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BIOREFINERY CONCEPT BASED ON GAMMA-VALEROLACTONE/WATER FRACTIONATION

Huy Quang Le*¹, Yibo Ma¹, Marc Borrega¹, Herbert Sixta¹.

¹ Aalto University, Department of Forest Products Technology, Vuorimiehentie 1, 02150 Espoo, Finland

ABSTRACT

This work describes a novel biorefinery concept based on the fractionation of woody biomass in a γ -valerolactone (GVL)/H₂O binary mixture. *Eucalyptus Globulus* wood can be effectively fractionated in a single step into its principal components without the addition of any catalyst or additives. The pulp fraction, characterized by high yield, high cellulose purity and high bleachability, can be directly spun to produce regenerated cellulose fibers. The spent liquor, rich in lignin, carbohydrates, furans and organic acids, may be a source for chemical and energy production.

KEYWORDS

Biorefinery, dissolving pulp, eucalyptus, gamma-valerolactone, organosolv fractionation.

INTRODUCTION

Nowadays, the production of materials, chemicals and energy, which continuously grows due to human needs, is almost exclusively dependent on the refining of oil. The insecurity and availability issues of fossil resources stimulates the research for alternative refinery processes employing renewable resources. Forest biomass consists of valuable biopolymers that can be refined into the above-mentioned products. Biorefinery, in which biomass is employed as renewable resource, emerges as basis for a sustainable bio-economy.

Kraft pulping has been the dominant chemical pulping process since the early 1930s. Kraft-based pulp mills can be upgraded to biorefineries [1], however, the kraft mills in temperate-climate regions are currently facing economic challenges due to the rise of new producers in sub-tropical and tropical regions [2]. Therefore, the need to develop innovative processes aiming at high value-added products and full utilization of raw material is crucial for increasing the competitiveness of the forest industry, especially in temperate-climate regions like Finland.

Recently it has been shown that birch sawdust, when treated at elevated temperature in a binary mixture of GVL and water, can be fractionated into its principal components: cellulose, hemicellulose and lignin [3]. Here, we suggest a biorefinery concept based on GVL/H₂O fractionation of Eucalyptus wood chips to fully utilize the biomass components: the cellulose fraction is targeted to be processed as dissolving pulp, the hemicelluloses fraction is targeted to be upgraded to furanic platform chemicals and to GVL, and the lignin fraction is targeted to be used as fuel or upgraded to value-added products.

EXPERIMENTAL

Eucalyptus globulus wood was fractionated in a binary mixture of GVL/H₂O. No catalyst or additives were added. Small scale trials with sawdust (particle size < 125 μ m) were conducted in 30mL vials heated in a microwave reactor (Anton Paar Monowave 300). Reaction temperature, time and liquor-to-wood (L:W) ratio were 180°C, 120 minutes and 10 L/kg, respectively. The GVL content in the fractionation liquor ranged from 0 – 98 wt%. The fractionation of wood chips was done in 225 mL bombs heated in a silicon oil-bath reactor (Haato-tuote 43427). The reaction temperature and L:W ratio were 180°C and 10 L/kg, respectively, the GVL content in the liquor was 50 and 60 wt%, and the fractionation time (retention time at 180°C) ranged from 60 to 180 minutes. For wood chips, an impregnation time of 60 minutes at 120°C was employed.

For each fractionation trial, the pulp was separated from the spent liquor by filtration, followed by washing. Yield was determined gravimetrically, and the pulp was analyzed for carbohydrate and lignin content, molar mass distribution (by Gel Permeation Chromatography) and intrinsic viscosity (only for pulps produced from wood chips). Spent liquor was analyzed for carbohydrate and dissolved lignin content. Washing liquid was analyzed for dissolved lignin content.

A short Elemental-Chlorine-Free (ECF) sequence was used to bleach a selected pulp sample produced from wood chips. The bleaching conditions are:

- D₀: 50°C, 60 minutes, 10% consistency, 0.25 Kappa factor
- E_p: 70°C, 60 minutes, 10% consistency, 1.5% NaOH, 0.5% peroxide
- P: 70°C, 120 minutes, 10% consistency, 0.6% NaOH, 0.5% peroxide

Selected bleached and unbleached pulps produced from wood chips were spun to regenerated cellulose fibers by the IONCELL-F spinning process [4]. Lignin was precipitated from spent liquor by addition of water, and the suspension was centrifuged at relative centrifugal force 3000g in 30 minutes for lignin collection.

RESULTS AND DISCUSSION

Eucalyptus Wood Fractionation

Small scale fractionation trials using sawdust were first conducted to determine the optimum GVL/H₂O ratio for delignification. The behavior of the wood main components, namely cellulose, hemicelluloses and lignin, in GVL/H₂O fractionation is summarized in Figure 1.

The results indicate that the cellulose fraction was recovered quantitatively at any GVL/H₂O content, while delignification reached a maximum when fractionation liquor contained about 50 – 60 wt% GVL. Hemicellulose removal increased with increasing the water content due to enhanced hydrolytic degradation. These results are in agreement with those reported by Fang and Sixta for the fractionation of birch wood meal [3].

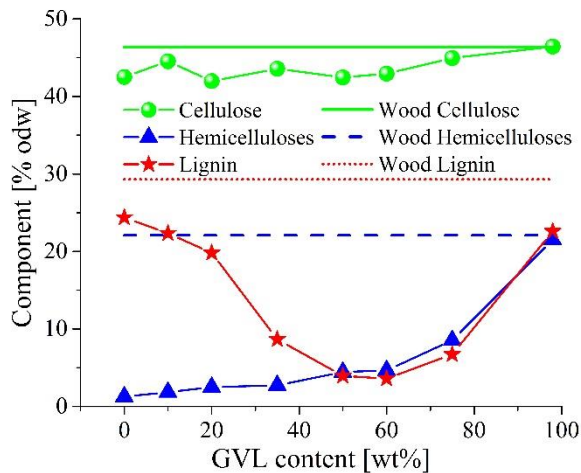


Figure 1. Effect of GVL content in fractionation liquor on the separation of eucalyptus sawdust main components. (odw: oven-dried wood).

The potential of GVL/H₂O fractionation in dissolving pulp manufacturing was investigated by fractionating wood chips in GVL/H₂O mixtures containing 50 and 60 wt% GVL. The removal of wood components and the viscosity of the pulps along the course of fractionation in 50 wt% GVL are shown in Figure 2. Wood defibrillation took place in the early stages of fractionation, with almost no rejects detected after 60 minutes of reaction. Extending the reaction time beyond 60 min slightly increased the removal of wood components, but the intrinsic viscosity decreased considerably.

In all cases, wood chips were effectively converted into pulps with high cellulose yield and purity. Delignification was more selective in wood chips than in sawdust, probably because of an additional washing stage with 50 wt% GVL solution in the case of chips, which further improved the removal of lignin from the pulp.

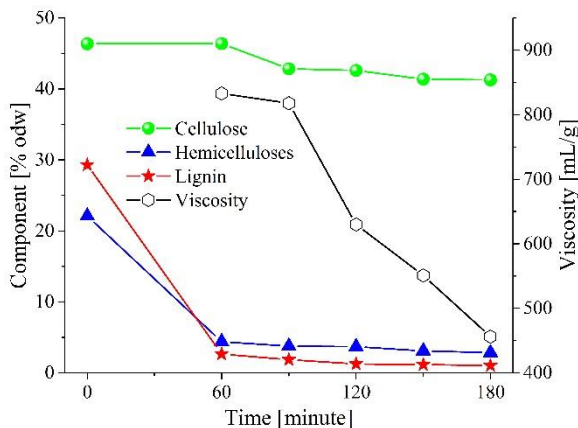


Figure 2. Effect of time on wood component removal during fractionation with 50 wt% GVL liquor in oil-bath reactor. (odw: oven-dried wood).

In comparison to fractionation with 60 wt% GVL liquor, using 50 wt% GVL liquor gave slight advantage on delignification and hemicellulose removal, at the expense of pulp viscosity.

Valorization of Pulp Fraction

The pulps produced after 150 and 180 minutes treatment in 50 wt% GVL/H₂O were selected for conversion into regenerated cellulose fibers. These pulps were spun using the IONCELL-F process [4], a dry-jet wet spinning process utilizing ionic liquids to dissolve the pulp for creating the spinning dope. The pulp produced after 180 minutes of fractionation (92.5% cellulose, 5.2% hemicellulose and viscosity 456 mL/g) was spun directly without bleaching. The pulp produced after 150 min fractionation time was bleached with a short ECF sequence prior to spinning (bleached pulp composition: 94.5% cellulose, 4.8% hemicelluloses and viscosity 470 mL/g). Similar to pulps produced by other acidic process, the GVL/H₂O pulps do not contain hexenuronic acid (HexA), and thus their bleachability was high (only a short ECF sequence of D₀-Ep-P required to reach viscose-grade). As can be seen from Figure 3, the molecular mass distribution of GVL/H₂O pulps closely resembles that of a commercial bleached hardwood dissolving pulp.

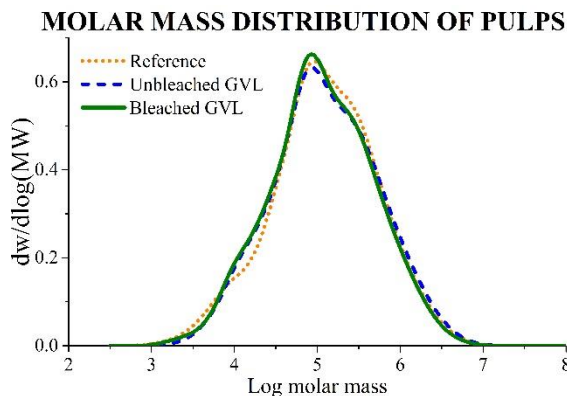


Figure 3. Molar mass distribution of unbleached and bleached GVL/H₂O pulps, in comparison with a commercial acid sulfite hardwood dissolving pulp (reference pulp). (dw/dlog(MW): differential mass fraction).

The mechanical properties of both unbleached and bleached regenerated fibers were comparable to other man-made cellulose fibers currently available in the market (Table 1).

Table 1. Comparison of IONCELL-F fibers produced from GVL/H₂O pulp with hardwood sulfite commercial fiber (reference fiber). Tenacity and elongation are determined at standard condition. (U-GVL: unbleached GVL/H₂O pulp; B-GVL: bleached GVL/H₂O pulp; ϵ : elongation).

Fibers	Titer dtex	Tenacity cN/tex	ϵ %	E-modulus GPa
U-GVL	1.3	41.3	8.2	18.3
B-GVL	1.3	43.0	9.5	21.4
Reference	1.2	40.1	8.7	20.6

Valorization of Spent Liquor

Most of the lignin in the chips was dissolved into the spent liquor, with some small amounts dissolved in the washing liquid after fractionation. By addition of water to spent liquor, more than 60% lignin readily precipitated. The mass balances for lignin for the 150 and 180 min fractionation trials in 50% GVL/ H₂O is given in Table 1. Lignin from the GVL/H₂O fractionation process is sulfur-free, and thus is a promising material for a wide range of applications. Valorization pathways of GVL/H₂O lignin is under investigation.

In addition to lignin, the spent liquor also contained extracted carbohydrates and their degradation products. Most of the hemicelluloses were extracted during the first hour of fractionation, and as time elapsed, the carbohydrates underwent degradation reactions to furans (furfural, hydroxymethylfurfural) and organic acids (formic acid, acetic acid and levulinic acid). The increase in furans content and quite stable organic acids content in spent liquor along the fractionation are in line with previous finding that GVL/H₂O system suppresses furan degradation, [5]. Furthermore, GVL can be catalytically synthesized from hexoses extracted from raw material, [6], which compensates for possible GVL loss during the process.

CONCLUSION

GVL/H₂O mixtures enable a quantitative and selective fractionation of all lignocellulosic components in just one single step, with a solid cellulose fraction that can be directly used as dissolving-grade pulp, and a liquid fraction that contains the extracted sugars and lignin which can be further processed to valuable chemical and energy. Furthermore, the process is sulfur-free and the high pulp bleachability offers the possibility for a Total-Chlorine-Free bleaching, thus making the process environmentally friendly. Altogether, our process fulfills the requirements of a modern biorefinery.

It is believed that no single bio-based process can match the wide product portfolio currently offered by the oil industry. Therefore, oil-refineries can only be replaced by a combination of different biorefineries types. This fractionation process would be one of the viable options when refining biomass to valuable products. The small-to-medium size of a typical organosolv biorefinery, together with the highly valued products we offer (textile fibers, platform chemicals), would reduce investment risk and pay-back time. More research is needed to fully exploit the potential of GVL/water biorefinery. The results obtained so far let us believe that this biorefinery concept could support the differentiation and the competitiveness of Finnish forest industry.

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