Solvent-Based Biorefinery of Lignocellulosic Biomass

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April 2015
ECN-B--15-001

Chapter 9

Solvent-Based Biorefinery of Lignocellulosic Biomass

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9.1 Introduction

9.1.1 Biomass as a Renewable Resource for Chemicals, Fuels, and Other Products

Our modern society is unsustainable because it very much depends on fossil resources for chemicals, fuels, materials, and energy. The unlimited exploitation of oil, natural gas, and coal by mankind increasingly causes global problems such as climate change, environmental pollution, depletion of natural resources, and geopolitical instability. While renewable resources such as sun, wind, geothermal energy, hydropower, and biomass all contribute to

Biomass Power for the World: Transformations to Effective Use
Edited by Wim van Swaaij, Sascha Kersten, and Wolfgang Palz

ISBN 978-981-4613-88-0 (Hardcover), 978-981-4669-24-5 (Paperback), 978-981-4613-89-7 (eBook)
www.panstanford.com

the transition to a sustainable energy system, biomass is the only source of renewable carbon for chemicals, fuels, and materials [1].

Most terrestrial biomass consists of three major biopolymers: cellulose, hemicellulose, and lignin. Depending on the type of biomass, inorganic constituents (ash) and organic extractable material may be present as well, albeit generally in smaller quantities. Cellulose is a primary sugar source for bioconversion processes and consists of tightly linked glucose monomers. Hemicellulose is a secondary sugar source and consists of shorter polymers of various carbohydrates. Lignin consists of phenolic moieties, polymerized in a complex three dimensional network structure. Inorganic constituents are predominantly salts of alkali and alkaline earth metals such as potassium, sodium, magnesium, and calcium. Also silicon compounds such as silicates can be present in significant quantities. Finally, lignocellulosic biomass contains a variety of extractable organic material (extractives) such as fatty acids, proteins, terpenes, macromolecular phenolics, and oligomeric sugar species.

Lignocellulosic biomass can be used as such for several applications such as construction timber, rubber, textiles, and heat and power. In addition, the chemical structure of lignocellulosic biomass merits its exploitation (as feedstock) for chemicals, fuels, and performance materials. However, this requires physicochemical treatments, analogous to the refining of fossil oil. Unfortunately, the oil refinery infrastructure in its present form cannot be deployed for biomass because of fundamental differences in chemical structure and characteristics between biomass and fossil oil. The intrinsic heterogeneity of lignocellulosic biomass requires the development of (a combination of) new transformation technologies in order to enable the production of chemicals, fuels, and performance materials.

9.1.2 Biomass Fractionation

Typical thermochemical biomass conversion technologies such as combustion, gasification, and pyrolysis are mostly targeted on energy applications, either directly (combustion) or via the production of secondary energy carriers (syngas from gasification, pyrolysis oil/gas). From an economic perspective, this is not very efficient

because the energy applications of biomass are generally low value and the added value of the generated heat and power likely does not make up for feedstock and processing costs. Although biomass locally can be deployed as a source for heat and power, large-scale energy applications seem better achieved from other renewable sources such as sun and wind for electricity. However, biomass is also a renewable source of carbon and its conversion into value-added materials, fuels, and chemicals can be economically much more attractive than its use for energy applications.

At present very few cost-effective processes exist for efficiently converting lignocellulosic biomass directly to components that are suited for producing chemicals, fuels, and other products. In general this is due to the fact that each of the major constituents (lignin, cellulose, and hemicellulose) demands distinct processing conditions such as temperature, pressure, catalysts, reaction environment, etc., in order to effectively break apart its polymer structure and selectively convert it into the desired product. In general, the highly intertwined character of lignocellulosic biomass, featuring a plethora of physicochemical linkages and (partly) overlapping thermochemical stabilities between the main biomass constituents, makes a selective and effective fractionation into its major constituents challenging. In addition, any deconstruction treatment inevitably leads to reactive species that often counteract further fractionation because of repolymerization and recondensation reactions.

A key issue for a successful biorefinery is a cost-effective and efficient fractionation of lignocellulosic biomass into its main constituents (hemicellulose, cellulose, and lignin), thus enabling dedicated further processing of each of the main fractions separately. This has been acknowledged for quite some time and already in the seventies and eighties of the last century (1st and 2nd oil crises) extensive R&D efforts took place to explore the (liquid-phase) fractionation of lignocellulosic biomass for chemicals, fuels, and other products [1]. Often, the starting point was the proven technology of biomass pulping in water at elevated temperatures and in the presence of certain “cooking” chemicals as practiced by the pulp and paper industry to liberate the cellulose fibres for further upgrading to paper. In general, lignin, hemicellulose, extractives, ash, and cooking chemicals end up in the so-called black

liquor that is partially dewatered and combusted to meet the energy requirements of the pulp mill and to recover the cooking chemicals. Although some companies (Metso, Domtar) recover lignin, post-treatment of the black liquor for higher-value materials is generally not pursued.

Within a biorefinery, the so-called organosolv process can be used to solubilize lignin and hemicellulose from lignocellulosic biomass in order to efficiently split the biopolymers cellulose, lignin, and hemicellulose, for example, for further hydrolytic processing of the carbohydrate polymers to liberate sugars for subsequent (bio)chemical processing. Organosolv involves high-temperature treatment (typically around 200°C) of the biomass with a water-miscible organic solvent such as ethanol or acetone and optionally an acidic catalyst such as sulphuric acid. During organosolv, the lignocellulosic biomass is fractionated into a cellulose-enriched solid product stream (pulp) and a liquid product stream (liquor), comprising lignin and hemicellulose derivatives.

9.1.3 Staged Solvolysis: Step-Wise Unraveling Lignocellulosic Biomass

Looking at the physicochemical differences between the main constituents of lignocellulosic biomass (extractives, inorganics, hemicellulose, cellulose, and lignin), it seems logical to explore the potential of a sequential multistep or staged fractionation approach to effectively unravel the complex biomass structure into its main fractions. Although few examples show the potential of a step-wise approach to unravel the major constituents within the complex lignocellulosic biomass (see Section 9.2.3), neglecting constituents such as inorganic matter (ash minerals) and extractives may lead to suboptimal fractionation results due to various and unknown interferences between inorganics, organic extractives, and the major fractions hemicellulose, cellulose, and lignin.

To improve the biorefinery of lignocellulosic biomass, a governing principle could be that each fraction (including inorganics and extractives) is targeted according to its specific physicochemical characteristics, starting with the least severe treatment conditions. This option offers some clear advantages compared to direct transformation of the whole biomass. Firstly, it enables the valorization of all important biomass constituents, including the

nonstructural fractions. Secondly, it offers the possibility to obtain the main biomass fractions (hemi)cellulose and lignin in superior quality because of the effective removal of the other (interfering) compounds and the prevention of undesired side reactions such as the formation of "pseudolignin."

The following sequence can be envisioned:

1. (Soluble) ash removal by washing with cold acidified water
2. Removal of extractives at elevated temperature with water and organic solvents
3. Hemicellulose auto- or catalytic hydrolysis
4. Lignin and cellulose separation by organosolv delignification

In an integrated biorefinery the sequence above could be seen as the solvent-based primary biorefinery in which lignocellulosic biomass is pretreated and fractionated into products that are further processed in a secondary biorefinery. This secondary biorefinery uses dedicated technologies for each of the fractions from the primary biorefinery, as visualized in Fig. 9.1. Basically, each step results in a product that can either be fractionated further or processed via a different route such as pyrolysis, gasification, chemical conversion, or biotechnological ways (e.g., anaerobic digestion and fermentation).

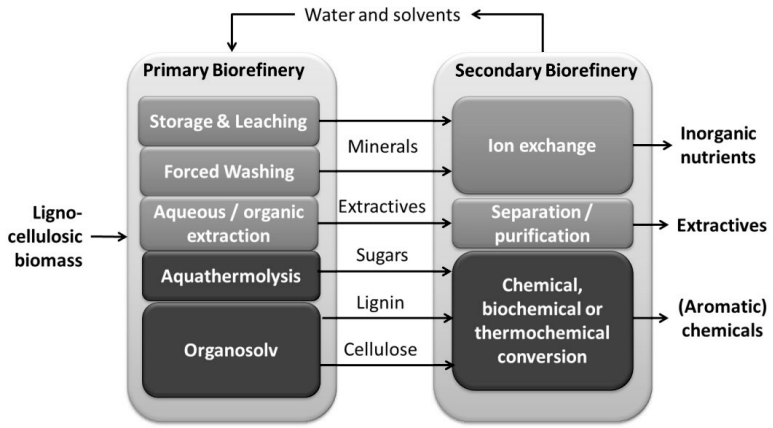

Figure 9.1 Two-step biorefinery concept featuring staged solvolysis in the primary biorefinery and dedicated processing in the secondary biorefinery. See also Color Insert.

This chapter describes solvent-based processes for the biorefinery of lignocellulosic biomass, both directly in a single step as well as in a staged approach. The focus will be on the latter as a fractionation concept that is targeted at sequential solvolytic processes to recover minerals, extractives, hemicellulose-derived sugars, cellulose, and lignin as primary fractions for further processing using dedicated technologies.

Figure 9.2 gives a schematic overview of the envisaged staged solvolysis concept. It should be noted that, depending on the location, size, and type of biomass, the first three stages may be bypassed.

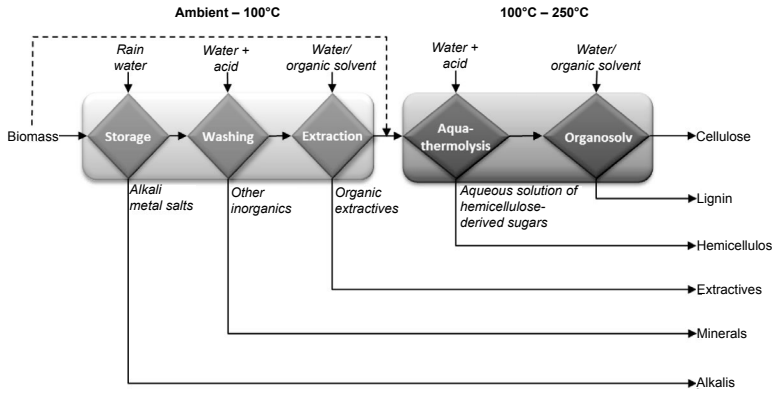

Figure 9.2 Staged solvolysis of lignocellulosic biomass for primary fractions.

9.2 Staged Solvolysis as a Solvent-Based Biorefinery Approach

9.2.1 Removal of Inorganic Matter (Ash) by Aqueous Leaching

The major and minor elements in biomass, in decreasing order of abundance, are generally C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti. Biomass is a complex heterogeneous mixture of organic matter and, to a lesser extent, inorganic matter. Table 9.1 presents a general overview of the composition of (lignocellulosic) biomass [2].

Table 9.1 Phase composition of biomass

Matter	State and type of constituents	Phases and components
Solid organic matter	Noncrystalline	Structural ingredients (hemicellulose, lignin), extractives, others
	Crystalline	Structural ingredients (cellulose), organic minerals such as Ca-Mg-K-Na oxalates, others
Solid inorganic matter	Crystalline	Mineral species from different mineral classes (silicates, oxyhydroxides, sulphates, phosphates, carbonates, chlorides, nitrates, others)
	Semicrystalline	Poorly crystallized mineraloids of some silicates, phosphates, hydroxides, chlorides, nitrates, others
	Amorphous	Amorphous phases such as various glasses, silicates, others
Fluid matter (mostly inorganic)	Liquid, gas	Moisture, gas, and gas–liquid inclusions associated with both organic and inorganic matter

Source: Taken from Ref. [2].

Alkali metals play a crucial role in thermal degradation of biomass. Especially, potassium catalyzes both volatile combustion and char burnout reactions, at least under low-temperature combustion [3]. In addition, experimental evidence suggests that alkaline additives act as homogeneous catalysts in various hydrothermal degradation reactions such as the conversion of glucose into formate salts [4].

Potassium is a key plant nutrient and present in varying amounts, depending upon the type of biomass, its growing conditions, and time of harvest. Of all the metals present in biomass, it is potassium that has the greatest influence on its thermal conversion properties. In general, the metal species in biomass are important in thermochemical conversion processes because of their impact on

secondary degradation reactions, slagging, fouling, and other ash-related problems [3].

Alkali metals can be removed from the biomass, for example to prevent their catalytic effects on the fractionation of biomass. Natural leaching by rainfall during the period between biomass harvest and collection can already substantially reduce the content of alkali metal salts, especially chlorides. Alkali metal salts are soluble in (acidified) water, and just leaving the biomass on the field and exposing it to rain during the period between harvesting and collecting can lead to a removal of 30%–45% of potassium and chloride, respectively [5]. So, on-field leaching can offer an additional low-cost, on-farm strategy option to improve biomass quality for further biorefinery purposes.

Industrially, leaching of minerals from biomass commonly takes place in the sugar refining industry, where leaching is applied to remove the sucrose from the solid bagasse residue. During this process, inorganic material is substantially removed as well. Design variables related to leaching are the ratio water to biomass (and the presence of acids), the temperature of the water, the leaching time, and the application of dedicated mechanical means to dewater the biomass. The addition of acid to the leaching water increases the efficiency of the alkali metal leaching, although most of the alkali metals can be removed by water only. The increased potassium content in the leachate might render this stream suitable as feed for the fertilizer industry provided that there are no heavy metals present [6].

9.2.2 Solvent Extraction of (Organic) Extractable Material

Lignocellulosic biomass such as wood and straw contains extractives, including lipids, phenolic compounds, terpenoids, fatty acids, resin acids, steryl esters, sterol, waxes, and proteins. Generally, the extractive content varies between 2% and 5% for woods and 5% and 15% for straws but can be as high as 30% for feedstocks like olive tree prunings [7]. Although extractives generally contribute little to the overall wood composition, they can exert a significant influence on properties such as mechanical strength, color, and thermochemical stability. For biorefinery it might be desirable to

remove the extractable compounds either to valorize them or to avoid interference of the extractives during the fractionation and/or conversion of the main constituents—hemicellulose, cellulose, and lignin.

Shebani et al. studied the effect of water-soluble and organic solvent–soluble extractives on the thermochemical stability of four wood species via an elaborate thermogravimetric analysis (TGA) study [8]. In general, the results suggest that a higher cellulose and lignin content leads to a better thermal stability of wood in different temperature regimes. It was also found that hot-water extractives decompose at lower temperatures than hemicelluloses and appear to protect the hemicelluloses. Ohtani et al. assumed that hot-water extractives suppress the decomposition and loss of hemicelluloses by acting as a protector for hemicelluloses during the alkaline cooking [9]. Removal of these extractives would render the hemicellulose more susceptible for thermochemical conversion such as acid-catalyzed hydrolysis.

Extractives can be removed from the biomass by solvent extraction, where the solvent can be water or a suitable and recoverable organic substance. For instance, Speaks et al. (1997) describe a process for extracting volatile organic compounds and higher-molecular-weight compounds ("pitch") from wood particulates. Thus, the emission of volatile organic compounds into the atmosphere during the processing of wood particulates into commercially useful products, such as oriented strand board, particle board, chipboard veneers, and various pulp and paper products is virtually eliminated [10]. In the extraction process, a solvent or mixture of solvents is used to remove wood extractives, including volatile organic compounds and pitch, from the wood particulates. The best results were obtained with acetone.

The example above merely illustrates the removal of extractives as undesired compounds for the further production of wood pulp. Within the framework of lignocellulosic biorefinery, an efficient removal of extractives is a desirable asset, too, because, in general, it enables the production of purer cellulose and lignin fractions, and it may increase the enzymatic digestibility (hydrolysis) of the cellulose when compared to the case in which extractives have not been removed.

Recently, Smit et al. (2014) described a treatment process for lignocellulosic biomass via an improved organosolv procedure that

involves removal of extractives (world patent WO 2014/126471) [11]. A preferred procedure consists of an aqueous pre-extraction at a temperature in between 20°C and 60°C followed by an extraction with an organic solvent such as ethanol or acetone at a temperature in between 30°C and 80°C. During the two-stage extraction procedure, nonstructural components such as salts, proteins, fatty acids, triglycerides, waxes, terpenes, and resin acids are removed, leading to an improved purity of the cellulose and lignin fractions, better lignin properties (less pseudolignin formation), and increased enzymatic cellulose digestibility. Hydrophilic components (e.g., salts and water-soluble proteins) are predominantly washed away during the aqueous pre-extraction. Lipophilic components (lipophilic proteins, fatty acids, triglycerides, waxes, terpenes, resin acids, etc.) are predominantly extracted during the treatment with an organic solvent. An example of an application of extractives within a biorefinery itself is given in patent WO2014/098589. In this patent, Smit and Huijgen present a method in which the protein containing aqueous extract from biomass types such as grass and straw is used later on to improve the enzymatic digestibility of cellulose [12]. The authors hypothesize that the extracted proteins adsorb on residual lignin present in the cellulosic substrate resulting after pretreatment. This presumed adsorption prevents inactivation of hydrolytic enzymes by irreversible binding to lignin.

It should be noted that the organosolv procedures, as described above, are particularly suitable for the production of high-purity cellulose and lignin. The hemicelluloses have relatively limited thermochemical stability and tend to break down as a result of the relatively high temperatures employed during organosolv. In general, hemicelluloses are hydrolyzed into C_5 and/or C_6 sugar monomers, which may be subsequently dehydrated to furans such as furfural and hydroxymethylfurfural (HMF) under the influence of acid. These furans are reactive and tend to be converted to other compounds via recondensation and repolymerization reactions among themselves or with lignin-derived species. These secondary products are undesired and in general less valuable than products such as monomeric hemicellulose sugars or their primary furanic conversion compounds. In addition, these degradation products can pollute the cellulose and lignin fractions, rendering them less suitable for direct application or further processing.

After the removal of inorganic and organic extractives from the lignocellulosic biomass by suitable aqueous and organic extraction schemes, a next step in a solvolysis cascade can be the selective hydrolysis and optional depolymerization of the hemicellulose constituent, leaving a purified solid lignocellulose complex for further processing.

9.2.3 Removal of Hemicellulose by (Auto-) Catalytic Hydrolysis

In 2009 De Wild et al. published research on a hybrid biorefinery concept. The concept encompassed the selective removal of hemicellulose by a so-called aquathermolysis approach (treatment with hot pressurized water) as a first process step, followed by a second pyrolysis step with the remaining lignin–cellulose complex [13]. The fact that hemicellulose can be quantitatively removed from biomass by treatment with hot pressurized water has been known for some time [14–20]. The treatment results in water-soluble oligomeric and monomeric sugars and their degradation products such as furfural and HMF, both of which are valuable chemicals [21, 22].

The hydrolysis and further dehydration of the hemicelluloses is catalyzed by acetic acid, originating from the acetyl groups of hemicellulose. Simultaneously, water-soluble components like alkali metal ions and water-soluble extractives are leached out from the solid biomass. Cellulose and lignin are relatively unaffected by the hot-water treatment, although parts of the lignin may be solubilized as well, especially when the product liquor is continuously removed from the solid biomass [23]. The amount of dissolved lignin depends on temperature and reaction time. Longer reaction times and/or higher temperatures render the lignin insoluble due to recondensation reactions [15, 24]. The recondensed structures could be thermally more stable than the parent material and less prone to thermal degradation under conditions where cellulose degrades. The removal of the hemicellulose and the apparent increase in thermochemical stability of the (recondensed) lignin implies that in a subsequent pyrolysis step a more selective depolymerization of cellulose is possible, for example, resulting in enhanced yields of levoglucosan and less lignin-derived degradation

fragments when compared to direct pyrolysis of the original feedstock. Supported by an extensive nuclear magnetic resonance (NMR) study, the work clearly showed that aquathermolysis results in removal of hemicellulose and that lignin ether bonds are broken. Apart from that, lignin seems hardly affected by the aquathermolysis [25]. Cellulose is also retained, although it seems to become more crystalline, probably due to a higher ordering of amorphous cellulose when the samples are cooled down after aquathermolysis. Figure 9.3 presents a schematic overview of a possible hybrid biorefinery in which aquathermolysis and pyrolysis are combined.

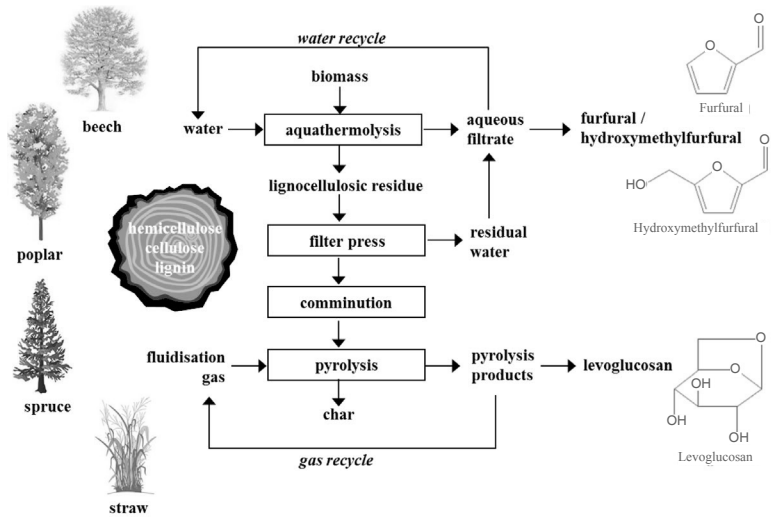

Figure 9.3 Hybrid biorefinery concept [1].

Alternatively, after the removal of the hemicellulose, the resulting (wet) cellulose–lignin complex can be further fractionated by the action of an organic solvent. This organosolv process uses a mixture of water and an organic solvent to extract and thereby separate the lignin from the cellulose.

In general, the aqueous ethanol organosolv process is conducted at conditions that lead to extensive degradation of the hemicellulose sugars. To prevent degradation and to eventually recover the sugars from the hemicellulose fraction, Huijgen et al. applied prehydrolysis, targeted at the hydrolysis of the hemicellulose polymer from wheat

straw into monomeric xylose [27]. Although the treatment resulted in a significant amount of xylose released, the lignin yield in the subsequent organosolv delignification step decreased due to the formation of so-called pseudolignin and lignin recondensation during the prehydrolysis step.

9.2.4 Separation of Lignin and Cellulose by Organosolv Fractionation

9.2.4.1 Organosolv fractionation

Organosolv is based on the treatment of biomass with an (aqueous) organic solvent at elevated temperatures [28–30].

Commonly used solvents are ethanol, methanol, acetone, and organic acids like acetic acid and formic acid or combinations thereof. Organosolv processes primarily delignify lignocellulose, with the organic solvent functioning as lignin extractant. Simultaneously, the hemicellulose fraction is depolymerized through acid-catalyzed hydrolysis. In general, organosolv processes aim to fractionate the lignocellulosic biomass as much as possible into its individual major fractions in contrast to other pretreatment technologies such as steam explosion and dilute acid hydrolysis.

While other pretreatment technologies merely make the cellulose fraction suitable for further processing without recovery of a purified lignin fraction, organosolv coproduces lignin with high purity (limited amounts of residual carbohydrates and minerals). In addition, organosolv lignins have a relatively low molecular weight with a narrow distribution and very low sulphur content. Consequently, their application spectrum is broader compared to the more impure lignin-containing residues derived from conventional pretreatments, which are targeted primarily toward the production of cellulose for paper or second-generation bioethanol. These lignin-containing residues are a complex mixture of unconverted carbohydrates, lignin, minerals, and process chemicals or microbial residues. Hardly any applications for such complex by-products have been identified other than combustion for combined heat and power (CHP). A block scheme of the aqueous ethanol organosolv

process as developed and practised at the Energy research Centre of the Netherlands (ECN) is presented in Fig. 9.4.

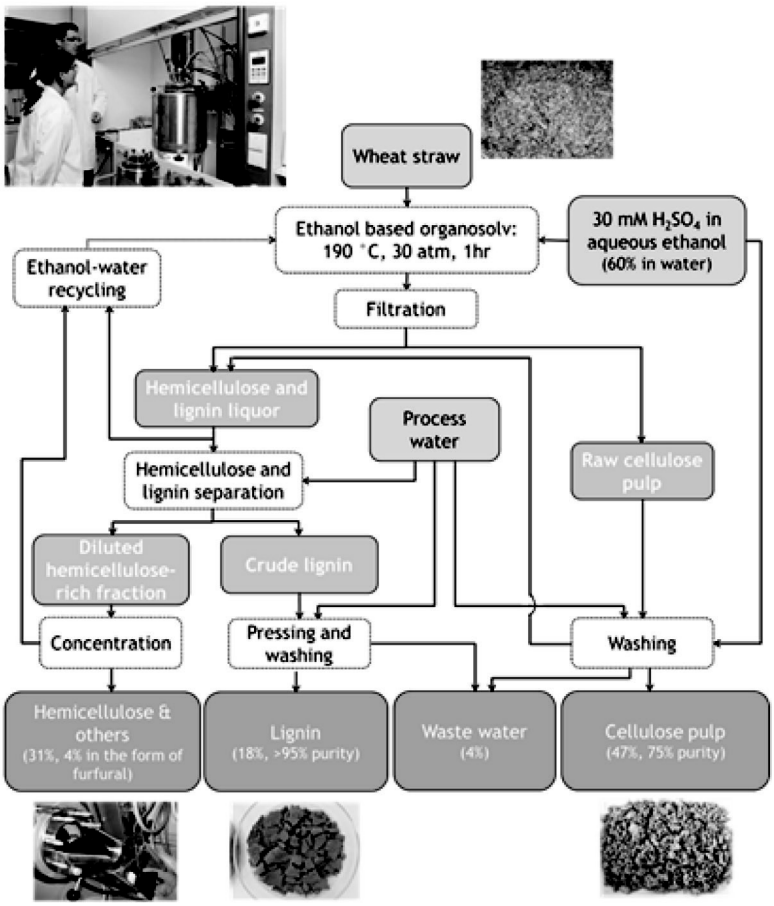

Figure 9.4 Fractionation of wheat straw by aqueous ethanol organosolv [31].

Another example of organosolv fractionation technology is the acetic acid/formic acid process, exploited by the French Compagnie Industrielle de la Matière Végétale (CIMV).

In Pomacle, France, the CIMV operates a pilot plant that takes in 100 kg/hr wheat straw that is treated with a mixture of acetic

acid and formic acid [29, 32]. The CIMV pilot plant differs from most other lignocellulosic biorefineries because it produces a high-quality lignin as a separate marketable product instead of a solid fuel. Figure 9.5 presents a schematic diagram of the CIMV biorefinery concept and a photograph of the pilot plant in France.

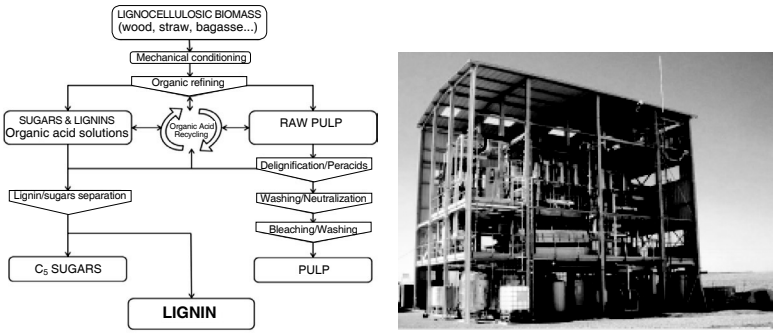

Figure 9.5 Process scheme and photograph of the CIMV organic acid–based organosolv process [33].

Figure 9.6 gives a photographic impression of the CIMV biorefinery products from wheat straw.

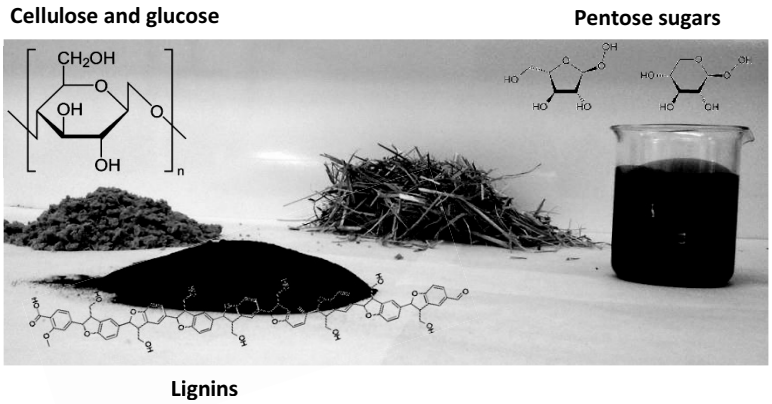

Figure 9.6 Typical biorefinery products from CIMV organosolv fractionation [33].

Both the ethanol and the organic acid organosolv processes are examples of modern fractionation technologies for lignocellulosic

biomass that are specifically aimed at the production of pure biomass fractions for further processing to value-added chemicals and other materials to enhance the profitability of the biorefinery. A generic view of future organosolv-based biorefineries is presented in Fig. 9.7.

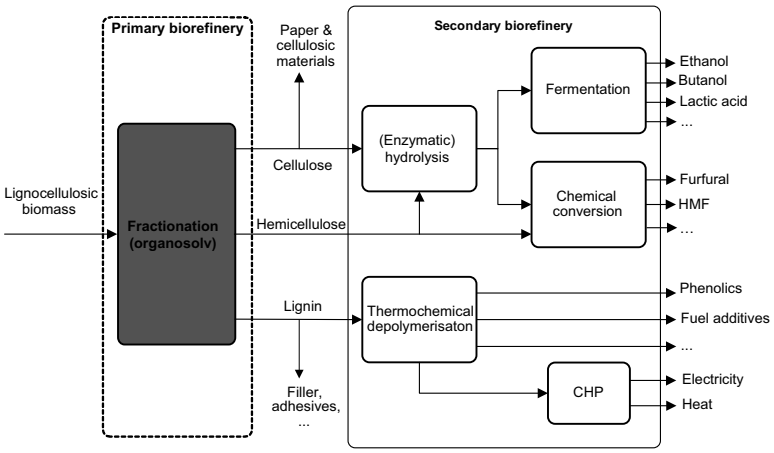

Figure 9.7 General layout of an organosolv-based biorefinery [30].

Finally, Fig. 9.8 is an example of a more detailed concept of an organosolv-based biorefinery, targeted at the fractionation of biomass into hemicellulose, cellulose, and lignin and the integrated further conversion of the hemicellulose pentoses into furfural.

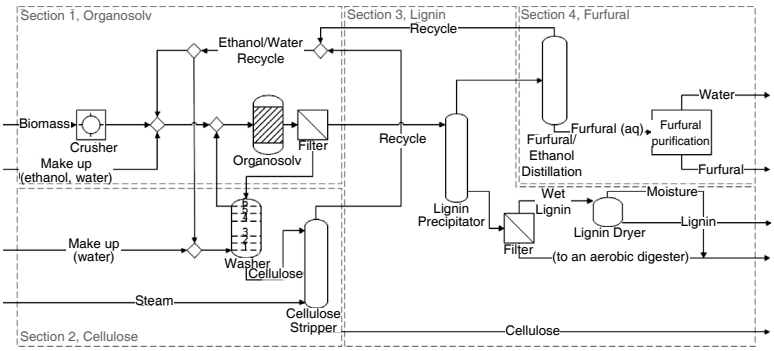

Figure 9.8 Ethanol-based organosolv biorefinery [34].

9.2.4.2 Prehydrolysis–organosolv approach

Various experimental studies on hydrolysis of hemicellulose prior to organosolv treatment have been published during the last years, such as with steam [35], dilute acid presoaking [36], and hydrothermal pretreatment [37–39]. In an approach to improve the ethanol-based organosolv fractionation of lignocellulose, Liu et al. also attempted a prehydrolysis step, aimed at the removal of the hemicelluloses prior to the separation of the lignin and the cellulose [40].

Recently, Huijgen et al. reported for wheat straw a staged approach targeted at the removal of hemicellulose, prior to the subsequent lignin–cellulose fractionation and enzymatic cellulose hydrolysis [27]. Wheat straw was fractionated using a three-step biorefining approach: (1) aqueous pretreatment for hemicellulose prehydrolysis into sugars, (2) organosolv delignification, and (3) enzymatic cellulose hydrolysis into glucose. Prehydrolysis was applied to avoid degradation of hemicellulose sugars during organosolv delignification.

The prehydrolysis–organosolv approach was compared to a direct one-step organosolv treatment (i.e., without prehydrolysis) to elucidate the influence of the prehydrolysis step on the delignification during subsequent organosolv treatment and the resulting enzymatic digestibility of the cellulose fraction. The experimental approach is illustrated in Fig. 9.9.

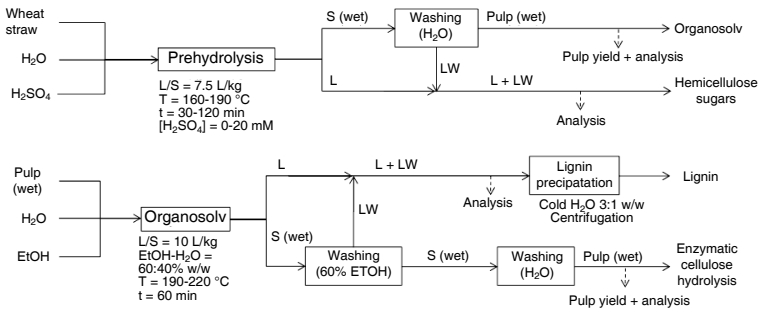

Figure 9.9 Experimental approach of direct organosolv vs. prehydrolysis—organosolv of wheat straw. Reprinted from Ref. [27], Copyright 2012, with permission from Elsevier.

The one-step organosolv treatment using a single arbitrary set of process conditions resulted in 67% lignin removal and 51%

xylan removal from the wheat straw. At the same time, 95% of the glucan remains in the solid fraction. In spite of the 51% xylan removal, the xylose yield is only 4% based on the xylan content of the feedstock. This xylose is mainly present in the form of oligomers. In total, residual xylan and identified xylan derivatives (including a furfural yield of 2%) account for only 56% of the original xylan in the feedstock. The remaining 44% has reacted into unidentified products, including possibly condensates with lignin [41]. The enzymatic digestibility of the produced cellulose-enriched pulp is 51% compared to 15% for untreated raw wheat straw.

Subsequently, prehydrolysis was performed prior to the organosolv delignification. Organosolv was performed at identical conditions as used for the organosolv experiment without prehydrolysis. The influence of prehydrolysis temperature (160°C, 175°C, 190°C), reaction time (30, 60, 120 min), and addition of H_2SO_4 (0, 10, 20 mM) as a catalyst was studied around the initial experiment. The use of a prehydrolysis step prior to organosolv delignification of wheat straw was found to improve the yield of xylose and the enzymatic cellulose digestibility. The maximum xylose yield obtained was 67% compared to 4% in the case of organosolv without prehydrolysis. However, prehydrolysis was found to reduce the lignin yield by organosolv delignification due to the formation of pseudolignin and lignin recondensation during prehydrolysis. This reduction could partly be compensated by increasing the temperature of the organosolv delignification step to 220°C. In addition, the application of a prehydrolysis step was found to substantially improve the enzymatic cellulose digestibility despite the recondensation of lignin and/or pseudolignin on the cellulose. Increasing the organosolv delignification temperature to 220°C resulted in a maximum enzymatic glucose yield of 93% or 0.36 kg/kg straw.

9.2.5 Conclusion: Staged Solvolysis

It is obvious that staged solvolysis can lead to relatively pure, separate fractions that can be further processed by dedicated technologies. However, the added value of the produced fractions should be counterbalanced by the costs related to the use of different solvents and processing technologies. Depending on the type of

biomass and the desired products, direct solvent-based liquefaction may be a viable alternative to valorize the biomass. The next section will briefly address some current developments in the field of direct solvolytic processing of lignocellulosic biomass.

9.3 Direct Solvolysis of Lignocellulosic Biomass for Fuels and Chemicals

9.3.1 Introduction

Direct solvolysis is a thermochemical liquefaction process using water and/or organic solvents to convert the solid lignocellulosic biomass into a liquid product. The objective of a total dissolution or liquefaction of biomass is to facilitate transportation, refining, and conversion. Liquefaction may enable the use of biomass as feedstock in conventional crude oil refineries with the use of conventional or modified processing/separation technologies. Currently, (fast) pyrolysis is intensively explored as liquefaction pretreatment for biomass processing in refineries. Despite the fact that modern state-of-the-art fast pyrolysis easily achieves liquid yields up to 80 wt.% (based on the dry biomass weight), the resulting fast pyrolysis oil is still unsuitable for direct processing in conventional crude oil refineries because of its acidity, water content, instability, solids content, etc. [42]. Direct solvolysis-based liquefaction may offer advantages compared to (fast) pyrolysis due to milder and more controlled process conditions.

In the case of water only, the solvolysis process is generally called hydrothermal liquefaction (HTL) which is performed at subcritical water process conditions (10–25 MPa pressure, 280°C–370°C) with or without catalysts. HTL is best suited for wet biomass and allows for the conversion of a wide range of feedstocks in a so-called liquid biocrude product. A detailed description of HTL can be found elsewhere [43, 44].

Wang and Wang recently reported a comprehensive review of the vast area of solvolysis [44]. Solvolysis has been studied with a variety of organic solvents such as (aromatic) alcohols, polyols, acetone, 1,4 dioxane, tetralin and other hydrogen donor solvents. In their review the authors clearly point out that the type of solvent

greatly influences yield and composition of the resulting bio-oil, although governing principles that determine the specific effects of solvents during liquefaction still require further understanding [44]. It was proposed that differences in density and polarity of the solvent might be a major reason for their different behaviour during liquefaction [45].

9.3.2 Alcoholysis

An example of the use of methanol and ethanol in liquefaction of biomass is given by Grisel et al., who investigated the acid-catalyzed alcoholysis of wheat straw in 95% methanol and in 94% ethanol (w/w) in the presence of various amounts of sulphuric acid and compared it to the alcoholysis of wheat straw-derived organosolv pulp and commercially available celluloses [46].

It was found that lignocellulosic biomass can be converted in a single step via acid-catalyzed alcoholysis using lower linear alcohols. Main products were furfural and alkyl glucosides. The major by-products were found to be levulinic acid and its alkyl ester. The amount of insoluble humins that are formed was limited. The depolymerization and alkylation of carbohydrates are mainly Brønsted acid-catalyzed and the presence of proton-consuming compounds, such as acid-neutralizing native minerals or chloride, hamper the liquefaction efficiency and the alkyl glucosides yields. The optimum acid dose needs to be adjusted to the acid neutralization capacity of the biomass. The amount of dimethyl ether formed from methanol under these conditions was limited but became readily more prominent at higher temperatures.

Solvent loss due to ether formation from ethanol condensation was much smaller. Delignification prior to alcoholysis did not influence the results much but allowed higher product concentrations and enables a separate lignin valorization. The glucosides can be separated, for example, by means of chromatography, and may be converted into furan building blocks, for example, for the production of plastic precursors, such as 2,5-furandicarboxylic acid.

Eerhart et al. compared direct alcoholysis of wheat straw for the production of furans with organosolv fractionation of wheat straw followed by (1) alcoholysis of the resulting cellulose pulp or (2) enzymatic hydrolysis of the cellulose [47]. It was concluded that all

three routes studied technically could be a viable option to produce biofuels and biobased plastics via the furan pathway at efficiencies generally higher than other biorefinery processes such as production of second-generation bioethanol.

9.3.3 Direct Solvolysis in the Presence of Hydrogen Donor Solvents

In the quest for so-called drop-in fuels from biomass, a major challenge is an effective removal of oxygen from the crude bio-oil product. In fast pyrolysis this is addressed by using specific in situ or ex situ catalytic approaches, often in the presence of hydrogen. Also the catalytic hydrodeoxygenation of fast pyrolysis oil is pursued to some extent [48]. Analogous to approaches in the fast pyrolysis field, in direct solvolysis processes the use of hydrogen is investigated, too, for oxygen removal from the solvolysis products. Hydrogen donor solvents such as tetralin or formic acid can be deployed to generate hydrogen in situ during the solvolysis.

Kleinert and Barth have reported on the conversion of lignin to liquids with the aim of obtaining liquid fuels. The high oxygen content and the dominance of aromatic structures in lignins require a high degree of chemical transformation and incorporation of additional hydrogen to give stable, nonpolar, petroleum-soluble liquid products [49]. The authors deployed formic acid/alcohol mixtures as the reaction medium for converting lignin to liquid "oils" in a solvolysis process. During the conversion, both depolymerization and removal of oxygen by formation of water occur in a single step. Formic acid serves as both the hydrogen donor and reaction medium in the solvolysis process. Using an alcohol as cosolvent can improve the liquid yields and H/C ratios. Very little coke (5%) was produced. The liquids produced comprise two phases that can be easily separated, where the lighter organic phase consists mainly of low-molecular-weight alkylphenols and C_8–C_{10} aliphatics. The process is developed to be combined with, for example, bioethanol production from lignocellulosic carbohydrates in a biorefinery concept aimed at converting all fractions of the wood into renewable liquid fuels. The solvolysis process uses formic acid as the reagent for both depolymerization and oxygen removal. Although formic acid is a costly chemical, it may be generated from biomass in an integrated oxidative process.

9.3.4 Direct Liquefaction with Biomass-Derived Phenolic Solvents

Preferred organic solvents for direct solvolysis can be derived from biomass itself and provide a good performance during liquefaction, including a good recoverability. For instance, Azadi et al. reported on an approach by which the hemicellulose and cellulose fractions of biomass are converted through catalytic processes into platform chemicals and transportation fuels using an organic solvent obtained by depolymerization of the lignin fraction [50].

In the paper, the authors aim at the production of second-generation biofuels from lignocellulosic biomass through the intermediate production of oxygenated platform molecules, such as furan intermediates (furfural [FuAl], furfuryl alcohol [FuOH], and HMF), levulinic acid (LA), and γ-valerolactone (GVL). The organic solvent is prepared by the catalytic depolymerization of the lignin part of poplar and consists of alkyl-substituted phenolics. Figure 9.10 shows the roadmap proposed by the authors for the conversion of lignocellulosic biomass to fuels and chemicals.

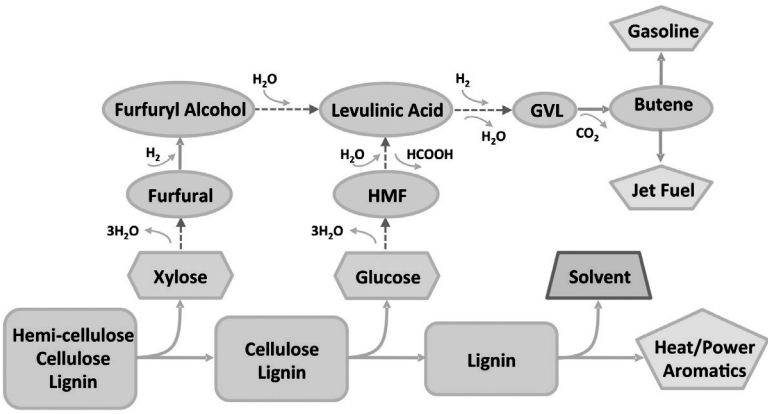

Figure 9.10 Roadmap for conversion of lignocellulosic biomass (rectangles) to chemicals (ovals) and fuels (pentagons), passing through the intermediate formation of C_5 and C_6 sugars (hexagons). Dashed arrows indicate processes that can be carried out using a lignin-derived organic solvent for the production of furfural, HMF, levulinic acid, and GVL [50].

Another example of the use of a lignin-derived solvent for biomass liquefaction is given by Kumar et al., who used guaiacol (2-methoxyphenol) as a solvent for direct liquefaction of lignocellulosic feedstock [51]. In an extensive parameter study, the authors showed that pine wood could be converted to bio-oil in guaiacol with an oil yield of >90% (based on C) at 300°C–350°C without catalysts or reactive atmospheres. Process conditions such as temperature, heating rate, reaction time, and water concentration were optimized to achieve the best compromise between maximizing the bio-oil yield and minimizing the fraction of heavy ends with a molecular weight >1000 Da. Best results were obtained at a temperature in the range of 320°C–350°C, a reaction time >200 seconds, and the addition of up to 10 wt.% of water. A remarkable mechanistic result was that the formation of undesired vacuum residue (heavy ends) apparently is not due to secondary condensation of bio-oil but rather to incomplete primary depolymerization of the reacting biomass with simultaneous dehydration of fragments. Water acts as a catalyst and accelerates liquefaction, but it seems not to affect the final product yields. Final conclusion of the work was that the 30% final vacuum residue is still too high to allow effective recycling of the bio-oil as a liquefaction medium. Alternative approaches are needed such as the use of catalysts or the removal and/or cracking the heavy ends prior to recycling.

These approaches are interesting and merit further research because the possibility to use bio-oil or fractions thereof as effective liquefaction solvents offer several advantages, both from a process and a fundamental chemical point of view. Biomass-derived fractions for solvolysis may be integrated in the whole process, thereby minimizing the need for an external solvent supply. Chemically, the principle "like dissolves like" offers interesting liquefaction possibilities. For instance, in the Noguchi process, phenol was used to liquefy lignin prior to hydrogenation to monophenolic compounds [52]. Kakemoto et al. patented a thermochemical method to manufacture phenols from lignin that was extracted in a solvolysis pulping process by a solvent containing phenols [53]. The subsequent thermochemical deconstruction of the lignin took place in a mixture with a double-ring aromatic solvent such as naphthalene. More recently, Okuda et al. selectively converted lignin

at 400°C into single-chemical species using a water–*p*-cresol mixture [54].

9.3.5 Direct Liquefaction with Ionic Liquids

Alternatively to organic solvents as described in previous paragraphs, also the use of ionic liquids (ILs) and deep eutectic solvents (DESs) has been explored for the pretreatment, fractionation, and/or liquefaction of lignocellulosic biomass. Vancov et al. recently reviewed a pretreatment method for lignocellulosic materials using ILs [55]. The authors focus on the use of ILs for dissolution of cellulose for further enzymatic hydrolysis and fermentation. ILs are nonvolatile solvents that exhibit unique solvating properties. In their review the authors describe the dissolution of cellulose and lignocellulose in various ILs, including key properties such as high hydrogen-bonding basicity, which increases the ability of the IL to dissolve cellulose. As a pretreatment in biofuel production, the review details aspects such as the regeneration of cellulose from ILs, structural changes that arise in the regenerated cellulose and their effect on enzymatic hydrolysis, the potential for IL recycling, and, finally, exploitation of ILs in an integrated bioprocess. ILs could hold the key to unlocking new and exciting processes for the production of biofuels from lignocellulosic materials. ILs have many advantages over traditional solvents, such as their low volatility, which arises from them having no vapor pressure, nonflammability, odorlessness, and thermal stability. ILs can be specifically designed and the liquid's ability to dissolve a variety of polar and nonpolar materials makes them useful for dissolving the complex structure of lignocellulose. Current literature on the use of ILs as a pretreatment in the production of bioethanol showed that the process seems promising because lignocellulose dissolved in ILs can be easily regenerated by the simple addition of an antisolvent. Regenerated cellulose is amorphous and porous and much more responsive to enzymatic saccharification. However, the use of ILs for biorefinery has major shortcomings, especially in process development (including difficulties in recycling of the IL due to build-up of contaminants) and current costs of the solvents.

Brandt et al. have critically reviewed the application of ILs for the deconstruction and fractionation of lignocellulosic biomass [56]. In their extensive review the authors address the solubility of lignocellulosic biomass (and the individual biopolymers within it) in ILs, the deconstruction effects brought about by the use of ILs as a solvent and practical considerations regarding the design of IL-based deconstruction processes.

In conclusion the authors state that ILs have as major advantage that they are able to decrystallize cellulose with a simultaneous disruption of the lignin–hemicellulose network. The possibility of removing lignin with the IL and recovering a separate, possibly more valuable lignin fraction is also an attractive feature. However, deconstruction with ILs will only be viable if its advantages outweigh the major drawback of ILs, their cost in relation to the cost of the feedstock that has to be treated and the revenues for the final products. Other important hurdles/research challenges are the relatively large amount of ILs needed to treat biomass, the recycling of the spent ILs, the end of use recovery of ILs, toxicity of residual ILs on downstream processing, and the health and environmental impacts of ILs in general.

Recently, also the use of DESs, also called low-transition-temperature mixtures (LTTMs), for biomass processing has been proposed [57, 58]. DESs are eutectic mixtures of solids that due to strong hydrogen bonding interactions show a very low transition temperature and are therefore liquid at low temperatures. Examples of DESs include mixtures of hydrogen bond donors, such as urea, oxalic acid, and lactic acid, and hydrogen bond acceptors, such as choline chloride, alanine, and proline. DESs are potentially much cheaper solvents than ILs and are, in principle, biorenewable. Fransisco et al. reported the ability of lactic acid–choline chloride mixtures to dissolve lignin [58]. Since the same DES showed no cellulose solubility, it might be used for lignin–cellulose separation purposes.

Both ILs and DESs have interesting characteristics, but it should be realized that research on the use of these solvents in lignocellulose pretreatment or as part of an integrated bioprocess

is obviously in its infancy. At the current stage, it is too early to draw any conclusions here whether, in the end, these solvents could be applied economically in industrial biorefinery processes.

9.3.6 Conclusion: Direct Solvolysis

Direct solvolysis is a thermochemical liquefaction process using water and/or organic solvents to convert the solid lignocellulosic biomass into a liquid product that enables easier transportation, refining, and conversion in conventional crude oil refineries with the use of conventional or modified process technologies. Currently, (fast) pyrolysis is intensively explored as liquefaction pretreatment for biomass processing in refineries. Despite the fact that modern state-of-the-art fast pyrolysis easily achieves liquid yields up to 80 wt.% (based on the dry biomass weight), the resulting fast pyrolysis oil is still unsuitable for direct processing in conventional crude oil refineries because of its acidity, water content, instability, solids content, etc. Due to milder and more controlled process conditions direct solvolysis-based liquefaction may offer clear advantages compared to (fast) pyrolysis. However, at the moment fast pyrolysis seems to be a more mature technology when compared to solvolysis. For example, fast pyrolysis is routinely performed in continuous-reactor systems, while solvolysis processes are currently generally still operated at a small scale and in batch mode. Which technology will prevail at the end of the day is difficult to predict and will depend on the balance between processing flexibility, costs, and quality of final products.

9.4 Conclusions

This chapter presents a perspective on the solvent-based fractionation and liquefaction of lignocellulosic biomass via a brief overview of staged and direct solvolysis processes. Staged approaches offer the clear benefit of separation of all major biomass fractions, enabling the deployment of dedicated upgrading technologies for each of the separate fractions. Of course, the revenues from the final products should provide a sufficient

economic margin for capital and operational expenses that come with the different process steps in the staged approach and the further upgrading. Therefore, staged approaches seem to be especially preferable when specific high-value chemicals are the desired products. On the other hand, when the target product is a drop-in biofuel, direct solvolysis may be the technology of choice, analogous to fast pyrolysis. Overall, significant progress has been made in the field of solvent-based biorefinery of lignocellulosic biomass in recent years and solvent-based processes might make a substantial future contribution to the biobased economy.

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