Özdenkçi, Karhan; De Blasio, Cataldo; Muddassar, Hassan R.; Melin, Kristian; Oinas, Pekka; Koskinen, Jukka; Sarwar, Golam; Järvinen, Mika

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A Novel Biorefinery Integration Concept for Lignocellulosic Biomass

Karhan Özdenkçi*
Department of Chemical and Metallurgical Engineering
Aalto University, Espoo, Finland
e–mail: karhan.ozdenkci@aalto.fi

Cataldo De Blasio
Department of Mechanical Engineering
Aalto University, Espoo, Finland
e–mail: cataldo.de.blasio@aalto.fi

Hassan R. Muddassar
Department of Chemical and Metallurgical Engineering
Aalto University, Espoo, Finland
e–mail: raja.hassan@aalto.fi

Kristian Melin
VTT, Technical Research Center of Finland
e–mail: kristian.melin@aalto.fi

Pekka Oinas, Jukka Koskinen, Golam Sarwar
Department of Chemical and Metallurgical Engineering
Aalto University, Espoo, Finland
e–mail: pekka.oinas@aalto.fi

Mika Järvinen
Department of Mechanical Engineering
Aalto University, Espoo, Finland
e–mail: mika.jarvinen@aalto.fi

ABSTRACT

The concept of an integrated biorefinery has increasing importance regarding sustainability aspects. However, the typical concepts have techno-economic issues: limited replacement in co-processing with fossil sources and high investment costs in integration to a specific plant. These issues have directed the current investigations to supply-chain network systems. On the other hand, these studies have the scope of a specific product and/or a feedstock type. This paper proposes a novel biorefinery concept for lignocellulosic biomass: sectoral integration network and a new hydrothermal process for biomass conversion. The sectoral integration concept has the potential for sustainable production from biomass: pre-treatment at the biomass sites, regional distributed conversion of biomass from various sectors (e.g. black liquor, sawdust, straw) and centralized upgrading/separation of crude biofuels. On the other hand, the conversion processes compose the vital part of such a concept. The new conversion involves partial wet oxidation - or simultaneous dissolution with partial wet oxidation for solid biomass-followed by lignin recovery with acidification and a reactor that can perform either hydrothermal liquefaction or supercritical water gasification. The process can intake both liquid and solid biomass to produce lignin as biomaterial and syngas or bio-oil. The new concept can contribute social development of rural areas by utilizing waste as valuable raw material for the production of multiple products and reduce the net greenhouse gas emissions by replacing fossil-based production.

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* Corresponding author

KEYWORDS

Supercritical water gasification, partial wet oxidation, hydrothermal liquefaction, biomass, integrated biorefinery, supply-chain network

INTRODUCTION

Sustainability aspects have driven the industry to renewable sources for energy and chemical production. Fossil fuel has the sustainability issues of depletion, carbon emission and other environmental impacts. Therefore, the current need of industrial production includes replacement of fossil fuels with renewable sources and accordingly process development. Regarding raw material, biomass presents promising potential for this purpose [1]. Especially, lignocellulosic biomass is the most abundant renewable source in the nature.

Biorefinery is classified as 1st generation (dedicated edible crops) and 2nd generation (non-edible feedstocks or side streams) with respect to the feedstock [1]. The 1st generation biorefinery provides close-to-uniform feedstock and conversion through inexpensive, simple processes. Two examples include biodiesel production from vegetable oils and bioethanol production from energy crops (such as sugar cane, corn and wheat). On the other hand, this approach compromises the needs of food production, water and land usage. Therefore, the emission calculations give much less carbon reduction or even negative (i.e. increase in carbon emission) with respect to fossil-based production when the aspects of plant growth are also counted, such as harvesting, machinery, fertilizers and distribution. Furthermore, the agricultural crops are available in certain seasons and spontaneous degradation can be an issue in case of long-time storage. As a result, it is evidently unsustainable to replace fossil fuels with 1st generation biofuels. In contrast, the 2nd generation biorefinery utilizes non-edible feedstocks (e.g. wood, grass or non-edible crops) and side or waste streams (e.g. black liquor, straw, bark, saw dust). Consequently, the 2nd generation biorefinery has the potential for sustainable production of energy and chemicals. This approach includes more advanced processes, enabling more value-added products. However, the 2nd generation biorefinery has techno-economic issues: variety in feedstock, high costs of advanced processes and other operational concerns in each process type.

The typical approaches to 2nd generation biomass utilization include co-processing with fossil-based sources and biorefinery integration to a specific plant. As an example for the co-processing approach, wood pellets or torrefied wood pellets are blended with coal as the feed of boilers in combined heat and power (CHP) plants [2]. However, this approach provides limited replacement of fossil source with biomass: around 10 % (by energy outcome) replacement without modifying the units. Full replacement or high ratio of biomass will require a secure biomass supply in high amounts and costly modifications in the process units. Integration to a specific plant involves inserting a biorefinery process utilizing the side/waste stream of the plant. This approach provides advantages in heat integration, infrastructure and raw material costs. For instance, in the wood industry, the current trend is to convert pulp mills into integrated biorefinery plants due to decreasing demand on paper. A recent development is integration of lignin recovery by acidification to pulp mills which utilizes part of the black liquor and recycle the residual liquid to the recovery boiler. When pH of black liquor is reduced to around 9-10 by carbon dioxide treatment, lignin precipitates and is recovered through filtration, namely LignoBoost process [3]. An improvement to this process involves partial wet oxidation prior to the acidification step in order to enhance the filtration step and to obtain sulphur-free lignin, namely LignoForce process [4]. However, it might be too costly to integrate a process with the complete chemical conversion and separation to a specific plant. For instance, black liquor gasification is another example investigated for either biofuel or energy production [5]. The integrated process includes gasification reactor, gas cleaning, and further reactors and separators together with upgrading units in case of chemical production or turbines in case of energy production. In addition, the recovery of cooking chemicals is an important aspect to address for integration. Kraft mills use sodium sulphide (Na_2S) and sodium hydroxide (NaOH) for cooking. However, sulphur is converted to hydrogen sulphide (H_2S) gas in gasification, thus requiring additional recovery operation. To sum up, each approach has some issues and the techno-economic aspects need improvements.

The future target of biomass processing would be sustainable production from biomass without the need of fossil fuels, considering the depletion of fossil fuels and biomass being renewable. For instance, co-processing biomass with fossil-based fuel can only be a short- or middle-term transition solution. Therefore, the current investigations have been directed towards the whole supply-chain network of biomass-to-products: the harvesting of biomass, transporting from field to conversion plants, the chemical conversion of biomass and finally transport of the products to the demand sites. In this chain, the chemical conversion is still the heart of the network: introducing the most influence to the optimum configuration of a supply-chain network and performance with respect to sustainability elements (economic feasibility, environmental impacts and social aspects). Therefore, the development of biorefinery concept involves two main subjects: chemical conversion of biomass and the optimization of whole supply-chain network of biomass-to-products. The sustainable biorefinery concept should fulfil the criteria listed below:

- no compromise with critical needs, such as food and animal feed
- maintaining the regeneration of biomass and biodiversity
- minimum environmental impacts
- the ability to adapt the variations in quality and quantity of biomass feedstock
- flexible operation to adapt the changes in market demand
- multi-feed-multi-product conversion processes

This paper proposes a novel biorefinery integration concept for lignocellulosic biomass: sectoral integration network and a new hydrothermal conversion process. The concept of sectoral integration network is developed for utilizing both solid and wet biomass from various sectors (e.g. black liquor, sawdust, straw and other residues from agriculture and forestry), and for flexible operation to adapt changes in market demand. To enable these features, a new hydrothermal conversion process is introduced for the production of lignin and syngas or bio-oil. This paper first discusses the current literature on the supply chain network and technologies for 2nd generation biomass conversion. Then, the novel biorefinery concept is presented including sectoral integration and the new hydrothermal conversion as well as sustainability remarks of the concept.

THE CURRENT STATE-OF-ART IN BIOREFINERY CONCEPT AND PROCESSES

The main steps of biomass processing include collection, pre-treatment, chemical conversion and upgrading/separation of products, and distribution of products. The complete process of 2nd generation biomass-to-product are usually determined to be unfeasible in case of single feedstock and single product, due to many operational steps and high costs of complicated conversion and separation. Therefore, the trend has been directed towards combination of biomass feedstock from several sources and multiple products in order to increase the production capacity and to ensure feed supply of each plant, i.e. supply-chain network. As a result, supply-chain network optimization and biomass conversion are the two main subjects that needs improvements in order to achieve sustainable biorefinery.

The Supply Chain Network

As a wider perspective of integrated biorefinery, the whole supply chain network is investigated from biomass to final products with respect to the elements of sustainability. Supply chain network development involves strategic, tactical and operational decisions and designs for each step of the network. Figure 1 shows the basic scheme of the biomass supply chain network development [6]. The strategical aspects include selections of biomass types, conversion technology, locations and capacities of source and demand sites, locations and capacities of biomass conversion processes as well as performance measures for sustainability evaluation. The tactical aspects include selection of collection and storage methods and planning for transportation and production, in accordance with the strategical decisions. The operational aspects include the implementation of tactical decisions: biomass harvesting at a time period, process control and operation for biomass conversion plants, and storage and transportation of feedstocks and products.

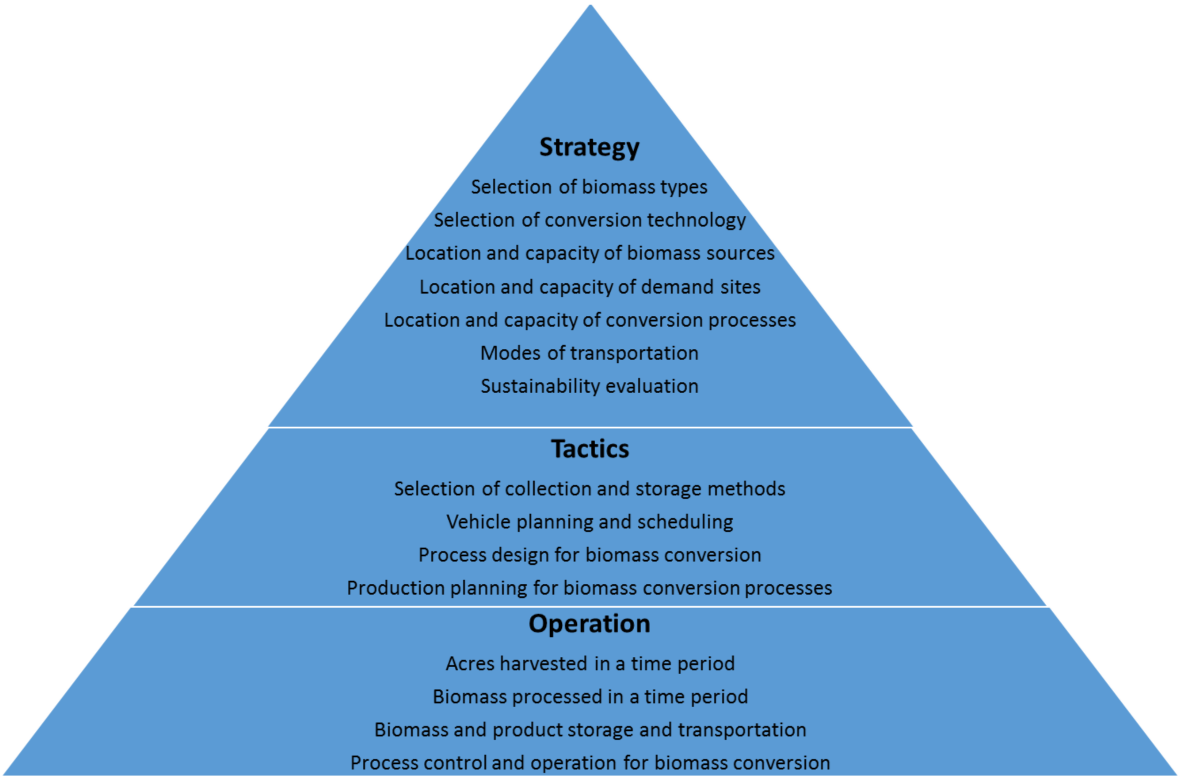

Figure 1. Development of supply chain network for biomass [6]

Supply chain network modelling refers to the optimization model that determines the location and capacities of biomass pre-treatment and conversion processes with respect to the sustainability issues as the objective, on the constraints of the amounts and the locations of biomass sources and product demand sites. These models use the decisions on strategical aspects (biomass type and technology selection, transportation modes and sustainability evaluation) and information from tactical and operational aspects (e.g., product yields of biomass conversion, fuel consumption and costs for transportation, biomass harvesting and storage). Sharma et al. (2013) [7] provided a detailed review of the literature studies on supply chain network modelling with respect to different aspects, such as objective functions, the model types, supply chain structure and biomass and product types. Regarding the objective functions, models can be formulated as single-objective or multi-objective optimization. Single-objective optimization provides ease in development and solution of a model due to less complications and less computational requirement. For instance, Marvin et al. (2012) [8] investigated lignocellulosic biomass-to-ethanol by maximizing the net present value and Kim et al. (2001) [9] modelled liquid fuels from biomass by maximizing the profit as the economical aspect. However, single-objective models can involve only one aspect of sustainability evaluation. The compromise between environmental performance and economic aspect is determined through multi-objective functions in an optimization model. For example, You and Wang (2011) [10] modelled biomass-to-liquid fuel network with respect to multi-objective function covering the minimization of greenhouse gas emissions and the annualized cost. In addition, bioethanol supply chain in the United Kingdom was modelled to minimize the total supply chain cost as single-objective [11] and to minimize the daily cost with the constraint of emission limits as well [12]. Regarding the model types, deterministic models comprises accurate and precise calculations. Mixed-integer linear programs are one of the usual optimization models. As an influential concern, uncertainties are the important part of supply chain networks, such as weather, biomass properties and moisture content, product demand and prices, biomass costs, changes in regulations and policies. The uncertainty aspects were reviewed in detail by Awudu and Zhang (2012) [13]. These aspects are dealt with stochastic models, e.g. Sharma et al. (2013) [14] studied scenario optimization for weather uncertainty in biomass supply chain.

The network structure is classified into two main chain systems: centralized and distributed networks, as shown in Figure 2. Centralized network refers to transporting biomass from all source places and processing to final product in a large-capacity single plant. However, even though this might provide more efficient processing, transport of biomass to processing plant becomes too costly and some biomass types can degrade spontaneously in case of long-time storage. On the other hand, a fully distributed network is not optimum either due to high transportation costs of products to demand sites and high operation costs of small-capacity plants. In this regard, Bowling et al. (2011) [15] proposed the distributed hubs for collection and pre-treatment, and centralized structure for biomass processing to the desired products. As a result, a balanced network provides the optimum production from biomass. However, transportation costs must be reduced further and long storage time can cause deterioration of biomass. These issues can be addressed by an intermediate conversion to increase the energy density of feedstock. Consequently, as further progress in the structure, the recently developed networks consist of pre-treatment and/or conversion to an intermediate compound on each set of biomass sites (i.e. regions) then centralized conversion of these intermediates to the final products, referred to as distributed-centralized network in the literature, as shown in Figure 2. For example, Kim et al. (2011) [9] compared centralized and distributed-centralized structures for gasification followed by Fischer-Tropsch synthesis in the absence or presence of pyrolysis as the intermediate conversion. The optimum result was distributed-centralized network; in addition, the same study showed that distributed-centralized network is more robust to the variations in market demand or prices than centralized network. Similarly, You and Wang (2011) [10] modelled biomass-to-liquid fuel network including biomass conversion and upgrading. The optimum result was distributed-centralized network in that study as well. Furthermore, as a social aspect, distributed-centralized approach contributes to the development of rural areas as well: more industrial production and employment [16]. Therefore, the population would be distributed to both rural and urban areas together with the social services, rather than high accumulation in certain industrial regions.

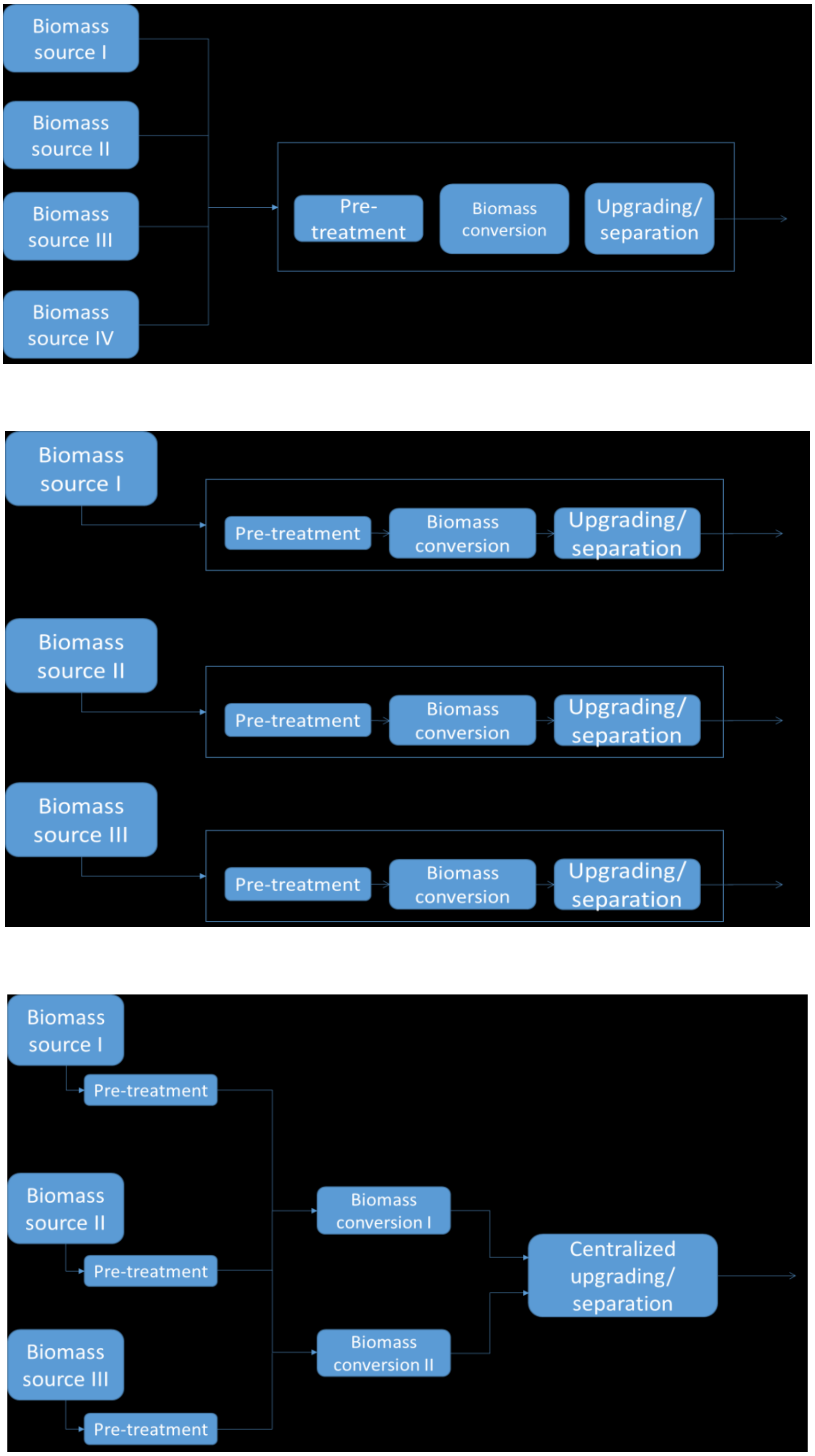

Figure 2. Centralized (top), distributed (middle) and distributed-centralized (bottom) supply chain network structures

However, the current literature on this subject is limited to specified feedstock and/or specified product and process. For instance, Kim et al. (2001) [9] and You and Wang (2011) [10] investigated only pyrolysis followed by gasification of bio-oil and Fischer-Tropsch synthesis. In addition, both studies utilized only solid biomass but not wet biomass. As another example, some studies considered only a single product. Marvin et al. (2012) [8] investigated economic optimization of a supply chain producing ethanol from lignocellulosic biomass. Akgul and Shah (2012) [11] investigated economic optimization of hybrid of 1st and 2nd generation biomass supply chain for ethanol production. Akgul and Shah (2012) [12] included multi-objective model in the hybrid supply chain: economic performance and environmental impact compiled in the objective function. However, ethanol is the only target product in these studies. Overcoming this issue requires biomass conversion processes enabling the production of multi-products and flexible transitions among different process conditions.

Biomass Conversion Processes for 2nd Generation Biomass

The chemical conversion approach and technology are the crucial aspects sharply influencing the techno-economic performance of a supply chain network. Regarding the chemistry, the conversion of lignocellulosic biomass occurs in three main approaches as illustrated in Figure 3: partial degradation followed by upgrading and/or separation, fractionation followed by processing of each fraction, complete decomposition to gas followed by catalytic synthesis. Fractionation usually involves the recovery of one component and the mixture other components as side stream, e.g. pulping process for papermaking. This approach provides uniform inlet for further processing. Partial degradation generates wide spectrum of liquid species, thus requiring upgrading and intensive separation for the final use. Production of bio-oil through pyrolysis or liquefaction is an example of partial degradation; afterwards, an upgrading process improves the fuel properties of bio-oil. The complete decomposition occurs at high temperature with faster reaction kinetics. Then, target products are selectively produced from syngas by adjusting the operating conditions including catalysts, temperature, pressure and residence time. Alternatively, syngas can be combusted in a gas engine to produce energy.

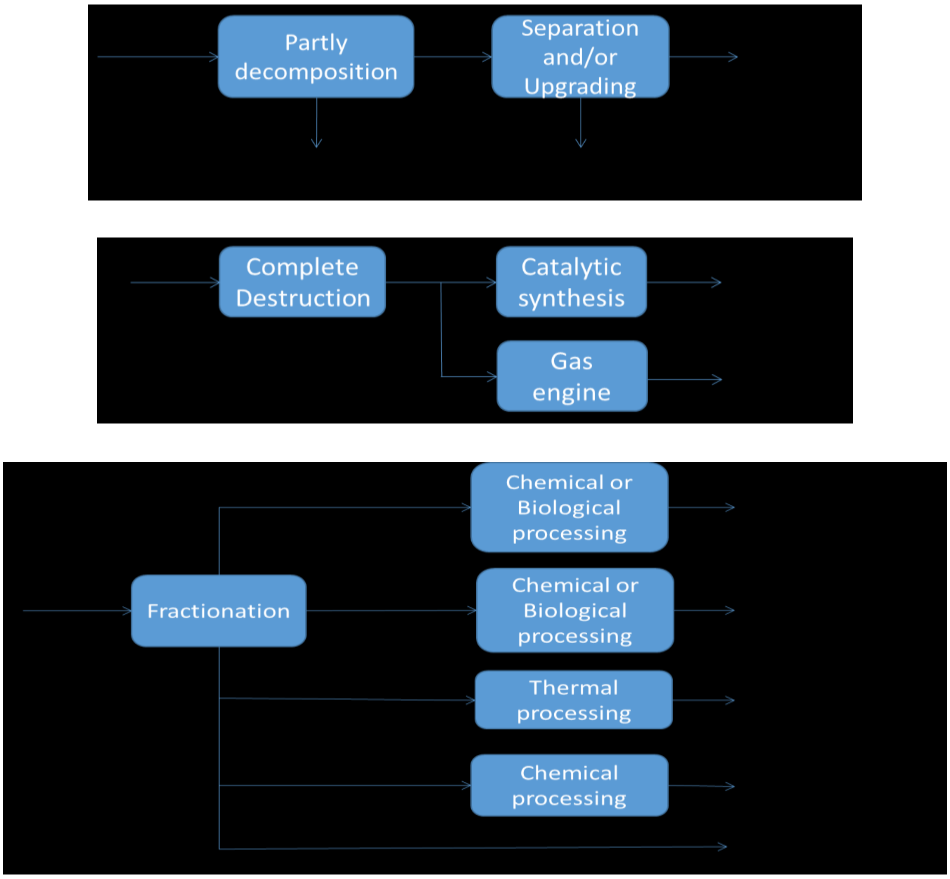

Figure 3. Chemical conversion approaches

The technology options include biological, thermal and hydrothermal conversion processes. The biological conversion uses enzymes or organisms to hydrolyse cellulose and hemicellulose and to ferment the sugar molecules for the production of liquid fuels (such as alcohols) or gases (such as methane). This can provide more purified production compared to thermal and hydrothermal degradation introducing many intermediate compounds. This conversion type has four main approaches [17]: simultaneous saccharification and fermentation (SSF), and separate hydrolysis and fermentation (SHF), simultaneous saccharification and co-fermentation, and consolidated bioprocessing (CBP). However, biological conversions have operational issues which prevent flexibility: very long residence time (days) due to cell culture growth, difficulty in process control, product inhibition in hydrolysis and intermediates inhibiting fermentation, and recovery of cell culture. As a new configuration, simultaneous saccharification, filtration and fermentation (SSFF) process was developed to combine benefits of SSF and SHF. This configuration was compared with SSF in case of wheat straw [18] and wood [19] feedstock. Despite increasing ethanol yields and enabling reuse of cell culture, this configuration has also the general issues of biological conversion which prevent the flexibility. Moreover, fermentation of glucose and hemicellulose sugars require genetically engineered yeast, e.g. as studied by Ishola et al. (2015) [18]. Therefore, this type of process is suitable only for 1st generation lignocellulosic biomass or food waste and require fractionation prior to biological conversion (as in Figure 3). Fractionation can be achieved by alkaline treatment [20] and organosolv treatment with alcohol or acid [21]. On the other hand, perfect fractionation of 2nd generation biomass might be unfeasible due to expensive solvents and solvent recovery operations [17].

Thermal conversion can decompose either partly or completely the biomass by heat treatment. These conversion processes are usually used for solid biomass. For instance, pyrolysis of wood generates char as solid fuel, bio-oil as liquid intermediate and gases including hydrogen and methane [22]. Fast pyrolysis maximizes the liquid yield up to 75 % whereas slow pyrolysis generates more charcoal. Slow pyrolysis occurs at moderate temperature (280-680 °C) with slow heating rate (0.1-10 K/s) and long residence time (450-550 s) whereas fast pyrolysis occurs at higher temperature (580-980 °C) with higher heating rate (10-200 K/s) and shorter residence time (10-200 s). Bio-oil is a major biofuel because fast pyrolysis has become a commercial process due to low investment cost and high energy efficiency. However, bio-oil needs upgrading because of high proportion of oxygenated compounds, high viscosity, high acidity and thermal instability. The upgrading options include hydrodeoxygenation (HDO) and zeolite upgrading [23]. Another thermal conversion is wood gasification to produce syngas for power, heat or chemical production [24]. On the other hand, thermal processes require drying as pre-treatment and include evaporation in the reaction phenomena, thus spending high energy for biomass processing. For instance, Brammer and Bridwater (2002) [25] investigated the economic performance of biomass gasification for a CHP system: for a feedstock with 50 % moisture content, the optimum result was obtained when the feedstock was dried to 10 % moisture content before gasification. Overall efficiency increases and cost of electricity decreases with decreasing moisture content in the gasifier feed (i.e. more intensive drying). However, increase in moisture content of the feedstock decreases the overall efficiency and increases the electricity cost. Moreover, the drying unit causes significant rise in the capital cost as well. In addition, black liquor gasification is the most investigated integration option to pulp mills [5]. For instance, Petterson and Harvey (2012) [26] compared black liquor gasification concepts including electricity, motor fuels and dimethyl ether production in terms of economic performances. However, despite increasing the electricity efficiency or the economic performance, this option has the same issues with the commercial recovery boiler treatment due to the evaporation step consuming one third of the energy required by the whole mill [5]. As a result, hydrothermal processes are potentially more suitable for biomass having high moisture content: e.g. around 40-50 % moisture in solid wood chips and around 80 % water in weak black liquor. Hydrothermal processes use water as the solvent (i.e. reaction medium) and the reactions occur in aqueous phase. In other words, no drying is required in these processes. For instance, an exergy analysis of biomass-based fuels stated the evaporation step as a main source of exergy loss in wood biomass processing and reported higher exergy efficiency for hydrothermal upgrading than thermal processes [27]. However, hydrothermal processes are rarely included in the overview schemes of biomass processing routes. These hydrothermal processes include aqueous phase reforming, carbonization, hydrothermal liquefaction, oxidation and gasification [28].

The properties of water play an important role in the hydrothermal conversion phenomena [29]. As a major feature, even though liquid water is polar under sub-critical conditions, polarity decreases with temperature and water becomes non-polar at supercritical conditions [29]. In other words, water becomes very effective solvent for organics and gases whereas the solubility of inorganic salts becomes very low. For instance, the oxygen solubility decreases with temperature at sub-critical conditions and increases with temperature at supercritical temperature [30]. In addition, the solubility of hydrocarbons in water increases dramatically when approaching critical temperature [31]. The negligible solubility of salts can cause deposition issue in the reactor; nevertheless, this might be converted into an opportunity to recover the inorganic salts with the suitable reactor configuration. As another feature, the dissociation constant increases with temperature under sub-critical conditions and reaches the highest values around critical point whereas supercritical water (SCW) has very low dissociation constant [32]. In other words, ionic mechanism is dominant in the reaction phenomena at sub-critical conditions and around critical point while radical mechanism becomes dominant in SCW. As flow properties, density and viscosity are also influenced mainly by temperature [33]. Viscosity decreases with temperature and is not affected significantly by pressure. Density changes very slightly with temperature after 500 °C and pressure influences slightly whereas temperature dramatically influences water density at around critical point. The dramatic influence of temperature on density and high dissociation constant around critical point cause difficulty in flow control and corrosion issue, respectively. Therefore, hydrothermal conversion processes are operated at well above or well below the critical point of water: e.g. partial wet oxidation (PWO) at 130-270 °C and over the corresponding vapor pressure, hydrothermal liquefaction (HTL) at 250-370 °C and 4-25 MPa, and supercritical water gasification (SCWG) at 500 °C or higher temperature and higher pressure than critical pressure of 22.1 MPa.

PWO is a liquid-phase hydrothermal process: oxygen is first dissolved in water and then reacts with the organics [34]. Muddassar et al. [35] investigated PWO of weak Kraft black liquor – KBL- (with 10.81 % solid dissolved by weight) and wheat straw black liquor –WSBL- (with 10.27 % solid dissolved by weight) under oxygen partial pressure of 0.5 MPa and the residence time of 30 minutes. The aim was to determine the generation of carboxylic acids. Acid content increases significantly for WSBL but very slightly for KBL and the downstreams are still very dilute. Consequently, the recovery of acids or sodium salts of these acids would be very challenging and require intensive evaporation as investigated by Özdenkci, et al. (2015) [36]. Regarding solid biomass, Sipponen et al. (2016) [37] and Muddassar et al. (2014) [38] investigated PWO of sawdust with 55 % moisture content. Sipponen et al. (2016) [37] investigated dissolution and PWO simultaneously in a single unit at temperature range of 130-270 °C with 30 minutes reaction time to determine the influences of oxygen (the absence or presence with 0.5 MPa partial pressure) and sodium carbonate (Na_2CO_3) on the process. The highest acid yields occurred in the case of PWO at 210 °C with sodium carbonate: further increase in temperature provided more dissolution of wood but no significant change in the yields. Muddassar~~,~~ et al.~~,~~ (2014) [38] experimented with a two-stage process of cooking with Na_2CO_3 or $Na_2CO_3/Na_2S.9H_2O$ followed by PWO at 210 °C under oxygen partial pressure of 0.6 MPa for 30 minutes. The single-stage operation provides higher yields and economically more advantageous due to less processing units and steps. PWO has both benefits and issues for industrial application. This is an exothermic process and oxygen dissolution can be accelerated via mixing rate, reactor configuration and feeding system. However, the separation and recovery of each acid might be a challenge due to dilute downstream [36]. Therefore, it can be more advantageous to use PWO as an intermediate step for the optimization of a biorefinery process rather than for chemical production. For instance, LignoForce process starts with PWO for oxidizing the sulphur content and this improves the lignin recovery: less resistance in filtering and sulphur-free lignin without sacrificing the mechanical properties of lignin significantly [4]. For using PWO as an intermediate step of a hydrothermal process, the criteria would be compromising between minimum reduction in TOC and the energy optimization: conversion of organic carbon and hydrogen into gas is undesirable in case of PWO being an intermediate step. Muddassar (2016) [39] investigated PWO of black liquor versus time (up to 40 minutes) and partial pressure of oxygen (0.5-1.5 MPa) as well. Higher oxygen pressure caused slightly lower TOC and COD values with time. In addition, pH decreased with time during PWO, indicating the formation of carboxylic acids, and remained almost constant after around 10-20 minutes. Higher temperature caused faster decrease in pH as temperature accelerates the reactions. The pH value has another importance as well: decreasing pH reduces the carbon dioxide need in the acidification step for lignin recovery. Lignin starts precipitating when pH decreases to around 9-10 while pH of KBL is around 13.

The HTL process produces bio-oil as the main product and aqueous phase, char and gas as the by-products. The proportion depends on the biomass type and the process conditions. For instance, cellulose is partly soluble in water at around 300 °C and becomes completely soluble at 330 °C [40]. Hemicellulose degrades more easily than cellulose whereas lignin has low solubility in water and is more stable but has more energy content. Even though upgrading process is still required for bio-oil usage as fuel, HTL provides bio-oil with less oxygen content compared to fast pyrolysis, thus requiring less hydrogen when upgrading [40]. Furthermore, among the developed HTL technologies, 30-40 % of oil yield (by weight on dry basis) is reached for lignocellulosic biomass, with the addition of alkaline (e.g. sodium carbonate) in moderate amounts and at the temperature range of 330-350 ºC (dramatically lower temperature than fast pyrolysis) [41]. In addition, the energy recovery is usually around 80 % in HTL process [41]. However, Zhu et al. (2014) [42] stated that HTL of wood biomass is not competitive compared to petroleum-based gasoline in terms of techno-economic analysis. Nevertheless, HTL investigated by Zhu et al. (2014) [42] has potential improvement aspects: wet biomass or wet biomass blended with solid biomass to reduce the pre-treatment cost, less feedstock price than wood in case of waste biomass, and a distributed HTL plant to reduce the capital cost.

SCWG is another hydrothermal process, which produces syngas. This is single-phase phenomena as well. Yakaboylu et al. (2015) [43] provided a review of SCWG technology for various biomass, involving the reaction mechanism and kinetics, catalyst impacts, modelling approaches in the literature as well as technology aspects and challenges. The hydrolysis occurs very fast under SCW as determined by kinetic studies. For instance, hydrolysis is the rate-determining step of cellulose decomposition under sub-critical water conditions; in contrast, the hydrolysis step occurs much faster than further decomposition of monomers under supercritical water temperature [44]. Similarly, decomposition of lignin to monomeric compounds occurs very fast in few seconds as well, i.e. the yield of phenol, guaiacol, cathecol and cresol increase very sharply in the first few seconds and decrease with time due to further decomposition of these compounds [45]. Since the reaction mechanism is complicated and not well understood yet, many studies investigated SCWG of model compounds. Hao et al. (2003) [46] investigated hydrothermal decomposition of glucose as the model compound for cellulose under supercritical water conditions. Kabyemela et al. (1999) [47] investigated pathways and kinetics of glucose and fructose decomposition in subcritical and supercritical water. Similarly, Binder et al. (2009) [48] investigated the decomposition of model compounds representing different function groups of lignin: eugenol representing guaiacyl aromatic structure, 2-phenylethyl phenyl ether representing β-aryl esters, 4-ethylguaiacol representing unfunctionalized alkyl structure. In addition, decomposition of guaiacol was investigated in subcritical and supercritical water as well [49]. Some studies investigated SCWG of one fraction of lignocellulosic biomass: for instance, cellulose decomposition with alkali or nickel catalyst [50] and lignin gasification in supercritical water [51]. Regarding the industrial purpose, SCWG of black liquor was investigated for the integration with a pulp and paper plant [52]. For large-scale wood mills, SCWG can address the capacity and efficiency limitations of the commercial recovery boiler treatment due to operational issues, such as salt deposition and increasing viscosity in the evaporation stage. However, an important aspect is sulphur for Kraft pulp mills since sodium sulphate (Na_2SO_4) is a cooking chemical. The sulphur content can occur in the outlet streams as hydrogen sulphide (H_2S) in the syngas, dissolved form in the liquid effluent, and in the solid residue. The liquid effluent is recycled to the recovery boiler, thus recovering sulphur. On the other hand, sulphur in the syngas causes the need of gas cleaning operation, and sulphur in the solid can lead to the need of chemical make-up in the cooking unit. For small-capacity non-wood mills, SCWG can be the solution for black liquor treatment as no feasible solution is currently available for those mills. The evaporation limit is only around 50 % organic content due to sharper increase in viscosity caused by silica content. This makes the recovery boiler unit inefficient and hence unfeasible. Nevertheless, SCWG does not require evaporation and viscosity of supercritical water decreases more dramatically with temperature. The experiments of De Blasio et al. (2016) [52] determined the influence of temperature and catalytic impact of nickel-chromium-molybdenum reactor on the product and the reaction mechanism: the experiments covered the temperature range of 500-700 °C in stainless steel and INCONEL 625 reactor under 25 MPa. Temperature enhances the efficiencies and gas yields. Carbon gasification efficiency (CGE – defined as the ratio of carbon in gas product to the carbon content of feedstock) reached around 70-75 % at 700 °C. Among the experiments, the highest hydrogen yield was obtained in INCONEL 625 reactor at 600 °C (as 32.9 moles of H_2 per kg dry-ash-free feedstock). The highest hot gas efficiency was obtained as 80 % in INCONEL 625 reactor at 700 °C. Nevertheless, the efficiencies in stainless steel reactor were also remarkable and stainless steel is cheaper material. Therefore, both reactors should still be investigated in feasibility analysis. Even though SCWG has advantages regarding high reaction rate, yields and efficiency; this process has some issues to be addressed for industrial application as well [43, 53]. These issues include high investment and operating costs due to high-pressure operation, char and tar formation, and precipitation of inorganic salts. In addition, sulphur outcome is another aspect as well: gas cleaning is required in further use of syngas in case of the presence of H_2S in gas product. On the other hand, reduced form of sulphur (Na_2S) is needed by Kraft pulp mills as the recycle of the cooking chemical and this is obtained in the recovery boiler unit. Regarding the readiness level of the technology, pilot-scale operation has been reached: Boukis et al. (2007) [54] introduced Verena pilot plant for SCWG of biomass. The feeding system of this plant involves biomass heated to sub-critical temperature and mixed with supercritical water. In addition, a vertical reactor with biomass feed from the top helps avoid the plugging problems associated with salt deposition: salts are transferred downwards by gravity, and gas product goes upwards through a vertical pipe inside the reactor.

To sum up, no commercialized technology has been achieved yet from 2nd generation biomass to fuels and value-added chemicals, even though pilot- or demonstration-scale processes exist for several technologies. Biological conversion is suitable only for biomass with high sugar content and does not enable flexibility. Thermal conversion has the issue of energy-consuming drying. Hydrothermal conversion has the issue of high operation cost due to high pressure. Therefore, further improvements are required to achieve the economic feasibility.

THE NOVEL BIOREFINERY CONCEPT

The core subjects of biorefinery concept are the supply-chain network and chemical conversion of biomass. This paper proposes sectoral integration as the network and a novel hydrothermal conversion process for biomass conversion. The main advantages of this concept are to ensure biomass supply and to convert all the waste/side streams from various sectors. Furthermore, the hydrothermal conversion process provides the flexibility. From the chemistry viewpoint, the conversion process mainly implements modification by partial degradation or complete destruction (but not complete fractionation except for specific feedstocks), depending on the market need, thus enabling conversion of different feedstocks in the same process. Last but not the least, the process produces intermediates for liquid fuels and biomaterials in an adjustable way regarding the product option and quantity.

Sectoral Integration

Sectoral integration network is an enhanced version of distributed-centralized network: utilizing both solid and wet biomass from various sectors (e.g. black liquor, sawdust, straw and other residues from agriculture and forestry), and flexible operation to adapt changes in market demand. For sustainable biorefinery systems, it is crucial to utilize the waste streams and by-products from all sectors; however, the majority of biomass energy is produced from wood, 64 %, whereas agricultural waste covers only 5 % of biomass energy [22]. Therefore, sustainable biorefinery requires an integration system and conversion processes for multiple and/or mixed feedstocks.

Sectoral integration is shown conceptually in Figure 4 for a wide area divided into regions. The network includes biomass pre-treatment at each source side, transport to the regional conversion plant, the conversion process at each region, transport to the centralized upgrading plant, upgrading to final product and finally transport to the demand places. The pre-treatment operations in source sites convert waste into suitable feedstock for regional conversion plants, thus providing additional income for rural areas. For instance, pre-treatment operations can involve physical-chemical and/or mechanical processes - e.g. removing inorganic salts through ion exchange to avoid salt deposition in the hydrothermal process, and dewatering and/or grinding to reduce the transportation costs. As a result, this network integrates the various sectors since the final products are combined contribution of each sector providing feedstock for the regional conversion plant. Afterwards, each regional conversion plant generates energy for its own region, products for other applications and intermediates for further valorisation in the centralized plants. Finally, the centralized plants produce the products transferred to demand sites.

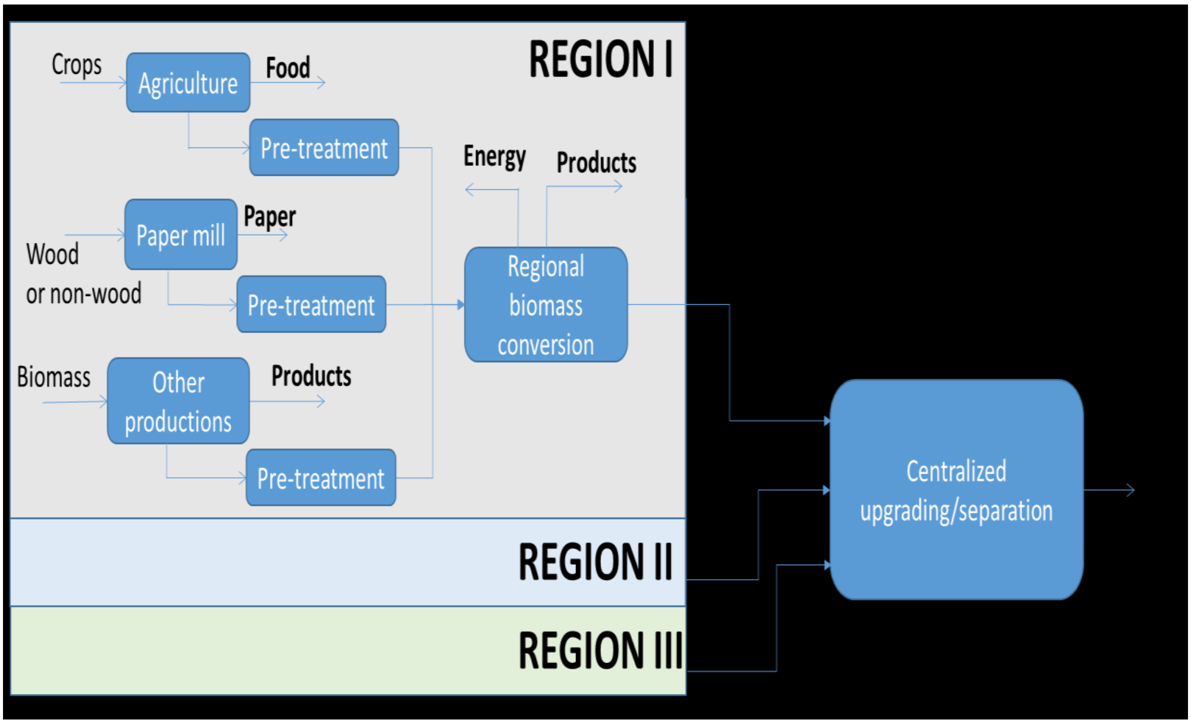

Figure 4. Sectoral integration concept for supply chain network

Supply chain network design determines the plant location and capacities by optimizing the total cost and environmental impacts. Total cost involves transportation costs of feedstock and products as well as operational costs of regional and centralized plants. The network design also defines the feedstock sources for biomass conversion plants, i.e. formulating the regions with a specific conversion plant for a set of biomass activity sites. Figure 5 briefly illustrates the network design with respect to locations: only for illustration, not a complete network design for a real case with all the data and optimization model. The biomass activity sites involve pre-treatment to prepare the feedstock from waste streams and by-products. Afterwards, in each region, the feedstock streams from the activity sites are transferred to the regional biomass conversion plant. These regional plants produce energy, products and intermediates. Then, the intermediates are transferred to the centralized upgrading/separation plants and converted into final products. Finally, those products are transferred to the demand sites. The top picture of Figure 5 shows the basic network design with one regional conversion plant per region and a single centralized plant in the whole network. Nevertheless, some case-specific improvements can result from the optimization model as illustrated in the bottom picture of Figure 5. For instance, the network can involve more than one centralized plants (of course, less than the number of regional conversion plants) in order to reduce the transportation costs of intermediates and products. For example, in the bottom picture of Figure 5, the centralized plant in the west side receives feedstock from the western regions and delivers the products to the demand sites in the west side. The same applies to the centralized plant in the east side as well. In addition, a centralized plant can be located nearby a regional conversion plant in case of difficult transfer of an intermediate. For instance, the centralized HDO plant can be located nearby a regional plant producing hydrogen gas, and bio-oil can be transferred from the other regional plants.

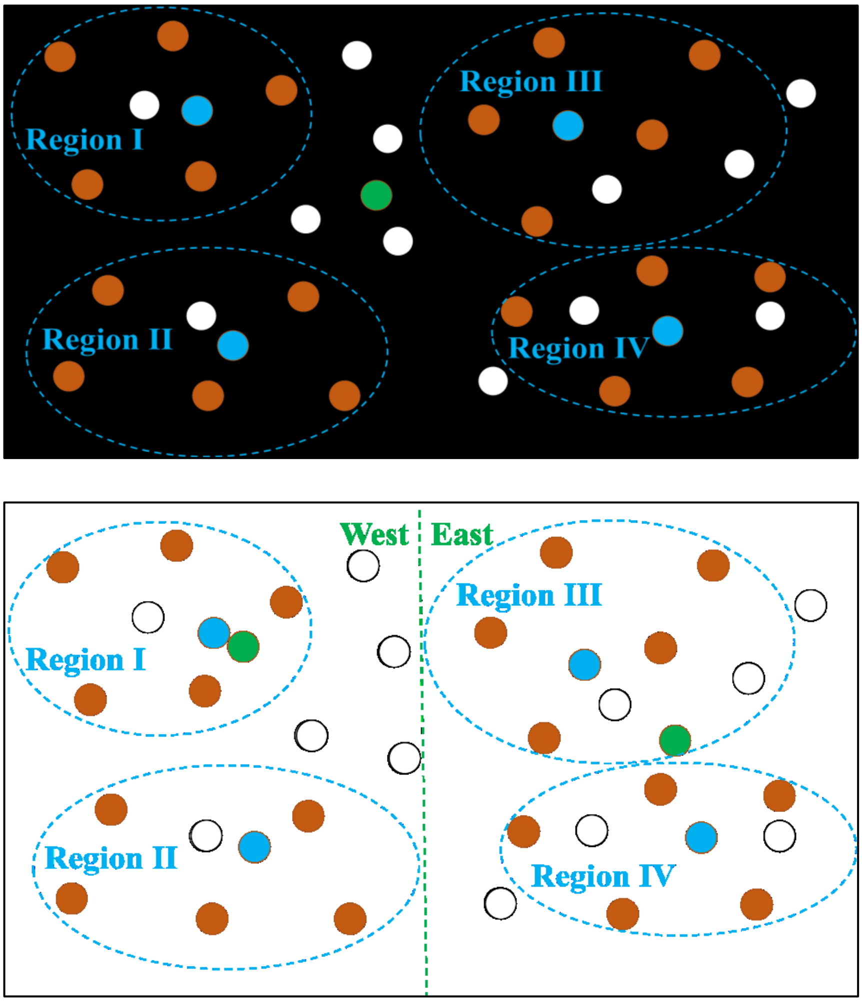

Figure 5. Illustrative example of plant locations through network design: brown circles for the biomass activity sites, blue circles for the regional biomass conversion plants and green circles for the centralized upgrading plants

The Hydrothermal Conversion Process

The sectoral integration concept requires multi-feedstock-multi-product processes as regional conversion of biomass, i.e. the ability to process different feedstocks and multi-functional process units for flexible production. Even though hydrothermal processes are suitable for biomass, no process option alone has been proven as sufficient for industrial application in terms of techno-economic performance.

Figure 6 shows the proposed regional biomass conversion process that produces lignin and syngas or bio-oil. The idea was filed as a provisional patent application as well [55]. The process starts with a unit of PWO for liquid feedstocks or simultaneous dissolution and PWO for solid feedstocks. In this way, the process can utilize both liquid and solid feedstocks from various sectors of agriculture and forestry. This unit can operate under oxygen partial pressure of 0.5-1.5 MPa and at temperature range of 180-240 °C, depending on the energy optimization of the process. Then, some portion of the downstream goes to lignin recovery through acidification. For alkaline biomass, lignin precipitates when pH reduces to 9-10. Then, washing and filtering steps are required to get lignin as a product. The other portion and residual liquid from the lignin recovery section are transferred to the thermochemical conversion reactor, which produces bio-oil through sub-critical liquefaction (under 4-22 MPa and at 250-350 °C) or syngas through

SCWG (supercritical water conditions, depending on the plant-wide optimization of the whole process). Then, the separation of the products and aqueous effluent is performed: two-stage syngas separation or drum. Based on the product demand, this conversion process operates in a flexible way by adjusting the flow rates and conditions in the units. Alternatively, for the feedstocks with high polysaccharide content, the first unit can include acid hydrolysis as well to recover sugars that can be processed separately, e.g. by fermentation in case of alcohol demand. Especially, agricultural feedstocks have less lignin and more cellulose and hemicellulose compared to woody biomass. Melin and Hurme (2010) [56] evaluated the conversion routes of lignocellulosic biomass and stated that anaerobic fermentation has high product yield. Afterwards, the proportion to lignin recovery section and the reactor can be adjusted based on the lignin demand. Then, the reactor can function SCWG or sub-critical hydrothermal liquefaction depending on temperature and pressure. The vertical reactor can address the deposition issue by removing char and tar: feed from top and product upwards through an internal pipe as in Verena pilot plant [54]. As further development, a cyclone can also be inserted as a separate unit for the gas outlet in order to provide more efficient solid removal. The cyclone unit can remove free-flowing solid particles based on Stoke's law by utilizing high difference in densities of particles and supercritical water phase. In addition, the reactor and the cyclone introduce pressure drop of 5-10 bars and 10-15 bars, respectively. Therefore, in case of SCWG, the reactor inlet should have high enough pressure to ensure supercritical phase, e.g. 250 bars is suitable. In the separation section, syngas is cooled and separated to hydrogen-rich and carbon dioxide-rich products in two stages: high-pressure and low-pressure gas/liquid separators. Temperature of separators can be set in accordance with the desired use of syngas and solubility of gases: maximizing the heating value of H_2-rich gas for energy production purpose or maximizing the mole fraction of H_2 for hydrogen production purpose. Low temperature around 80 °C gives higher H_2 mole fraction in H_2-rich gas since the solubility of other gases in water increase with decreasing temperature. In contrast, high temperature provides higher fraction of combustible gases in H_2-rich gas; however, the amount of water vapour also increases with temperature. Therefore, temperature of "HP G/L Separator" unit can be around 200-250 °C in case of the energy production purpose, depending on the plant-wide optimization. In case of bio-oil production, the cooled product can go to low pressure separator which would function as drum in that case. Finally, some or all of the aqueous effluent can also be recycled for dilution purposes for hydrothermal conversion, e.g. SCWG operates with less than 10 % organic content.

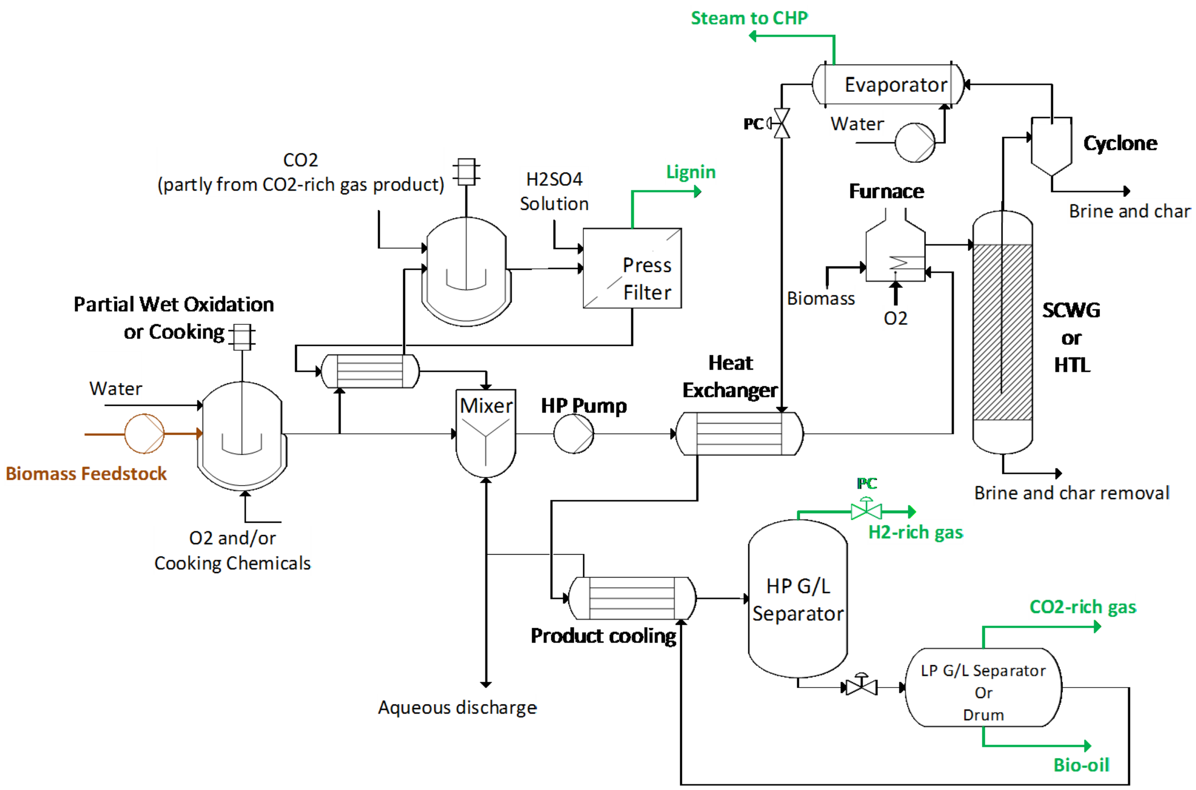

Figure 6. The proposed process of regional biomass conversion for sectoral integration [55]

The ranges of process conditions are given in Table 1. PWO can be implemented at 170-240 °C and 0.5-1 MPa of oxygen partial pressure. The residence time of 10-20 minutes can be sufficient for liquid biomass. In case of solid biomass, 30 minutes time can be applied or the solid can be blended with liquid feedstock in relatively low amounts to ensure the dissolution in 10-20 minutes, depending on the relative amounts of solid and wet biomass received by the regional conversion plant. The reactor conditions depend on the feedstock and the desirable product. HTL occurs at 4-22 MPa and 250-350 °C. The conditions can be selected based on the product quality and plant-wide optimization. SCWG conditions are selected based on the further use of syngas. For instance, based on the experimental conditions presented by De Blasio et al. (2016) [52], the yields and energy efficiency are very low at 500 °C for black liquor. For the purpose of energy generation, higher temperature provides higher hot gas efficiency; however, the heat needed to maintain the reactor temperature would be also higher [52]. Thus, temperature should be selected based on the optimum compromise between hot gas efficiency and the heat needed in the reactor. For the purpose of hydrogen production, temperature can be 600 or 700 °C depending on the reactor material and plant-wide optimization. The hydrogen yield increased with temperature in stainless steel reactor; in contrast, the yield of hydrogen decreased in Inconel reactor at 700 °C compared to 600 °C in case of SCWG of black liquor [52]. The pressure has no major influence on gas yields even though it affects water properties associated with energy and flow, such as viscosity, specific heat and density; therefore, pressure in the reactor can be selected based on plant-wide optimization. The feed to reactor will be pressurized by high-pressure liquid pumps; thus, no gas compressors are needed.

Table 1. Process conditions of the proposed hydrothermal conversion process as illustrated in Figure 6

The unit	**The conditions**	**Remarks**
PWO	T: 170-240 °C P_{O2}: 0.5-1 MPa t: 10-20 min.	Self-heating of the feedstock
Acidification	T: 80 °C P:1 atm	Lignin precipitation at pH 9-10
The conversion reactor	T: 600-700 °C P: 25 MPa or above t: 1-5 min.	SCWG
The conversion reactor	T: 250-350 °C P: 4-22 MPa t: 1-12 min.	HTL
HP G/L Separator	T: 80-250 °C P: 25 MPa or above	Separation of H_2-rich gas in case of SCWG
LP G/L Separator	T: 80 °C or less P: 1 atm	Separation of CO_2-rich gas in case of SCWG or Phase separation of aqueous effluent and bio-oil in case of HTL

This process would potentially have improved techno-economic performance. The process combines the advantages of exothermic PWO and fast hydrothermal conversion. First, the energy integration and optimization can determine the extent of oxidation in the first unit, thus reducing the energy need for heating prior to SCWG or hydrothermal liquefaction. In addition, oxidation of sulphur enables sulphur-free lignin recovery with less filtering resistance. Afterwards, the reactor can produce either syngas or crude bio-oil.

The heat integration is briefly involved as well in Figure 6 and can be improved further when designing the process. The reactor outlet heats the reactor feed in “Heat Exchanger” unit. However, in case of SCWG, temperature of the feed stream should not exceed the critical water temperature to avoid salt deposition in the pipelines and in the heat exchanger. Therefore, a furnace is included to increase the reactor inlet temperature further. The extra internal energy of product gas can further be used to generate steam for turbines: the reactor outlet first can exchange heat with water in another unit then can pass through “Heat Exchanger” unit as in Figure 6. In addition, the purpose for further use of H_2-rich gas can influence “Product cooling” unit. The fractions of combustible gases in the H_2-rich gas stream are maximized for the purpose of energy production in gas engine. In contrast, the fraction of hydrogen is maximized for the purpose of hydrogen production. In other words, the purpose determines temperature in “HP G/L Separator” unit. In case of HTL, temperature difference between two inlets of “Heat Exchanger” unit would be less, thus influencing the heat integration and introducing less heat duty to the furnace.

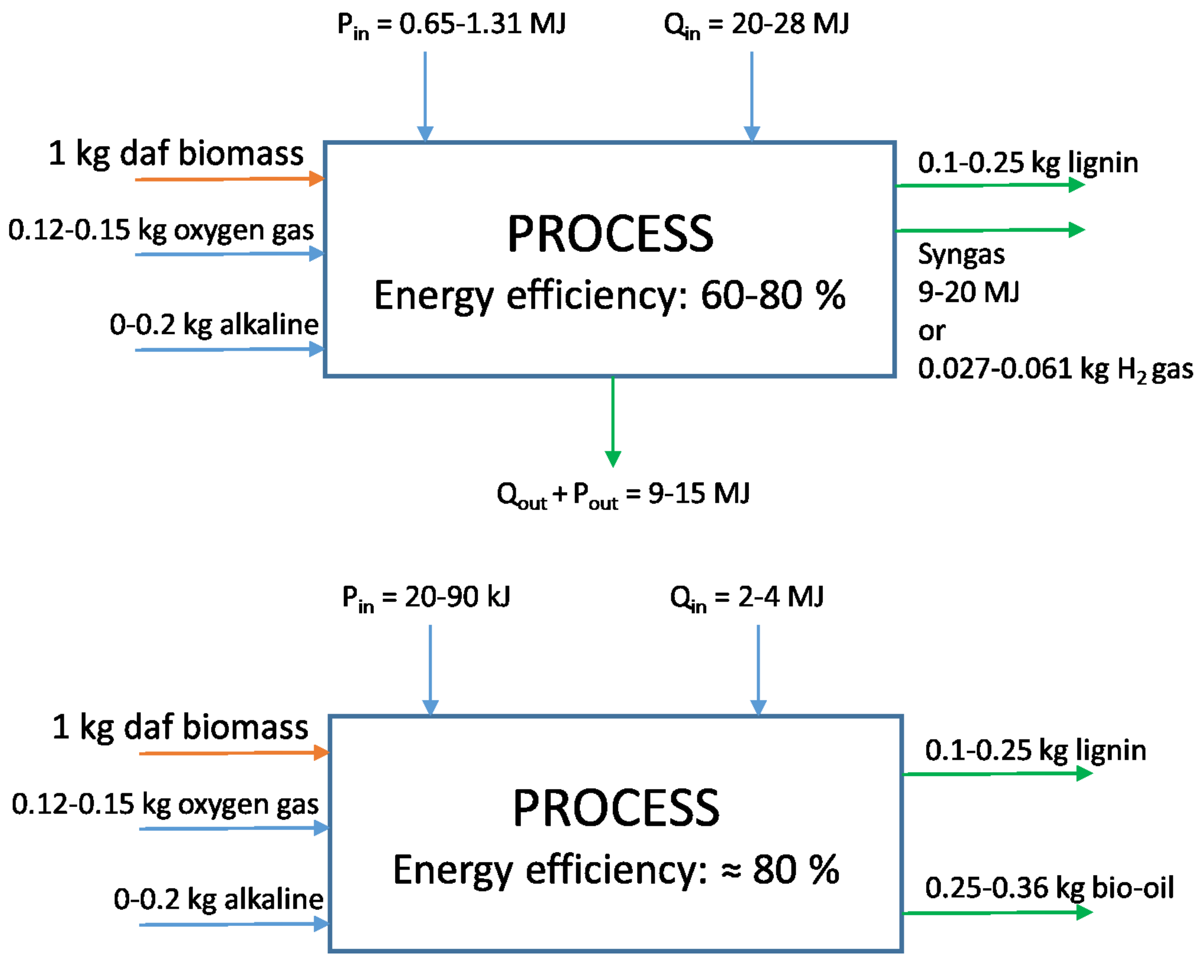

Figure 7. The input-output diagrams of the proposed hydrothermal conversion as illustrated in Figure 6 (per kg of dry-ash-free "Biomass Feedstock" stream) for the cases of SCWG (top) and HTL (bottom) operations in the reactor

Figure 7 shows the ranges of product yields and utility needs for the process as illustrated in Figure 6: the minimum and maximum values are approximately calculated based on the operational ranges given in Table 1. Oxygen gas inlet shows the amount needed in the PWO unit. P_{in} shows the electricity needed by the mixer and the high pressure pump. Q_{in} shows the amount of heat needed in the furnace. Q_{out} + P_{out} shows the amount of excess heat in the reactor outlet: transferred to "Steam to CHP" stream for combined heat and power production. On the other hand, it should be noted that these values are case-dependent and vary depending on the operating conditions as well as biomass type. Therefore, approximate ranges are given in Figure 7. The oxygen need in PWO is calculated assuming 20 % solid content in the "Biomass Feedstock" stream, based on the solubility of oxygen in water and some degradation of organics. The values have the basis of unit mass dry-ash-free (daf) content in the "Biomass Feedstock" stream in Figure 6. In other words, depending on the portion transferred to acidification, 0.9-0.75 kg organic content remains for the hydrothermal reaction. Then, the yields reported in the literature are adjusted accordingly. For instance, HTL giving 40 % yield on mass means 40 % of 0.9 kg and leads to 0.36 kg bio-oil/kg daf biomass feedstock. For SCWG, the reactor inlet is assumed to have 5 % organic content and the identical heat transfer-related properties with pure supercritical water. The heat available for CHP process and needed in furnace are calculated accordingly. The syngas product is listed as hydrogen yield and the energy amount when used in combustion. The H_2-rich gas has lower heating value of 20-25 MJ/kg dry syngas in case of separation for maximizing the heating value.

The proposed hydrothermal process gives promising figures compared to the alternative conversion processes. Even though high amount of energy is needed in the furnace, SCWG of wet biomass can reach the energy efficiency of 60-80 %. The energy need in furnace can be fulfilled by burning 1-1.5 kg of biomass per kg daf biomass in the "Biomass Feedstock" stream. Nevertheless, the energy efficiency can be improved further by operating with more concentrated reactor feed (e.g. 10 % solid content provided that the gas yields are maintained either by longer residence time or more effective catalyst). As an alternative to produce the same product, thermal gasification of wet biomass consumes high energy as well for evaporation as a pre-treatment process and drying step in the gasifier. For instance, 8-10 MJ per kg daf biomass is the energy cost due to water content of concentrating biomass feed from 20 % to 80 % solid content and gasifying this stream afterwards. In addition, thermal gasification occurs very high temperature; therefore, oxygen is introduced into the gasifier. Introducing air to gasifier does not help reduce the cost since the syngas becomes dilute in the presence of nitrogen. Moreover, the syngas from thermal gasification requires gas cooling and cleaning to remove the sulphur content, thus reducing the efficiency of post-processing of the gas. In contrast, the syngas from the proposed process may not require gas cleaning if sulphur remains as the oxidized form and occurs in the liquid effluent after the separation stages. Furthermore, the combustible gases can be separated more effectively, giving H_2-rich gas at high pressure. Regarding bio-oil, HTL produces bio-oil in higher quality than pyrolysis, thus requiring less hydrogen in upgrading. For instance, the oxygen content of bio-oil is 10-20 % by weight and the heating value is in the range of 30-37 MJ/kg in case of HTL [41]. In contrast, biomass pyrolysis produces bio-oil having the heating value range of 18-29 MJ/kg [57]. Furthermore, HTL occurs at lower temperature than pyrolysis and avoids the need of evaporation as well.

Regarding the development of sectoral integration supply chain, this process is very suitable for regional conversion of biomass. Due to biomass inlets from several sectors, the continuous feedstock supply is secured unless there is sharp decline in all sectors simultaneously. In addition, the process can respond changes in market demand: switching between liquid biofuel production and syngas besides adjusting the proportion passing through lignin recovery section. The process can perform all the chemical concepts of lignocellulosic biomass conversion shown in Figure 3.

For deeper process development of the proposed hydrothermal conversion, future studies will involve several aspects: further experimental data, kinetic modelling of hydrothermal decomposition of biomass, preliminary process design for a selected region with forestry and agricultural activities, feasibility and environmental performance evaluations. More data are available in the literature for a technology option alone. However, the future experiments will cover HTL and SCWG of PWO downstream for various feedstocks.

Sustainability Evaluation

The sustainability consists of environmental, economic and social aspects. A process is evaluated as sustainable when it succeeds in all these three aspects. The proposed sectoral integration together with the novel hydrothermal conversion process has the potential to be sustainable.

From the environmental viewpoint, the proposed sectoral integration concept utilizes the by-products and waste streams from various sectors, thus improving the environmental performance of the operations of those sectors as well. For instance, non-wood pulp mills have no commercial treatment solution for black liquor due to high content of silica causing extreme increase in viscosity when concentrating. The proposed hydrothermal process can include non-wood black liquor as feedstock as well, thus enabling non-wood mill operation. The agricultural residues become valuable raw material rather than waste with this concept and the proposed conversion process, thus improving LCA (life cycle assessment) results of agricultural activities. In addition, lignin can replace fossil-based phenol and phenol derivatives in various applications, thus providing further improvement in the environmental assessment [58]. As a future aspect, further integration can be implemented by utilizing waste streams from other biomass sectors than lignocellulosic ones. For instance, some studies investigate SCWG of mixed feedstocks, e.g. manure-eucalyptus wood [59] and waste paper sludge-black liquor [60]. As another perspective, there is a potential for integration through CO_2 utilization as well. For instance, Sharifzadeh et al. (2015) [61] investigated the utilization of CO_2 emission from biomass pyrolysis in microalgae production and reported improved product yield as well as environmental performance. Regarding the sectoral integration network, CO_2 generated in the regional conversion can go to a biomass processing at source site, such as algae production. Then, algae can possibly be used in the proposed hydrothermal process together with lignocellulosic biomass. Alternatively, Michalak et al. (2015) [62] studied the applications of supercritical algal extracts in animal feed and food supplement, pharmaceutical and plant protection products.

The environmental evaluation can be performed with LCA for the whole system covered by the concept including biomass fields, regional conversions and centralized upgrading plants. Alternatively, regional evaluation can be performed for the combination of all involved sectors with the system boundary from biomass fields to the regional conversion process in a specific region. The new biomass implementation can be evaluated by comparing the combined LCA results with and without the new implementation, rather than LCA analysis for a proposed implementation alone.

From the economic viewpoint, the proposed concept and conversion process provide value-added products from by-products and waste streams. In other words, pre-treatment operations in biomass activity sites convert waste into raw material for regional conversion plants, i.e. providing additional revenue for rural areas. Furthermore, regional conversion plants can provide energy for the region or intermediates converted into biofuels and other valuable products in the centralized upgrading plants. Considering the depletion in fossil resources and increasing energy demand, biorefinery will potentially have increasing economic value. In addition, regional conversion plants can recover lignin as well. Lignin is a valuable material for 3-D printing [63] carbon fibers [64] and other composite material applications [65]. For example, the sectoral integration provides the improvements below compared to the distributed-centralized network presented by Kim et al. (2011) [9]:

- possible reduction in transportation costs from biomass site to the regional conversion plant by pre-treatment at biomass sites, e.g. mechanical dewatering or grinding
- increasing the revenue by 1.1-1.4 times through lignin recovery in the regional conversion plants (assuming that lignin has the prices of 1000 $/ton [4]): 352.4 million-1.4 billion dollars of additional revenue
- saving transportation cost of bio-oil from the regional biomass sites to the centralized plant: around 30 % reduction in cost per transferred energy content, i.e. from 128.7 million dollars to 92.7 million dollars and saving 36 million dollars

- reducing the operation costs of bio-oil upgrading, that is one of the main costs
- reducing the acquisition costs of biomass by using waste biomass rather than chips and grass, another main cost
- more secured feed supply by introducing the agricultural wastes as well
- instead of relying on a single product; adapting market demand by switching among the products of lignin, bio-oil derived liquid fuels and syngas derived heat and power or chemicals

Even further improvements can be achieved by re-designing the network with these pieces of information. However, the operation costs of the proposed hydrothermal process are to be calculated more precisely as a future aspect, requiring more experimental data and feasibility studies. Then, the whole supply-chain network can be designed for a real case with the sectoral integration network and the proposed hydrothermal process for the regional conversion plants.

The sectoral integration network provides regional development as well regarding the social aspect. The biomass source sites (rural areas) can provide valuable feedstock for the regional conversion processes. Therefore, regional processes provide industrial employment in rural areas: local farming people, engineers, scientists and other associated business management people. Consequently, the concept will provide distributed population over the rural and urban areas as well as mixing people with urban and rural backgrounds, thus facilitating the social services reaching everybody and everywhere. In addition, supporting this concept also with local wind turbines and solar panels, this concept has potential to switch the energy policy from central power plants distributing electricity to very large areas to energy-independent smaller areas, thus saving energy distribution losses. Furthermore, the potential implementation of the sectoral integration would provide independence with respect to energy to the countries with biomass activities [66]. Especially, agricultural countries can fulfil energy and food need simultaneously, thus securing the most critical two sectors.

CONCLUSION

Due to sustainability issues of fossil fuels, biomass has increasing importance as a renewable source. However, chemical and energy production from biomass should not compete with the food sector, i.e. 2nd generation biorefinery is more suitable. In addition, sustainable biorefinery requires flexible and multi-feed-multi-product conversion processes in order to adapt the variations in product demand and feedstock properties. On the other hand, regarding the supply chain network, neither centralized nor fully distributed network provides the optimum value chain with respect to profitability and environmental performance. The distributed-centralized approach has been investigated in the literature; however, most studies are limited to single product and/or single biomass type. Moreover, each conversion process has drawbacks and no commercial technology has been achieved for 2nd generation biorefinery.

This paper proposes sectoral integration as the concept for biorefinery value chain: distributed pre-treatment at the harvesting sides, regional chemical conversion of side products or waste streams of all forestry and agricultural activities, and finally centralized upgrading to final products. This network integrates the various sectors since all the sectors providing biomass to the regional conversion process contributes to the final product. Furthermore, this integration concept can address the variations in feedstock and market demand as well as reducing the transport costs.

The biomass conversion part is the crucial part of the sectoral integration network concept. This paper proposes a novel hydrothermal conversion for lignocellulosic biomass. The proposed process enables multi-feedstock-multi-product and flexible operation, producing lignin and syngas or bio-oil. The process uses the benefits of hydrothermal conversion methods and potentially provides energy efficient production. This process concept can also overcome the concerns of the availability of feedstock since it utilizes biomass from various sectors.

The future aspects from the scientific viewpoint include obtaining more experimental data on hydrothermal processes and designing the sectoral integration network with the proposed regional conversion process for a real case as well as feasibility and environmental analysis. The future aspect from an application viewpoint includes the lignocellulose-aquatic biomass mixture integration as the feedstock and carbon dioxide utilization, e.g. integration with algae growth for the coastal areas.

NOMENCLATURE

AC: Activated carbon
CGE: Carbon gasification efficiency in percentage
CHP: Combined heat and power
COD: Chemical oxygen demand in g/L
daf: dry-ash-free
HP G/L Separator: High pressure gas/liquid separator
KBL: Kraft black liquor
LCA: Life cycle assessment
LHV: lower heating value in kJ/kg dry-ash-free
LP G/L Separator: Low pressure gas/liquid separator
LRP: the portion to lignin recovery
LY: lignin recovery yield in acidification and filtration
P_{O2}: Partial pressure of oxygen in MPa
PWO: Partial wet oxidation
SCW: Supercritical water
SCWG: Supercritical water gasification
TOC: Total organic carbon in g/L
WSBL: Wheat straw black liquor

η: Hot gas efficiency

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