate Change (CC), Ozone layer depletion potential (OD), Human toxicity, non-cancer effects (HT (non-cancer)); Human toxicity, cancer effects (HT (cancer)), Particulate matter formation (PMF), Ionizing radiation HH (IR HH), Ionizing radiation E (interim) (IR E), Photochemical ozone formation (POF), Acidification (AC), Terrestrial eutrophication (TE), Freshwater eutrophication (FE), Marine eutrophication (ME), Freshwater ecotoxicity (FET), Land use (LU), Water resource depletion (WD) and Mineral, fossil & renewable resource depletion (MRD & FD). The aim was to cover as much as different types of impacts as possible. This include the harmful effects of effluent discharges and the emissions because of the energy use. The selection of these impact categories has been made in accordance with one of the available impact assessment methods included in SimaPro Software: ILCD 2011 Midpoint+.

In Figure 3, the LCIA for the production of high added-value products through fermentation by Clostridia is shown. Main impact in this process is derived from the enzymatic hydrolysis into monosaccharides (red), while the impact of the fermentation tends to be low (around 30% or less).

Regarding the enzymatic hydrolysis it can be concluded that their main contributions to impact are on mineral, fossil & renewable resource depletion (MRD&FD) with more than 90% of the total impact, on human toxicity and land use (LU). This contribution is mainly caused by the use of enzymes and determinate chemical reagents.

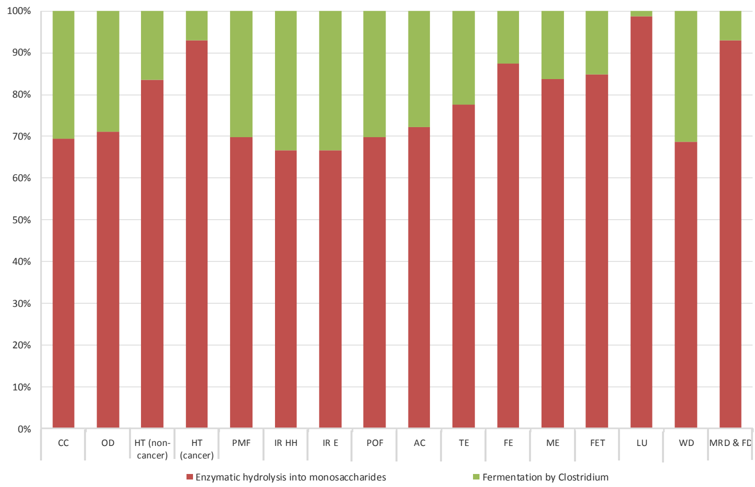

Figure 3. LCIA results. High added-value products production

Figure shows the results obtained for the pathway of production of single cell proteins by aerobic fermentation by yeast.

In this case, the aerobic fermentation by yeast represents the major environmental impacts in almost all the categories, except for human toxicity (HT) (non-cancer effects) with more than 80% of the total, due to the chemical reagents use in the process.

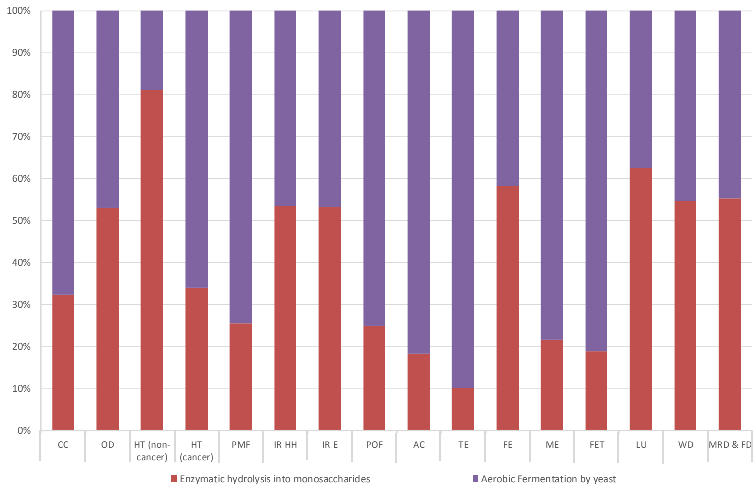

Figure 4. LCIA results. Single Cell Proteins production

Figure shows the impacts related to the different steps of production of xylitol, where the main contributions are the enzymatic hydrolysis into monosaccharides (red), while the contribution of the anaerobic fermentation represents less than 30% in all the impact categories.

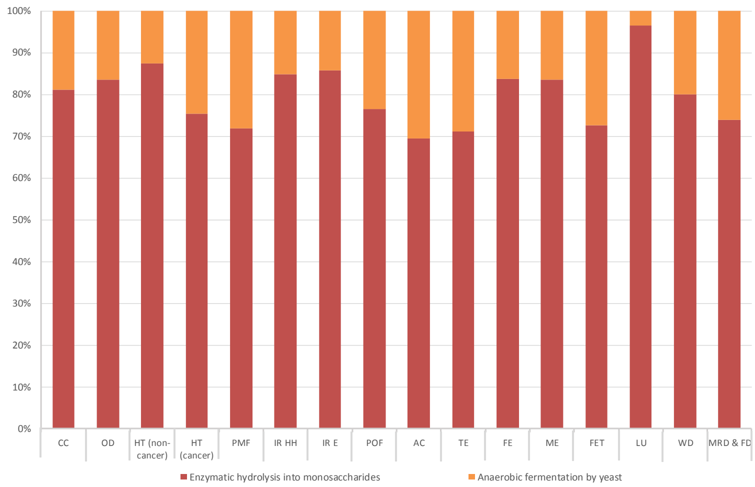

Figure 5. LCIA results. Xylitol production

Regarding the lignin valorisation process to obtain PHAs, looking at the Figure 6, it can be concluded that most of the impacts are concentrated in the downstream steps after PHA production: further development of these processes is necessary, especially with the use of chloroform as solvent during the extraction step (red colour). The latter process represents more than 60% of the total impact in all the impact categories except the water depletion (WD), where it has a compensating effect with more than 70% negative impact. The reason for that compensation is related to the water saved by composting. However, even though the chloroform extraction has this compensation effect, it is the biggest contribution to the environmental impact of the whole lignin value chain, and it would be necessary to find alternatives to reduce its impact.

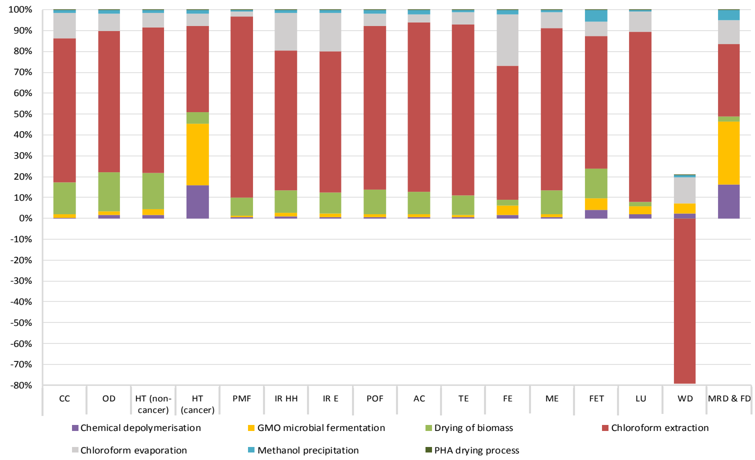

Figure 6. LCIA results. PHA production from lignin valorisation

Conclusions

A life cycle assessment (LCA) of novel hemicellulose and lignin pilot-scale valorisation processes into high-added value products has been developed. As can be drawn from the above-mentioned results, novel strategies on bioprocesses for both hemicellulose and lignin at pilot scale require of further refinement, and the LCA methodology is suitable to detect where there is room for improvement.

Acknowledgements

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Bioforever project for the conversion of woody biomass to chemicals

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BIOFOREVER (BIO-based products from FORestry via Economically Viable European Routes) – a consortium of 14 European companies – using EU funding under the Horizon 2020 program - aims at the conversion of woody biomass to value adding chemical building blocks (www.bioforever.eu).

The demonstration project started in September 2016 and will run for 3 years. Woody biomass, including spruce, poplar and waste wood A and B will be converted to (hemi-) cellulosic sugars, nano-cellulose and lignin and further converted to enzymes and chemicals such as butanol, 2,5 - furandicarboxylic acid and resin acids on pre-industrial scale. Typically, the BIOFOREVER bio-refinery will be projected in logistic hubs such as the Port of Rotterdam or other European ports.

DSM and BPF are customizing dilute acid pre-treatment and enzyme hydrolysis for maximum sugar output from these woody sources via a concerted work-flow, at scales ranging from high throughput millilitre scale pre-treatment and hydrolysis, through bench scale (~10 kg/ day) towards pilot scale demonstration (~1 ton/day). In analogy to BPF, API, Borregaard and Avantium are also customizing wood pre-treatment towards cellulosic sugars, based on different technologies.

Furthermore the cellulosic sugars obtained are being tested by DSM for the fermentative production of an (hemi) cellulytic enzyme cocktail. For testing of the fermentation capacity of the cellulosic sugars, millilitre scale fermentation screening for growth is performed, followed by 50-500 ml scale fed-batch fermentations, which are compared to references fed with 1G glucose syrup. Ideally enzymes will be made “on-site” of the envisaged BIOFOREVER bio-refinery and from lignocellulosic sugars, representing a true circularity.

Most desirable combinations of feedstock – dilute acid pre-treatment conditions – enzymatic hydrolysis – sugar fermentability are selected via design of experiments (DoE) coupled to mechanistic modelling and techno-economic modelling. Results of the feedstock screening will be presented. So far woody hydrolysates have shown to be promising feedstock for the production of (hemi) cellulytic enzymes.

Techno - economic evaluation of biofuel production from black liquor by hydrothermal liquefaction

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Kraft black liquor, a side product of pulp and paper industry, is available in huge amounts at pulp mills in northern countries. Conversion of black liquor into transportation fuel via hydrothermal liquefaction is a promising pathway, which has been demonstrated in the laboratory scale in the LIGNOHTL project (2013-17)[1]. In this poster presentation, the techno-economic performance estimate of biocrude production from black liquor based on the measured laboratory scale yields is presented and the importance of different variables on the profitability is illustrated. According to the results, the cost of transportation fuels production from black liquor is roughly 1000 €/ton with mature production technology hence similar range than i.e. for Fischer-Tropsch or Methanol to Gasoline routes from lignocellulosic biomass. However, both the production technology and the profitability could be significantly improved if the organic losses particularly in the washing of the HTL crude product are reduced. Because the process has only been demonstrated in laboratory scale, the assumptions behind the techno-economic analysis particularly product yields should be verified in bigger scale and in continuous reactors.

Introduction

The fundamental objective of the HTL (Hydro Thermal Liquefaction) process is to convert a wet feedstock into biocrude, an oil-like product. Although the biocrude from HTL also has potential applications as a fuel oil, its further upgrading into transportation fuels is to be the most preferable goal. The advantages of using black liquor are that it is available in huge amount and it already contains sodium hydroxide that catalyses the hydrothermal liquefaction reaction, and it is easier to pump towards a high pressure than fully solid biomass. In addition, by-products such as water phase can be treated in the chemical recycle of the pulp mill as long as additional sulphur intake can be handled. A challenge of the process is that, more expensive materials in process equipment such as Hastelloy are needed, at typical operating conditions near the critical point of water. Also additional sulphur originating from washing of the HTL crude with sulphuric acid, might increase sodium losses in the pulp mill.

In this study, the production chain shown in Figure 1 was considered. Here black liquor was converted by HTL into biocrude, which was further washed with sulphuric acid to reduce its alkali content so that it could further be catalytically hydro deoxygenated (HDO) and co-refined with vacuum gasoil into transportation fuel using existing oil refinery process Fluid Catalytic Cracking (FCC) unit. Here the objective was to study the techno-economic performance of the production pathway from feedstock to upgraded product, which is available in the open literature for wood and some other feedstocks, but not for black liquor.

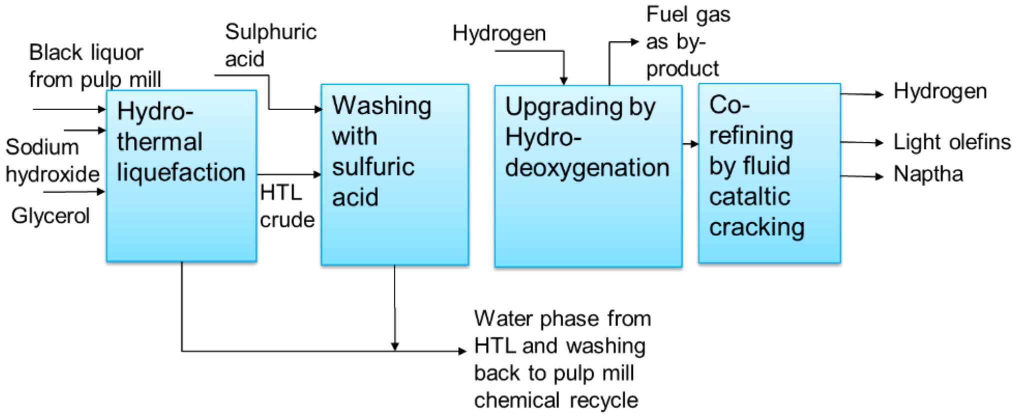
Black liquor from pulp mill
Sodium hydroxide
Glycerol
Sulphuric acid
Hydro-thermal liquefaction
HTL crude
Washing with sulfuric acid
Hydrogen
Upgrading by Hydro-deoxygenation
Fuel gas as by-product
Co-refining by fluid cataltic cracking
Hydrogen
Light olefins
Naptha
Water phase from HTL and washing back to pulp mill chemical recycle

Figure 1. Block diagram of the studied production process

The techno-economic analysis (TEA) was calculated with the technical parameters shown in Table 1 and economic parameters shown in Table 2.

Experimental

The techno-economic feasibility of the case was evaluated where 50 % of black liquor from a typical pulp mill with the capacity of 600,000 t/a of air-dried pulp production was treated in HTL process according to the technical parameters shown in Table 1. The aqueous phase from the HTL process was sent back to the chemical recycle. The yields for the HTL, HDO and co-refining processes are based on laboratory experiments. The prices of products (Table 2) have been considered according to typical market prices and the energy value of the product they could substitute. The investment cost for HTL was estimated based on the reported cost by PNNL (Pacific Northwest National Laboratories) for a HTL plant, recalculating the investment cost for the plant scale considered here with a capacity exponent of 0.6[2].

Table 1. The technical parameters used in the calculations

Technical Parameters	Value	Unit
Kraft pulp capacity	600000	Air dried ton (ADt) pulp per annum
BL solids per ADT pulp	1.8	ton/ton
BL fraction to HTL	50	%
Charge of BL solids	12	% NaOH
Charge of BL solids	50	% Glycerol
Washing acid used	100	kg H2SO4 /t HTL Crude
Residual oxygen after HDO	4.1	wt.%
Washed HTL crude energy yield	53	wt.%
HTL crude Heating value	34	MJ/kg
HTL crude oxygen content	16	wt.%
HTL crude carbon content	67	wt.%
Mass yield in HDO to liquid product	80	wt.%
Mass yield in HDO to fuel gas	20	wt.%
Mass yield of rest coke etc.	0	wt.%

Technical Parameters	Value	Unit
Light olefins mass yield in the FCC step	40	wt.%
Naptha mass yield in the FCC step	43	wt.%
Hydrogen mass yield in the FCC step	0.6	wt.%
CO+CO_2 gas mass yield in the FCC step	2	wt.%
Coke mass yield in the FCC step	5	wt.%

Table 2. The economic parameters used in the calculations

HTL water phase value	14	eur/MWh
Black liquor value	14	eur /MWh
Fuel gas (side product value)	60	eur MWh
Hydrogen price	3000	eur per ton
Light olefins	1300	eur per ton
Naphtha	800	eur per ton
Coke	0	eur per ton
Estimated HTL and further upgrading plant cost	290	MEUR
Annuity factor	10	%
Maintenance cost	5	% of investment cost annually

Results and discussion

With the prices calculated according to Table 2, the profitability of the process was close to 0 MEUR per year as seen in Figure 2. The bigger is the difference in the annual profit when a variable is changed 30 %, the more impact the corresponding variable has on the profitability of the process. It could be observed that the yield of washed HTL crude oil, value of the olefin products and CAPEX effected most on the profitability. On the opposite, the hydrogen needed had least influence due to the relatively small amount of hydrogen needed. In addition, the fuel gas value from HDO and the HTL aqueous phase had a minor influence on the profitability.

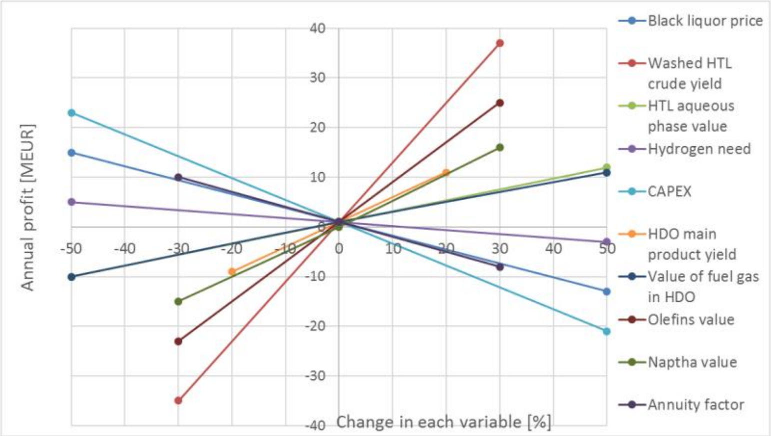

Figure 2 Sensitivity analysis showing annual profit versus change in each variable

Conclusions

The production cost transportation fuels by the process was around 1000 € /ton which is in similar range as earlier calculated for Fischer-Tropsch and Methanol to Gasoline routes [3]. However reducing the losses particularly in washing of HTL crude product and utilising the water phase could significantly improve the profitability. The concept was calculated based on the experimental data generated in the project. However due to the early stage of the studied process concept (TRL 4), it is difficult to estimate accurately the techno-economic feasibility at this stage. Product yields should be optimised and demonstrated applying continuous operation and long term performance of catalysts should also be demonstrated.

Acknowledgements

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Characterization of hemicelluloses extracted from mixed hardwood chips by an autohydrolysis. Effect of enzymatic post - treatments

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Hemicelluloses which make up 30% of wood composition are of great interest because they are made of polysaccharides that can be used to produce platform chemicals. Those saccharides can be derived in numerous different biobased value-added products fulfilling numerous functions, some of them being equivalent to those of petrol-based products such as chemicals, biofuels and biomaterials.

Hemicelluloses as such cannot be exploited. They first need to be extracted from wood chips generally by hot water extraction. In the case where monomeric sugars are looked for, a depolymerization treatment must be applied to convert them from polysaccharides or oligosaccharides to monosaccharides.

In this study, the degree of polymerization of hemicelluloses as well as their side-groups were compared in autohydrolysates obtained under different autohydrolysis conditions. Post-treatments of the autohydrolysates with enzymes were done to tune the size and structure of hemicelluloses. To investigate the effects of these different treatments, Matrix- Assisted Laser Desorption/Ionisation – Time of Flight (MALDI-ToF) analysis was performed.

Experimental and economical case study: Competitive odor - free lignin from an aquasolv biorefinery

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A Liquid Hot Water (LHW) biorefinery concept focusing on the production of lignin from non-woody lignocellulose was developed at the TUHH. Results from the cosortial project "Biorefinery 2021" are represented in this work. In a process cascade based on high pressure, hot water and enzymatic hydrolysis, hemicellulose and cellulose sugars are removed from the substrate to leave a near-natural high molecular weight lignin fraction, which is not cytotoxic and possesses several proven bioactive properties. Lignin powder formulations are developed according to the applications requirements from industry and academia.

Introduction

Lignin and carbohydrates from non-edible biomass are promising and widely abundant raw materials for the production of platform chemical for the substitution of fossil carbon in the chemical industry. Effective disintegration and separation technologies are needed to provide material streams that can be further processed into valuable goods. The biorefinery concept under investigation works on the basis of organic solvent-free and acid-free pretreatment. The model substrate is wheat straw, but further annual lignocelluloses have been tested successfully.

An interdisciplinary consortium, consisting of three academic institutions and three SME's jointly worked within three phases of the project "Biorefinery2021" towards the process and product development, namely purification of the sugar streams, synthesis of levulinic acid, lignin formulation, lignin compounding, reactor modelling, lignin aerogel production, plant design and economic evaluation.

The Aquasolv Process

The developed technology is a substrate and product tailored cascade of hydrolysis and extraction processes, that only uses water, enzymes and carbon dioxide as processing agent, see Figure 1.

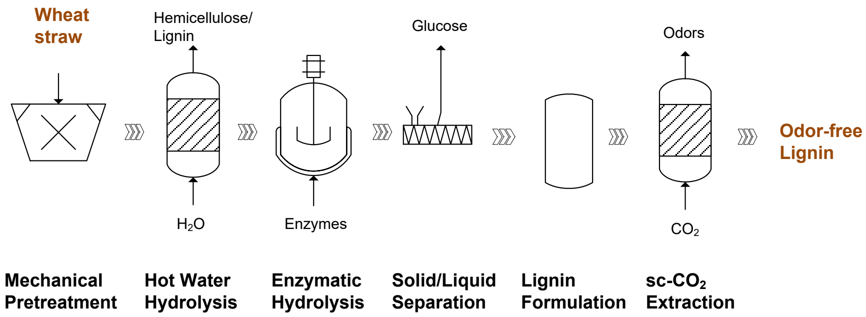

Figure 1. Aquasolv biorefinery cascade under investigation, TUHH facilities
Hydrolysis fixed bed : volume 40 L

The process agents are environmentally friendly and their adaptable properties at high temperatures and pressures are exploited. First, the substrate is pelletized, which reduces the size of the primary particles and increases the bulk density significantly, thus allowing a high reactor loading of the consequent unit. The LHW is performed in a fixed bed reactor, operated at 200°C, 40 bar and 35 minutes residence time. The hemicellulose sugars are separated and obtained in a liquid hydrolysate form, with a conversion of larger than 90 mass percent and a minor lignin rich fine particle fraction. The remaining solids are treated via enzymatic hydrolysis at 50°C and pH 5 for 48 h, converting cellulose to soluble glucose which are removed afterwards to obtain the solid lignin fraction. The lignin powder can be deodorized using supercritical carbon dioxide extraction[1] [1].

Odor-free Lignin

A high-quality product was achieved with following mass fractions: Klason-lignin 88.3 %, acid-soluble lignin 1.7 % and residual sugars 4.3 %. The powder possesses a large molecular weight and is thermally stable. The particle size can be adapted between 15 - 150 µm, depending on the lignin formulation process parameters. The lignin powder, which is produced with a yield of 30 wt%, is free flowing and possesses a Hausner ratio of 1.2.

Table 1. TUHH aquasolv solid lignin properties

Free phenolic groups	1.84	mmol/g
Radical Scavenging Capacity against DPPH	76	RSA%
Moisture content	5	wt%
Surface energy	87	mN/m

Techno-Economic evaluation

For a scale-up to a throughput of 30,000 t/a wheat straw[2], a hot water hydrolysis unit was integrated into a lignin-biorefinery plant design, also considering different hydrolysate stream valorization strategies. The hot water hydrolysis process modes like flow through or partial circulation, and parameter variations in a fixed-bed reactor were tested and optimized using a flow sheet simulation. The economic evaluations found the Minimum Lignin Selling Price (MLSP) to be competitive in regard to other technical lignins as well as to polymers, which were used for compounding with AS-lignin, nevertheless depending on the hydrolysate stream valorization. In **Error! Reference source not found.** a comparison of common polymer and lignin prices are made.

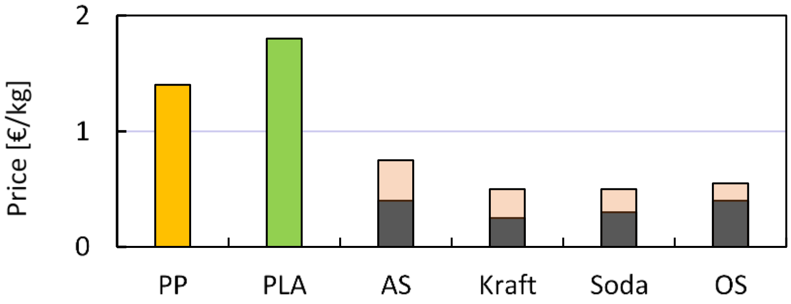

Figure 2. Prices of polymers and technical lignin, for lignin types upper and lower limits are indicated. PP: polypropylene, PLA: Poly lactic acid (technical grade), AS: aquasolv lignin, AS Acet.: acetylated AS lignin, Kraft: kraft-lignin, Soda: soda-lignin, OS: organosolv lignin

Outlook

A consortium from academia and industry will continue the research focusing on the valorization of sugar-rich side streams from the same lignin production chain. The separation of oligomeric polysaccharides from the complex media, biogas production from the remains and the biotechnological conversion to lactic acid (LA) and propionic acid (PA) will be investigated. The support of the Federal Ministry of Education and Research (BMBF), ref. 031B0091 and ref. 031B0660 is gratefully acknowledged.

The BioMP

BioMP, a competence center at Hamburg University of Technology (TUHH) is using the know-how and technology to advance the lignin applications for commercial use. BioMP is looking for partners for new lignin applications and investors to scale-up the production facilities.

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Chlorine dioxide stage at near-neutral pH for AOX reduction

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Chlorine dioxide (ClO_2) is a commonly used bleaching agent in kraft pulp production. Depending on the pH during the ClO_2 bleaching (D stage), either delignification or brightening reactions are favored. When ClO_2 reacts with the pulp acids are formed, resulting in a rapid decrease of the pH. A low ending pH (below 3) results in significant formation of hypochlorous acid (HOCl) and elemental chlorine (Cl_2). HOCl and Cl_2 are most responsible for the formation of adsorbable organically bound halogens (AOX), which can negatively affect the environment. A high starting pH (above 10) causes the formation of hypochlorite ion (ClO^-), a non-selective bleaching agent, and chlorate ion (ClO_3^-), which consumes ClO_2. Due to the problems connected with extreme pH levels, it has been proposed that ClO_2 bleaching should be performed at near-neutral pH.[1,2,3]. To control the ending pH of a D stage, many mills today use NaOH and/or H_2SO_4. For near-neutral D stage applications, this pH controlling method would not be suitable, since the starting pH would have to be quite high in order to end the stage at neutral pH. Therefore, the use of a pH buffer has been considered as an alternative pH controlling method.

This work examines the effect of a pH buffer on the AOX formation in a well-defined intermediate D stage. Carbon dioxide was added to the pulp in the form of dry ice, generating a bicarbonate buffer system in situ, and thus stabilizing the pH at 6.5 before chlorine dioxide addition. The stabilization of the ending pH around near-neutral is hypothesized to decrease the formation of strongly chlorinating species, such as Cl_2 and HOCl, so that the AOX formation is reduced. A fixed chlorine dioxide charge of 3.8 kg/ton dry pulp was used. The standard methods were used to determine pulp kappa number, viscosity and ISO brightness. The fiber charge and chemical structure, before and after D stage, were determined by conductometric titration and FTIR spectroscopy.

Obtained results show that an addition of 10 and 30 kg CO_2/ton dry pulp reduced the AOX content of the D stage filtrate with 55 and 75 %, correspondently. Such reductions could be related to variations of the pH profile, which in turn is related to the fiber charge. There were no significant differences in the ISO brightness, kappa number and pulp viscosity for the bleached pulp samples.

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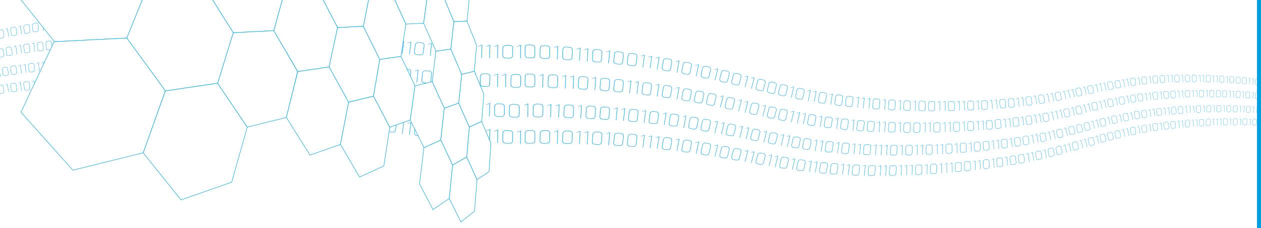

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