Biomass Pyrolysis for Hybrid Biorefineries

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Upper picture: Oleochemical Biorefinerie of Avril, Grand-Couronne/France, photo credit: Cédric Helsly, with kind permission
Lower picture: Rapeseed cultivation in the Picardie region/France, photo credit: Philippe Montigny, with kind permission
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CHAPTER 8

Biomass Pyrolysis for Hybrid Biorefineries

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1. INTRODUCTION

Biomass such as lignocellulose (e.g., woods and grasses) and aquatic resources (e.g., seaweeds and microalgae) is the only renewable carbon source for the production of chemicals, materials, and fuels. Decreasing fossil resources, global warming, and environmental

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pollution associated with the use of fossil fuels are growing incentives for the transition to renewable energy including solar, wind, hydrogeothermal, and biomass. Biomass is particularly suited as an abundant, low-cost feedstock for the production of biobased chemicals, fuels, and energy to substitute fossil resources. Although the global biomass resources alone might be insufficient to accommodate the world's ever-increasing power needs, it can provide carbon-containing raw materials because its unique composition makes it especially suitable for the extraction of value-added chemicals and materials that can replace petrochemicals including fuels.[1,2] Analogous to the processing of fossil oil in an oil refinery, a biorefinery uses different types of biomass feedstocks that are processed via different technologies into heat, power, and various products. The biorefinery is self-sustainable with respect to heat and power and puts no burden on the environment. The pyrolysis-based processes that are described in this chapter can play an important role in biorefineries, either as a central processing unit or as a more peripheral unit, to process biorefinery side streams.

2. PYROLYSIS-BASED FRACTIONATION OF BIOMASS

2.1 Introduction: Pyrolysis

In general, the main biomass fractions hemicellulose, cellulose, and lignin react differently when subjected to different temperatures to yield different products.[3–6] This can be exploited to extract value-added chemicals by pyrolysis, the thermal degradation of organic material in the absence of (molecular) oxygen. Pyrolysis is a versatile thermal conversion technology in several varieties, such as slow, intermediate and fast pyrolysis, depending on the desired products. Table 8.1 summarizes the main pyrolysis technologies and their major products. Table 8.1 shows that several temperature and heating rate regimes are used, depending on the desired product slate.

In general, charcoal is the main product from carbonization of wood or other lignocellulosic biomass types, and when appropriate, by-products such as acetic acid and wood tars are recovered.[8] Torrefaction generates an enhanced fuel for heat and power via a mild thermal treatment that transforms lignocellulosic biomass into a solid material with a higher energy density, a better grindability, and a lower moisture susceptibility than the original biomass.[9] Finally, fast and intermediate pyrolysis is developed to generate high liquid yields from biomass.[7] The so-called pyrolysis oils or biooils can be used as liquid fuels for heat and power generation and also as a feedstock for chemicals.[10] Since the late 1970s, fast pyrolysis technology has been developed as a thermochemical conversion technology to produce high yields of biooil from biomass.[11–14] Fast pyrolysis rapidly heats the usually finely ground and dry biomass (typically 10 wt% of moisture) to temperatures around 500 °C, causing a release of a multitude of thermal degradation products that are quenched within a few seconds to produce the so-called "pyrolysis oil" or "biooil," a mixture of condensed organic compounds and water. In addition, char and permanent gases are formed. Table 8.2 gives an example of the average chemical

Table 8.1 Modes of pyrolysis and major products

Mode	Reaction conditions	Reactor technology	Liquid	Solid	Gas
Fast	Reactor temperature 500 °C, high heating rates >1000 °C/s, short hot vapor residence ~1 s	Fluidized bed, entrained flow, ablative (contact pyrolysis)	75%	12% char	13%
Intermediate	Reactor temperature 400–500 °C, heating rate range 1–1000 °C/s, hot vapor residence ~10–30 s	Same as for fast pyrolysis plus auger type of reactors	50%	25% char	25%
Slow Carbonization	Reactor temperature 400–500 °C, heating rate up to 1 °C/s, long solid residence hours–days	Moving bed retorts, augers, batch fixed bed reactors	30%	33% char	35%
Slow Torrefaction	Reactor temperature ~290 °C, heating rate up to 1 °C/s, solids residence time ~30 min	Same as for carbonization	0–5%	77% solid	23%

Adapted from Ref. 7.

Table 8.2 Compound classes in biooil[10]

Compound class	Composition range (wt% based on the organic fraction of biooil)
C_1 compounds (formic acid, methanol, formaldehyde)	5–10
C_2–C_4 linear hydroxyl and oxosubstituted aldehydes and ketones	15–35
Hydroxyl, hydroxymethyl, and/or oxosubstituted furans, furanoses, and pyranones (C_5–C_6)	10–20
Anhydrosugars including anhydrooligosaccharides (C_6)	6–10
Water-soluble oligomeric and polymeric carbohydrate fragments of uncertain composition	5–10
Monomeric methoxyl substituted phenols	6–15
Pyrolytic lignin	15–30

composition of biooils from hardwood and softwood. It is obvious that the extraction of value-added chemicals from the complex biooil mixture is difficult and complex. Other challenges for further development of pyrolysis include improvement of the reliability of reactors and processes and the demonstration of the suitability of the oil as a fuel for

boilers, engines, and turbines. Knowledge and control of the type of oxygen functionalities in the pyrolysis oil (i.e., aldehyde, ketone, alcohol, ether, ester, and acid) are needed in relation to the further processing of the oil for different purposes (fuel, feedstock for chemicals, etc.).[14]

2.2 Value-Added Products from Lignocellulosic Biomass Pyrolysis

The different thermal stabilities of hemicellulose, cellulose, and lignin provide an opportunity to use pyrolysis for the thermal fractionation of biomass.[15,16] The bar graph in Figure 8.1 presents a schematic overview of the different thermal stabilities of each of the main biomass fractions.[17] The height of the bars corresponds to the approximate temperature level at which the thermal degradation rate of the biomass constituent under isothermal conditions and in an inert atmosphere reaches a maximum as can be measured by thermogravimetric analysis.[18]

Figure 8.1 indicates the potential for thermal fractionation of the biomass. The order of thermochemical stability of the individual biomass constituents ranges from hemicellulose (fast degassing/decomposition from 200 to 300 °C) as the least stable polymer to

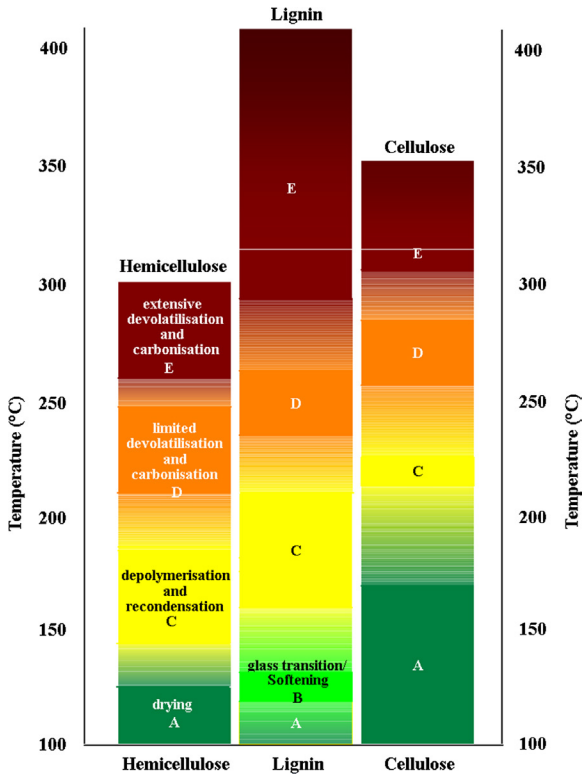

Figure 8.1 Thermal stability regimes for hemicellulose, lignin, and cellulose.[17]

the more stable cellulose (fast degassing/decomposition from 300 to 400 °C). Lignin exhibits intermediate thermal degradation behavior (gradual degassing/decomposition from 250 to 500 °C). This order determines the rate of thermal breakdown and the product slate. Table 8.3 presents an overview of value-added chemicals that can be obtained from each of the main biomass fractions via pyrolysis.[2,8,19]

2.3 Pyrolysis of Algae

2.3.1 General

Aquatic biomass types such as microalgae and macroalgae (seaweeds) have been suggested as good candidates for the production of fuels and value-added chemicals because of their advantages of higher photosynthetic efficiency, higher biomass production, and

Table 8.3 Major chemicals from the pyrolysis of lignocellulosic biomass[2,8,19]

Biomass constituent (thermal degradation range)	Pyrolysis products (major value-added chemicals underlined)	Market application examples of the underlined chemicals
Hemicellulose (150–300 °C)	*Acetic acid*	Bulk chemical, vinegar (food), cleansing agent, vinyl acetate, acetic anhydride, esters, solvent, road deicer (as calcium acetate)
	Furfural	Intermediate commodity chemical, solvent, resins, adhesives, food flavoring agent, precursor for specialty chemicals
	Furan, furanone, methanol, other C_1–C_4 oxygenates (e.g., formaldehyde, hydroxyacetaldehyde, acetone, acetol, lactones, etc.), C_5 and C_6-anhydro-sugars, humic substances	
Cellulose (200–400 °C)	*Levoglucosan*, *Hydroxyacetaldehyde*,	Glucose, polymers, antibiotics food browning agent in "liquid smoke"
	1,6 anhydro-β-D-glucofuranose, furfural, hydroxymethylfurfural, furan, other C_1–C_4 oxygenates (e.g., methanol, formaldehyde, formic acid, acetone, acetol, lactones, etc.)	

Continued

Table 8.3 Major chemicals from the pyrolysis of lignocellulosic biomass[2,8,19]—cont'd

Biomass constituent (thermal degradation range)	Pyrolysis products (major value-added chemicals underlined)	Market application examples of the underlined chemicals
Lignin (150–600 °C)	*2-Methoxyphenols (e.g., guaiacol)*, *2,6-Dimethoxyphenols (e.g., syringol)*, *Catechols*, *Phenol*, *Alkyl phenols*, *Methanol*, Other oxygenated aromatics (e.g., coumaran), furfural, acetic acid, other C_1–C_4 oxygenates (e.g., formaldehyde, formic acid, acetone, acetol, lactones, etc.), pyrolytic lignin	Fine chemicals, pharmaceuticals, food flavoring agents in "liquid smoke," fragrance industry, bulk chemical, wood adhesives, resins, plastics, fuel additives, bulk chemical, solvent, fuel, antifreeze, ethanol denaturant, second energy carrier for H_2, biodiesel
Whole biomass (100–600 °C)	*Extractives (e.g., terpenes)*, *Charcoal*, *Pyrolysis oil*, Gases (e.g., CO, CO_2, CH_4)	Fine chemicals, pharmaceuticals, turpentine, fuel, soil improver, active carbon, metallurgy, cooking (barbecue), liquid fuel, feedstock for chemicals such as organic acids, and phenolic compounds fuel

faster growth when compared to lignocellulosic biomass types. The composition of algae (macroalgae and microalgae) is different from the composition of lignocellulosic biomass types. While lignocellulosic biomass is mainly made up of cellulose, hemicellulose, lignin, and variable amounts of inorganics and organic extractive compounds, algae consist of different types of carbohydrates in combination with various proteins, lipids, and inorganic material. In addition, algae do not contain lignin. Consequently, the pyrolysis products from algae are different. Thermal liquefaction via pyrolysis or hydrothermal processing is a suitable option for the production of biooils and chemicals from algal biomass. Both microalgae and macroalgae can be pyrolyzed using slow and fast pyrolysis technologies to obtain an energy-rich biooil (fast pyrolysis) and biochar (slow pyrolysis).

The presence of a large amount of ash minerals in macroalgae can be tackled by a pretreatment in which a significant part of the minerals are washed out. Subsequent pyrolysis yields a better (i.e., higher heating value) oil. Relatively little information is available on the continuous pyrolysis of algae in, for example, a fluidized bed. The high content of carbohydrates makes algae a possible feedstock for the pyrolytic production of furfural (especially from alginate) and/or other chemicals.

2.3.2 Microalgae

Several studies have shown that microalgae can be pyrolyzed using slow and fast pyrolysis technologies to obtain an energy-rich biooil (fast pyrolysis) and biochar (slow pyrolysis). Typical conditions are relatively mild, that is, atmospheric pressure, inert atmosphere, and process temperatures in the range of 300–600 °C. Typical oil yields of algae pyrolysis are 20–40 wt%.[20–22] In general, the oil produced has a heating value between wood biooils and petrochemical diesel. The use of catalysts in pyrolysis or thermal liquefaction offers good prospects to modify the yield and quality of oils produced.[20,23–25] Pyrolysis of lipid-rich microalgae produces a liquid hydrocarbon mixture rich in free fatty acids and other compounds that can be further purified. The remaining biooil fraction can be used for fuel production or other applications, for example, via catalytic hydroprocessing.[26] Suitable reactor types for pyrolysis include fluidized bed and entrained flow reactors. For biomass with a higher water content, prior drying is usually required. Methods for the processing of wet biomass such as hydrothermal liquefaction may offer attractive conversion options in particular for microalgae and can utilize both carbohydrate and lipid fractions. The development of staged processing comprising an aqueous step in which minerals are removed followed by a higher temperature pyrolytic phase may offer attractive solutions as has been shown for lignocellulose.[27] Further, pyrolysis can be a suitable technology for the upgrading of oils from microalgae to enhance their quality, for example, by decarboxylation to reduce the oxygen content.[28]

2.3.3 Macroalgae (Seaweeds)

It has been known for a long time that dry distillation of seaweed produces oily products. Around 1930 attempts were made to identify the nature of the distillation products in order to assess possibilities to increase the profits in the potash production industry. Direct pyrolysis produces useful organic products such as hydrocarbon gases, phenols, carboxylic acids, organic bases, and neutral molecules and also some valuable inorganic by-products such as ammonia, CO, and potassium chloride. However, in general, the amounts produced are small. So, at the time, it seemed unlikely that simple pyrolysis of seaweeds would be an economic prospect in the future.[29] Ross et al.[30] studied the production of liquid fuels and chemical commodities using analytical flash pyrolysis technology.

They concluded that flash pyrolysis produces interesting compound fingerprints and a range of low molecular weight oxygenated and nitrogen-containing compounds. The fate of nitrogen might pose a drawback in fuel applications and further denitrogenation may be necessary. Probably the most suitable conversion technologies for macroalgae will be those that are most tolerant to the (high content of) ash components in the fuel. So hydrothermal treatments or digestion methods may be better suited for the exploitation of these resources for fuels and chemicals than anhydrous pyrolysis, gasification, or combustion. From an investigation of the pyrolysis behavior of brown macroalgae, Ross

et al.[31] revealed the effect of different pretreatment schemes on the subsequent pyrolysis. It was shown that specific pretreatments (e.g., with acid) can remove a significant proportion of the mineral matter and halogens, although they also selectively extract polymeric materials such as mannitol (water pretreatment) and fucoidan, mannitol, and partially laminarin (acid pretreatment). Residues from the pretreatment appeared to contain less ash and nitrogen. In a recent approach, Anastasakis and Ross[32] hydrothermally liquefied the brown macroalga *Laminaria saccharina* into a biocrude in an autoclave reactor. A maximum yield of 19.3 wt% was obtained. The biocrude had an higher heating value (HHV) of 36 MJ/kg and appeared to be similar in nature to that of a heavy crude oil or bitumen. Also, the biocrude was shown to contain appreciable amounts of nitrogen. Much higher oil yields from macroalgae were obtained by Bae et al.[33] Maxima of 37.5–47.4 wt% of biooil were achieved at a pyrolysis temperature of 500 °C. Bae et al. concluded that the biooil might be better suited as a chemical feedstock than as a fuel due to its high nitrogen content.[33]

3. BIOMASS PYROLYSIS FOR BIOREFINERIES

3.1 Introduction: Biorefineries

Biorefining is the sustainable processing of biomass into a spectrum of marketable products.[34,35] This definition involves a multitude of possibilities to convert biomass into bioproducts via (combinations of) different processing technologies including (bio) chemical and thermochemical processes. Hybrid biorefineries refer to biorefineries that use a combination of processes to convert biomass into heat and/or power, fuels and/or chemicals. Biorefinery concepts can be classified according to platforms, products, feedstocks, and processes. Platforms are based on (1) intermediates from raw materials toward the final biorefinery products, for example, "sugar" or "lignin platform," (2) linkages between different biorefinery concepts, and (3) final products of a biorefinery. Combined platforms are possible (e.g., C_6 and lignin, C_5 and C_6). Intermediates from biomass can be substances such as syngas, biogas, sugars, lignin, and pyrolysis oil. These intermediates are building blocks for the final products of the biorefinery including fuels, chemicals, and (performance) materials.

For example, in a (thermochemical) biorefinery, biomass is converted into energy carriers such as transportation fuels (e.g., ethanol), heat, and power and/or chemicals. In terms of energy content, the amount of biomass for (transportation) fuels and CHP (e.g., by combustion) is much higher than the amount used for the production of chemicals. However, in terms of added value, chemicals can provide a significant contribution to the overall cost effectiveness of the refinery. When the main product of a biorefinery is (hemi)cellulose bioethanol, the lignin ends up in a residue that mostly is used as a fuel to generate heat. The economics of the biorefinery will benefit much from the valorization of this lignin-rich residue to value-added aromatic chemicals.

3.2 European Lignocellulosic Biorefinery Examples

The intrinsic heterogeneity and complexity of biomass call for biorefinery approaches that are adapted to the feedstock and that are impossible to match with current petrochemical technologies. An efficient (thermal) fractionation of the biomass into its main constituents is a key issue.[36] An effective fractionation ensures that each of the main fractions is less heterogeneous than the original material and can be processed further into less complex product mixtures with higher concentrations of the desired chemicals, making their isolation from the mixture more efficient and cheaper.

Examples of fractionation technologies are the several biomass pulping processes that are common practice in the pulp and paper industry (e.g., kraft pulping, sulfite pulping, soda pulping, and organosolv pulping). Here, the biomass is essentially fractionated into cellulose (for paper) and black liquor, a waste stream that predominantly contains residual carbohydrates, and their degradation products (e.g., from the hemicellulose), partly degraded lignin and inorganics from the pulping process. The main application to date of this black liquor is combustion for heat. Another example is the production of bioethanol by fermentation of glucose that is obtained from the acid or enzymatic hydrolysis of cellulose and the production of furfural by dehydration of hemicellulose-derived xylose. In general, these fractionation technologies are complex, time consuming, and expensive. In most cases, they focus on the separation of one or two biomass fractions only (e.g., cellulose pulp and precipitated lignin from organosolv pulping).

In Europe, a limited number of (demo) biorefineries that use lignocellulosic biomass for the production of second-generation bioethanol is currently in operation. For example, the demonstration plant of Abengoa Bioenergy New Technologies (ABNT) in Salamanca, Spain,[37] uses steam explosion of lignocellulosic biomass such as wheat straw to process up to 70 t/d to produce >5 Ml of fuel grade ethanol per year. Another development is the biorefinery of Chempolis in Oulu, Finland[38] (fractionation of agricultural residues using formic acid).

The plant can process 25,000 t/yr of nonwood, nonfood raw material, and will also be used for testing raw materials and producing samples of bioethanol. In Denmark, the Inbicon Biomass Refinery is demonstrating the production of up to 5.4 Ml per year cellulosic ethanol from 30,000 t/yr straw with energy integration with a power station.[39] Inbicon's core technology is a three-stage process consisting of mechanical conditioning of the biomass, hydrothermal pretreatment, and enzymatic hydrolysis. The process releases cellulose, hemicellulose, and a lignin-rich residue and converts them for useful purposes. Steam from the power plant will cook the straw, and the lignin from the ethanol plant will be burned by the power plant. Recently, a commercial biorefinery was commissioned in Crescentino, Italy, by Beta Renewables. This plant uses the patented PROESA™ technology.[40] PROESA is based on steam explosion and enzymatic hydrolysis of agricultural residues. The annual production capacity amounts to 51 Ml/year. Additionally, lignin will be produced as a by-product at some 165 t/year on a wet basis. The

residual lignin or lignin containing side streams from the biorefineries mentioned above is generally used for the generation of heat and power. An exception is the pilot plant of Compagnie Industrielle de la Matière Végétale (CIMV) in Pomacle, France[41] (organosolv fractionation of 100 kg/hr wheat straw using a mixture of acetic acid and formic acid). The CIMV plant differs from most other lignocellulosic biorefineries, because it produces a high-quality lignin as a separate marketable product instead of a solid fuel.

3.3 Introduction: Biomass Pyrolysis for Biorefineries

Pyrolysis is an important conversion technology for biorefineries and can be applied as a primary unit to convert biomass into pyrolysis oil as feedstock for further processes. In biorefineries that first fractionate the biomass in hemicellulose, cellulose, and lignin, pyrolysis can play a central role as a processing unit for one or more of these fractions. Finally, pyrolysis can be used as a more peripheral unit, for example, to treat side streams that originate from other processes within the biorefinery. It is expected that (fast) pyrolysis will play an important role in biorefineries because of its versatility and the advantage of a storable and transportable biooil product that permits economies of scale.[42] Fast pyrolysis has been developed to convert biomass into high yields of biooil (typically up to 80 wt% of the dry feedstock), gas, and char. This is not a fractionation in main constituents, but merely an efficient liquefaction of the solid biomass in a liquid product that can be regarded as a sort of molecular debris that contains thermal degradation products from all the main biomass parts. Although this "soup" contains many valuable chemicals, separation and purification is not a trivial task.

3.4 Pyrolysis as the Primary or Central Unit in a Biorefinery

3.4.1 Historical Background of Pyrolysis-Based Biorefineries

Pyrolysis of lignocellulosic biomass leads to an array of useful products including liquid and solid derivatives and fuel gases. At the beginning of the twentieth century, pyrolysis processes were utilized for the commercial production of a wide range of fuels, solvents, chemicals, and other products from biomass feedstocks.[43–46] At the time, the dry distillation of wood for the production of charcoal was the mainstay of the chemical industry.

Many variations exist of pyrolysis-based biorefineries,[47,48] and an early (1920s) example is the production of charcoal and various other products in the continuous wood distillation plant of the Ford Motor Company in Michigan, USA.[45] This plant used 400 tons per day of scrap wood from the automobile body plant. The Ford plant not only produced make acetic acid (among charcoal and other products) but also ethyl acetate (via esterification with bioethanol), which the company required in its lacquer and artificial leather departments. The first T-Fords used bioethanol as their transportation fuel. Figure 8.2 gives a schematic overview of the plant that was completely self-sufficient with regard to its heat demand.

Pyrolysis can also play an important role in hybrid biorefineries that first fractionate the biomass into its main constituents hemicellulose, cellulose, and lignin. Depending on

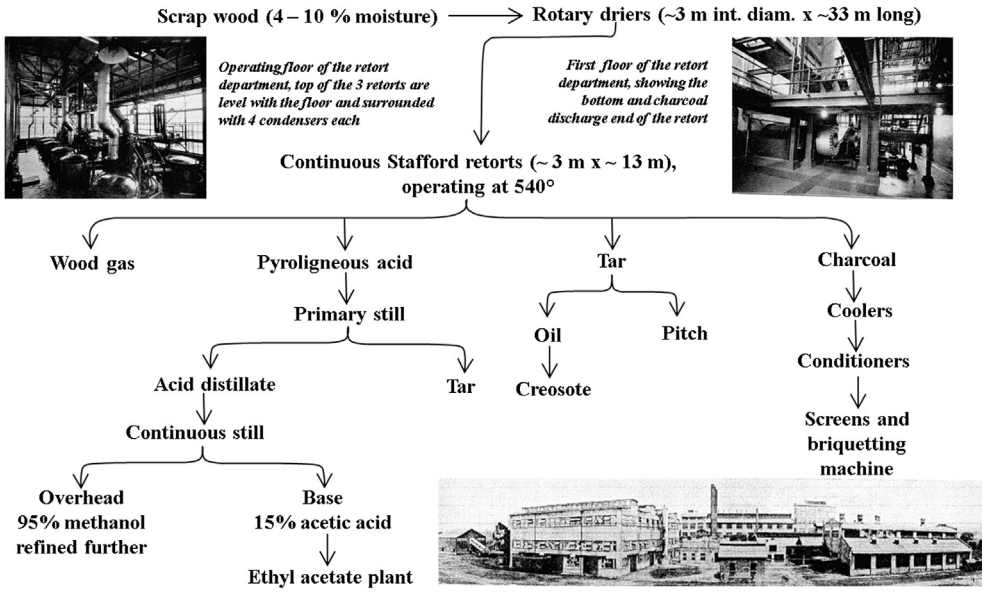

Figure 8.2 An example from the 1920s of a thermochemical biorefinery; the flow sheet for the Ford continuous wood distillation plant, Iron Mountain, Michigan, USA.[45]

the desired products, pyrolysis can be applied to one or more of these fractions. In the 1960s, Russian workers laid the foundations of a technology for a hybrid combination of thermochemical processes to convert biomass into value-added chemicals.[49] Furfural was obtained from the hydrolysis of hemicellulose. Levoglucosan, phenolics, and a residual char were subsequently produced via a one-stage pyrolysis of the hydrolysis residue. The total cumulative yield of these products was claimed to be 88–93%, containing 10–15% char. The Latvian State Institute of Wood Chemistry (LSIWC)[50] developed a pyrolysis technology for birch-derived lignocellulose in a tubular coil reactor at approximately 320–400 °C. The applied pyrolysis with steam yields a water-soluble tar that contains up to 64 wt% of levoglucosan and almost no lignin-derived impurities. The birch lignocellulose contains approximately 0.1 wt% of sulfuric acid and is prepared by washing the residue from the sulfuric acid-catalyzed production of furfural from birch.

The results are partly attributed to the relatively low pyrolysis temperature (preventing an excessive degradation of the lignin) and the relatively long residence time (10 s to make up for the decreased kinetics of levoglucosan formation at lower temperatures) when compared to the state-of-the-art fast pyrolysis. Figure 8.3 presents an example of the integrated LSIWC biorefinery system.[51]

In the 1980s, a hybrid process was developed in which the fast pyrolysis of biomass for levoglucosan is preceded by the removal of the hemicellulose via a mild sulfuric acid hydrolysis.[4] The acid hydrolysis transforms the hemicellulose in water-soluble carbohydrates while the subsequent fast pyrolysis step converts the resulting

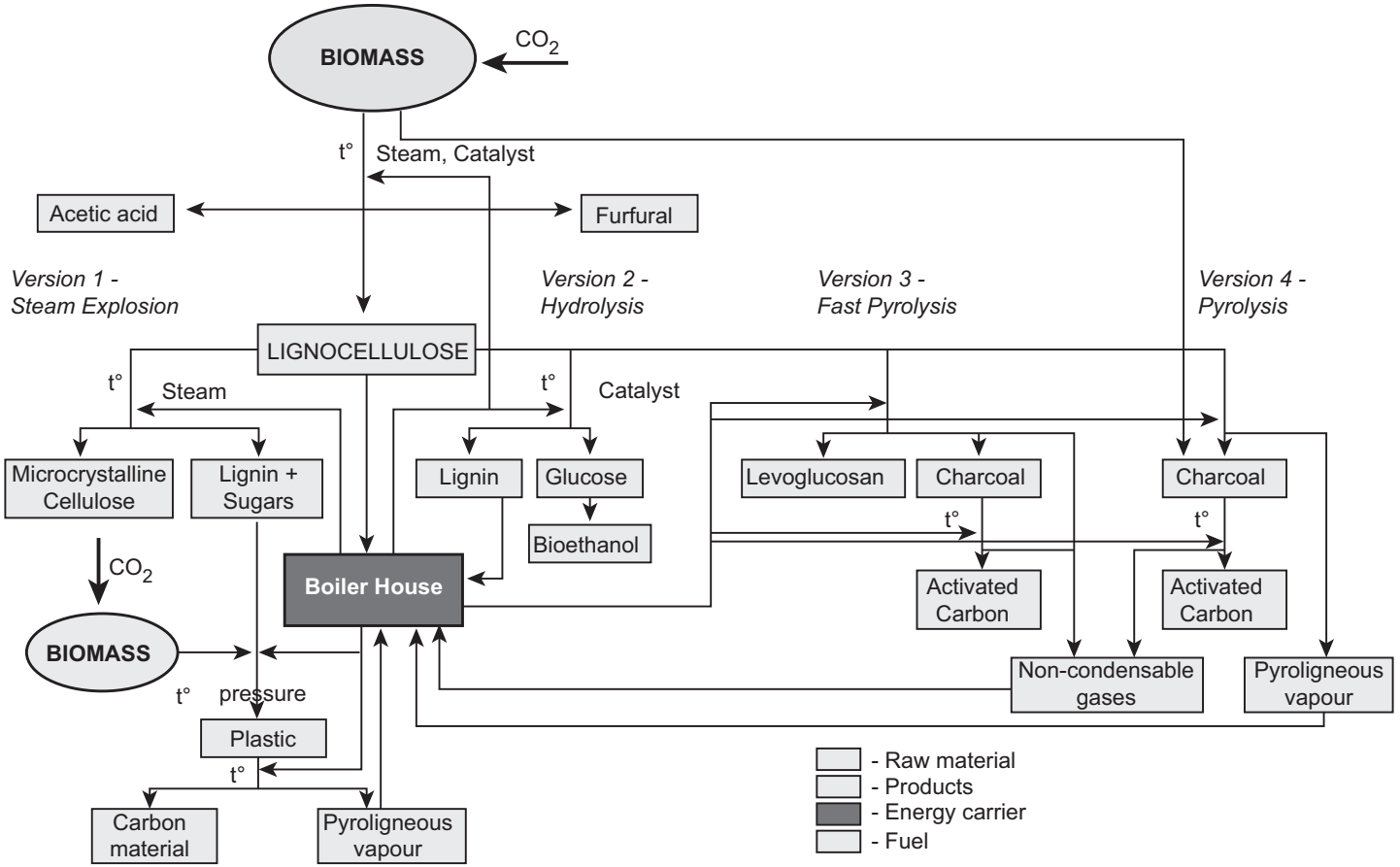

Figure 8.3 Biomass-based integrated technologies cluster.[51]

lignocellulose complex into a high levoglucosan-containing biooil. The process was developed as a hybrid pyrolytic route to fermentable sugars, that is, C_6 sugars. The highest yield of this process was found especially for softwoods, since their hemicelluloses contain a large fraction of (fermentable) C_6 sugars (mannose and galactose). The existence of anhydropolysaccharides in the tar was anticipated, and consequently, a significant increase in the yield of glucose by a mild acid hydrolysis of the pyrolysis tar was obtained. On the laboratory scale, the processing of extracted and ground Douglas-fir heartwood yielded 38 wt% of hexoses, 24 wt% from the hemicellulose hydrolysis and 14 wt% from the (vacuum) pyrolysis (yields based on the original feedstock weight). Figure 8.4 presents a conceptual design of the process as a pyrolytic route to fermentable sugars from softwood.

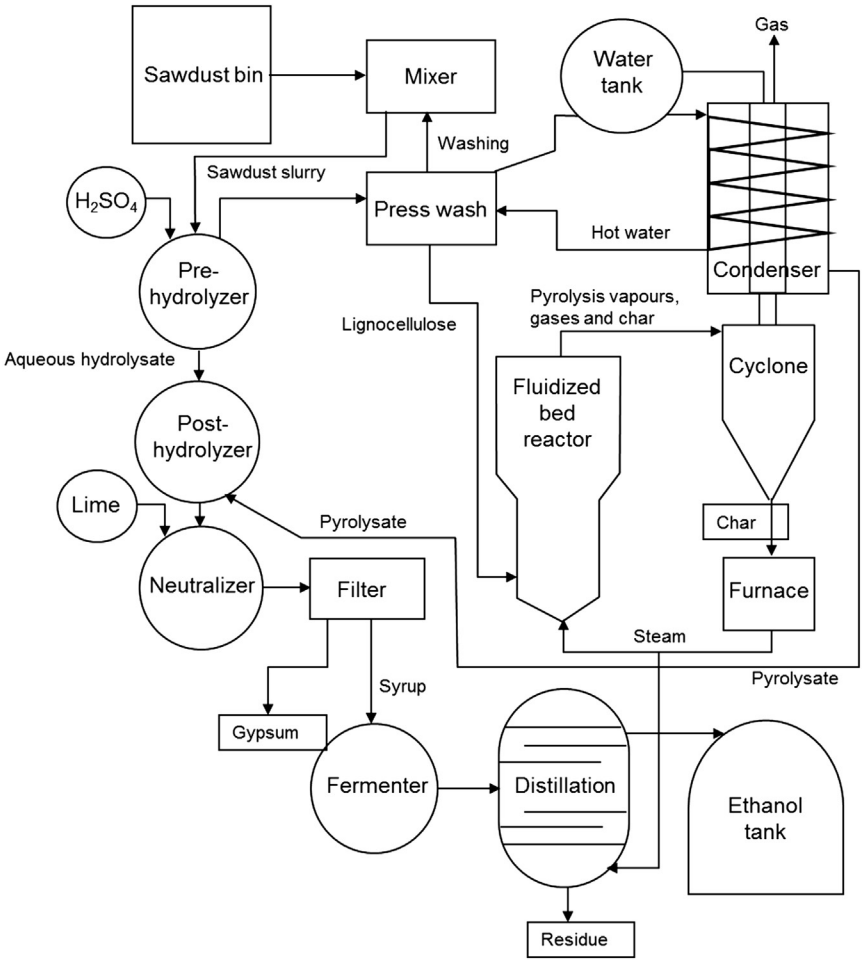

Figure 8.4 Acid hydrolysis and pyrolysis for production of fermentable sugars.

The University of Waterloo continued the development in greater detail and showed from an economic evaluation that the process is an interesting alternative for the conventional production of ethanol.[52–54] In 1999, they compared the cost of producing ethanol from cellulosic biomass via the hybrid thermochemical biorefinery approach, to acid hydrolysis and enzymatic hydrolysis technologies. The results indicate that the production cost of ethanol via the fast pyrolysis-based concept is competitive with the production cost via the conventional approaches.

3.4.2 Current Developments in the Field of Pyrolysis-Based Biorefineries

Recently, the global problems that are associated with the intensive use of fossil fuels have led to a renewed interest in (modern varieties of) these processes. For instance, the interest in slow pyrolysis technology (both carbonization and torrefaction) is growing rapidly again because of the need for renewable fuels from biomass.[9,55]

Figure 8.5 presents a view of the Energy Research Center of the Netherlands (ECN) on the layout of a future thermochemical biomass refinery might look like. As can be seen from the figure, pyrolysis, torrefaction, and gasification play an important role and the valorization of several side streams is important here too.[47]

The Dutch Biomass Technology Group (BTG) is currently developing a pyrolysis-based biorefinery concept that uses fast pyrolysis as the primary process to convert biomass into biooil that is subsequently fractionated in a secondary processing step. A tertiary upgrading step produces the final marketable products. Figure 8.6 gives a photographic impression of the Bioliquid Refinery concept.[56]

As can be seen from Figure 8.6, fast pyrolysis is the primary technology to convert lignocellulosic biomass into biooil, char, and gas. The biooil is feedstock for a subsequent biorefinery approach that aims to further process the biooil into a spectrum of value-added products. This elegant concept is further schematically presented in Figure 8.7.

Much attention is presently focussed on the production, application, and upgrading of biooil from the fast pyrolysis of whole biomass for fuels and chemicals.[57,58] The organic fraction in the pyrolysis liquid consists of hundreds of both small and large highly oxygenated and reactive compounds. The extraction of specific chemicals with added value and/or upgrading of this complex mixture to usable and valuable bulk products and/or fuels is a difficult task. Recent developments show encouraging results, although yields are often limited.[59–62] However, given the complexity of the biooil, it is already promising that some chemicals can be separated at all. Limited yields are not necessarily a drawback for economic viability. This depends on many variables such as oil price, market situation (price, volume) for the specific chemical, and a full technoeconomic evaluation of the separation procedure, including a life cycle analysis is required to assess the prospects of the recovery of individual chemicals.

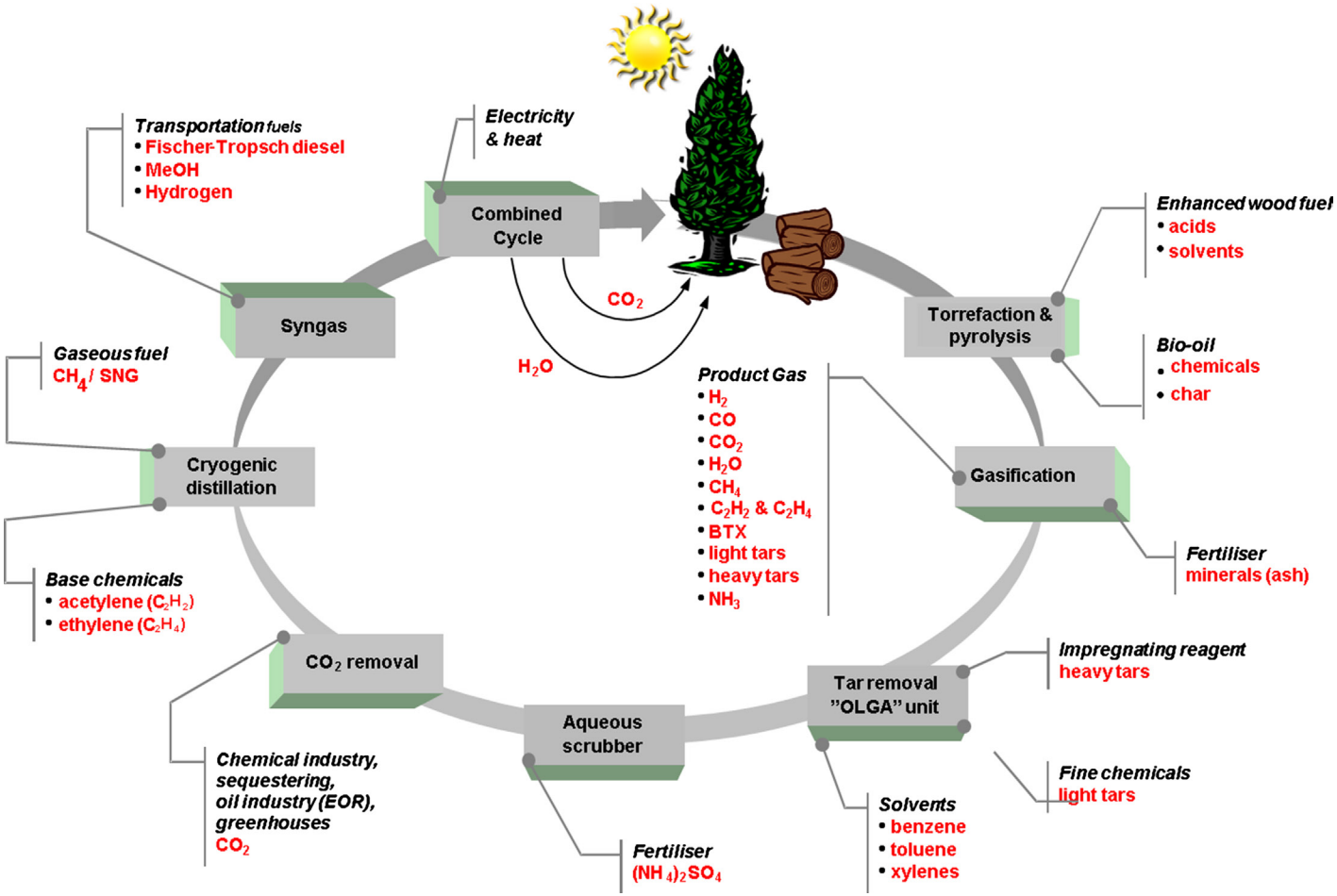

Figure 8.5 Thermochemical biorefinery concept ECN.[47]

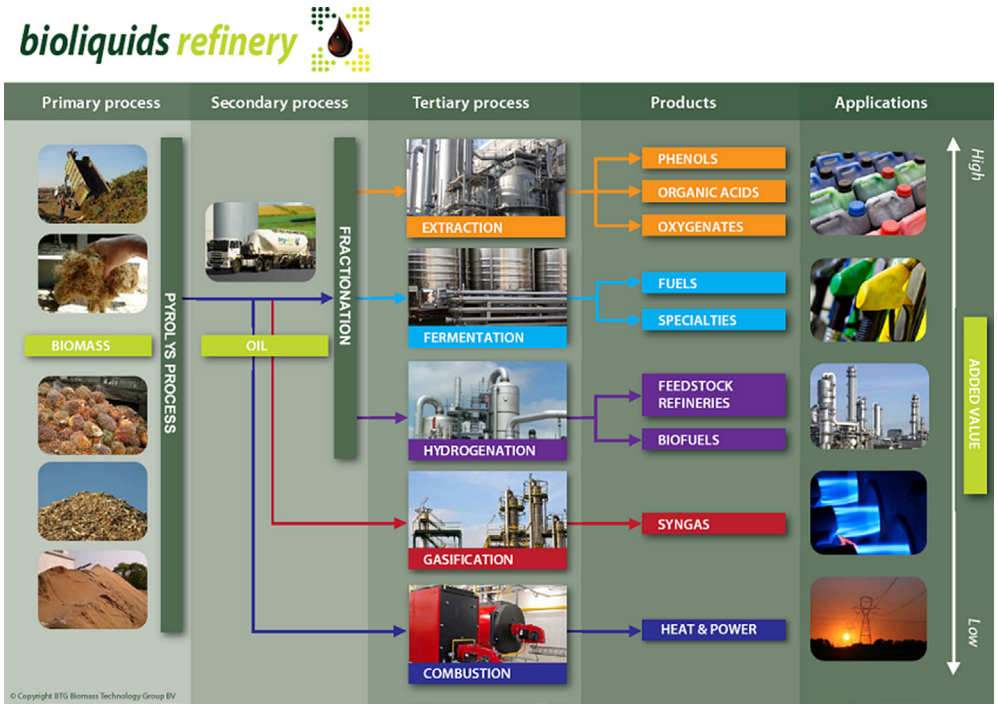

Figure 8.6 Bioliquid refinery; the BTG concept of a pyrolysis-based biorefinery.[56]

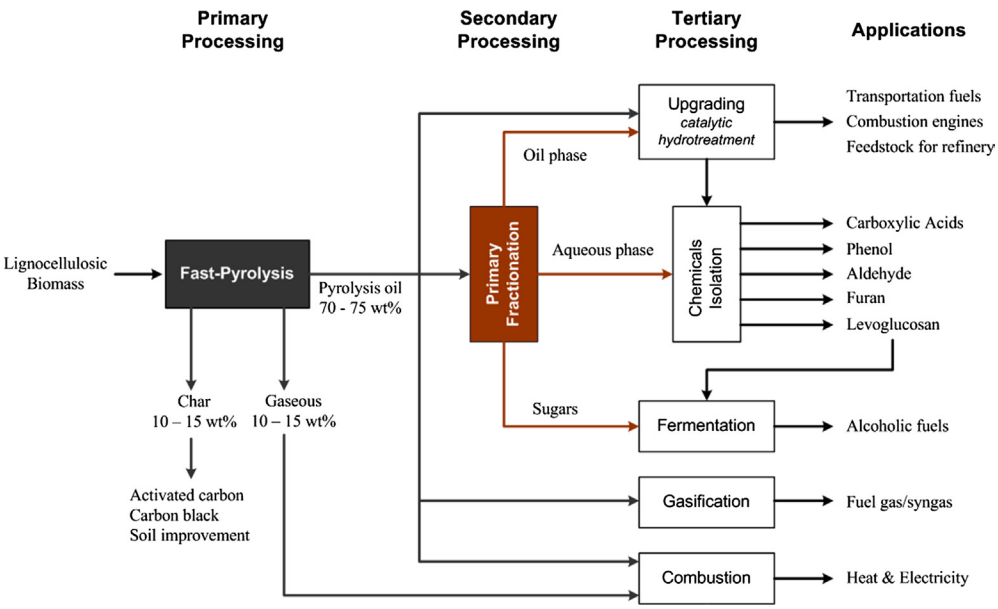

Figure 8.7 Pyrolysis as the primary unit to provide biooil for further processing.

A new development at BTG is the EMPYRO project aimed at the construction and demonstration of a pyrolysis polygeneration plant to produce electricity, process steam, organic acids (acetic acid), and fuel oil for burner applications from woody biomass.[63]

The pyrolysis plant will be built near Hengelo in The Netherlands and has a processing capacity of 120 t/d biomass (~25 MW_{th}). Recently (February 8, 2014), it was announced by Empyro BV through a press release that construction of the first pyrolysis plant (biomass to liquid) has started at the AkzoNobel site in Hengelo (The Netherlands). By the end of this year, construction will have been completed. The production capacity will then be gradually increased to its maximum of >20 million liters of pyrolysis oil per year. This amount of renewable oil will replace 12 million cubic meters of natural gas, the equivalent annual consumption of 8000 Dutch households, which saves up to 20,000 tonnes of CO_2 emissions per year.

Additionally, the project creates approximately 100 person-years of work in the Dutch province of Overijssel. This project has been made possible through the financial support of the European Commission (FP7 program), the Ministry of Economic Affairs, via the Topsector Energie TKI-BBE program, the province of Overijssel, the Energy Fund of Overijssel, and a private investor from Enschede. Investments for design and construction of the Empyro plant are 19 million Euros. Internationally, there is interest to develop more pyrolysis plants, but first, the plant in Hengelo will be erected. In the Empyro pyrolysis process, biomass (e.g., wood chips) is mixed with hot sand and converted within 2 s to pyrolysis oil, char, and gas. This process was invented at the University of Twente and has been further developed in 1995–2015 by BTG in Enschede, the Netherlands. Empyro BV has been founded by BTG Bioliquids BV (supplier of the technology) and Tree Power (long term investor in renewables) to demonstrate the technology on a commercial scale. Empyro intends to convert in the plant every hour 5 tonne of biomass to 3.5 tonne of pyrolysis oil. The plant will also produce enough electricity for its own use, and steam is supplied to the salt production of AkzoNobel located next to Empyro. This will reduce their annual CO_2 emissions with 6000 tonne as well. The pyrolysis oil will be purchased by the company FrieslandCampina, which has signed a long-term off-take agreement. FrieslandCampina will use the oil in its production location in the city of Borculo to replace 10 million cubic meters of natural gas annually. This is in line with its policy goals of climate neutral growth, use of renewable energy, and efficient and sustainable production, as laid down in its strategy route2020. With the choice for this fuel, the share of renewable energy grows and the CO_2 emissions decrease by 15% for the Borculo location.

Another actual pyrolysis-based biorefinery concept is the Bioliq® process that was developed at the Karlsruhe Institute of Technology (KIT). Bioliq® aims at the production of synthetic fuels such as Fischer–Tropsch diesel and chemicals from biomass.[64] Synthesis based on synthesis gas requires pressures of up to 10 MPa. High-pressure entrained flow gasification provides high-quality tar-free syngas with low methane contents.

Entrained flow gasification requires a feed that can easily be fed into the gasifier at elevated pressures. Fast pyrolysis was chosen to obtain such a feed by mixing pyrolysis condensates and char to the so-called bioliqSyncrude®, exhibiting a sufficiently high heating value, and being suitable for transport, storage, and processing. This slurry-gasification concept has been extended to a complete process chain via a pilot plant erected on site at KIT. The plant uses a twin-screw pyrolysis reactor and is designed to process up to 500 kg/h (~2 MW_{th}) of air-dry biomass at a pyrolysis temperature of 550 °C. The main operation target is to achieve full operation of the plant with straw as feed material. Figure 8.8 presents a photographic impression of the bioliq® plant at KIT.

In a recent press release (September 2013), KIT announced that for the first time gasoline is produced by KIT. The synthesis stage of the bioliq® pilot plant successfully started operation. Hence, KIT, in cooperation with Chemieanlagenbau Chemnitz GmbH, has progressed further in the production of environmentally compatible fuels from residual biomass. Now, all stages of the bioliq® process, that is, flash pyrolysis, high-pressure entrained flow gasification, and synthesis, have been realized. The project will now be completed by testing the entire process chain and optimizing it for the large industrial scale. As soon as all stages of the bioliq® process will have been linked, the pilot plant will supply high-quality fuel from straw, probably in mid-2014. The four-staged bioliq® process developed by KIT accounts for the fact that straw and other biogenous residues have a low-energy density and arise in a widely distributed

Figure 8.8 The bioliq® plant at KIT: In a multistage process, high-quality synthetic fuels are produced from straw and other biogenous residues. *(Photograph: KIT/Tom Zevaco.)*

manner. Moreover, the bioliq® process allows for the economically efficient large-scale production of high-quality engine-compatible designer fuels. The bioliq® synthesis stage now is the last section of the bioliq® pilot plant on KIT Campus North to successfully start operation. Upstream of hot gas cleaning, the synthesis stage converts synthesis gas into high-quality Otto fuel based on two reaction steps. Plant design is specially adapted to CO-rich synthesis gas produced by gasification of sustainable biomass. Maximum utilization of the carbon contained in the biomass with a minimum investment volume is achieved by direct conversion of the synthesis gas into dimethyl ether in the first reaction step. The complete bioliq® process (Biomass to Liquid Karlsruhe) comprises four stages. In the first stage, the dry residual biomass that arises in a widely distributed manner and possesses a low-energy content is subjected to decentralized conversion by flash pyrolysis into a substance of high-energy density similar to crude oil. This substance, the so-called bioliqSynCrude®, can be transported over long distances in an economically efficient manner and is subjected to further central processing.

A high-pressure entrained flow gasifier converts the bioliqSynCrude® to a tar-free syngas at temperatures >1200 °C and pressures of up to 80 bar. This synthesis gas is mainly composed of carbon monoxide and hydrogen. By means of downstream hot gas cleaning, impurities like particular matter, chlorine, and nitrogen compounds are separated from the syngas. In the synthesis stage, this synthetic gas is specifically composed to high-quality fuels. In Figure 8.9, a schematic of the process in given.

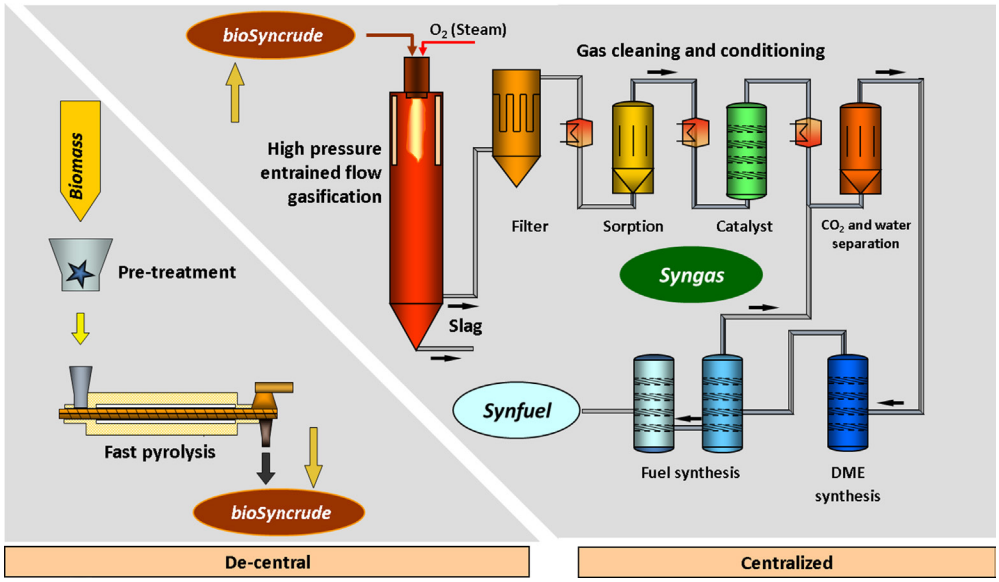

Figure 8.9 KIT's bioliq® process. *(N. Dahmen, KIT/IKFT.)*

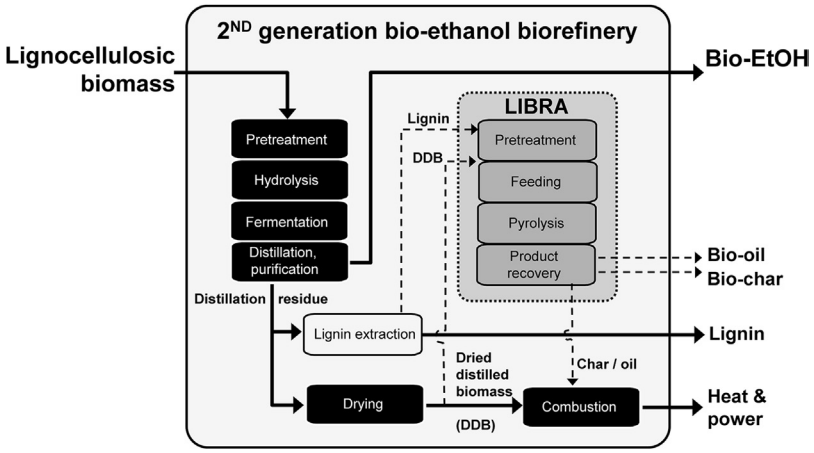

Figure 8.10 Lignin Biorefinery Approach (LIBRA), under development at ECN.

3.5 Pyrolysis as a Peripheral Unit for Biorefinery Side Streams

The production of pulp and paper and bioethanol from lignocellulosic biomass generates a large lignin-enriched side stream. The main practiced option to date is the combustion of this stream to meet heat (and power) demands of the biobased industry. Figure 8.10 illustrates the pyrolysis of lignin-enriched side streams in the biorefinery. Integration of the lignin-pyrolysis section[65,66] (LIBRA: Lignin BioRefinery Approach) with the other biorefinery sections enables an optimal use of material and heat.[67]

The black parts in Figure 8.10 depict the current state-of-the-art processing of biomass for the production of bioethanol. Lignin is separated by means of a caustic wash, in which pH is increased to dissolve lignin. Then an S/L separation takes place to separate dissolved lignin, which is afterward precipitated by acid addition.

4. A PYROLYSIS-BASED HYBRID BIOREFINERY CONCEPT

4.1 General Scheme

Figure 8.11 presents a general scheme of how a hybrid biorefinery for lignocellulosic biomass could look like. It encompasses pyrolysis next to biomass fractionation, two relevant examples of a chemical and biochemical conversion route, product upgrading, and by-product utilization. Figure 8.11 can be regarded as a flexible biorefinery concept for the conversion of different types of lignocellulosic biomass to different products (chemicals, secondary energy carriers, heat, and power) via different conversion technologies.

4.2 Feedstock and Feedstock Fractionation

The feedstock for the biorefinery is lignocellulosic biomass that contains variable amounts of hemicellulose, cellulose, and lignin as the main fractions with smaller amounts

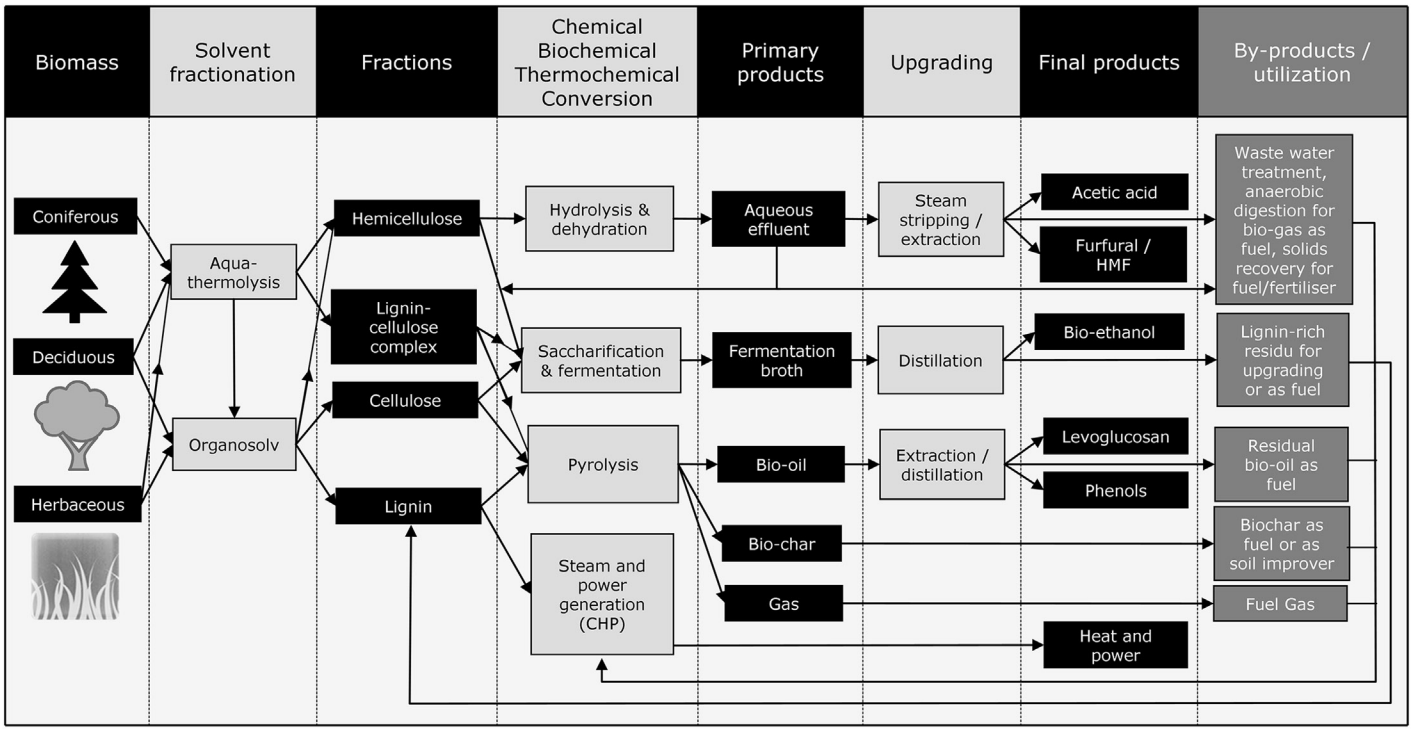

Figure 8.11 General scheme for a lignocellulosic biomass-based hybrid biorefinery.

of organic extractives and inorganic ash minerals. The differences in biomass composition are important for (the (choice of)) the fractionation process that forms the heart of the biorefinery.

Aquathermolysis or hydrothermal treatment (treatment with hot pressurized water, typically at temperatures of around 200 °C and reaction times of 30 min) can be applied to all three types of biomass, and is effective in separation of the hemicellulose from the lignin–cellulose complex. The aquathermolysis basically converts the biomass in two fractions, an aqueous solution that contains mainly hemicellulose derivatives (e.g., acetic acid, oligomeric and monomeric sugars, and their degradation products like furfural), extractives, and water-soluble ash minerals (e.g., KCl) and a solid residue that contains lignin, cellulose, and water insoluble inorganics (e.g., silicates in herbaceous types of biomass). Depending on the specific type of biomass and the reaction conditions, acetic acid and furfural yields up to, respectively, 5 wt% and 8 wt% of the dry feedstock are possible.[68]

Organosolv fractionation is a biomass pretreatment with a mixture of water and an organic solvent at elevated temperatures (around 200 °C) and pressure. The main goal of Organosolv is the delignification of the biomass to liberate the cellulose for further processing, for example, to bioethanol. Organosolv treatment also removes the hemicellulose, although less efficiently when compared to aquathermolysis because of the presence of an organic solvent. Organosolv fractionation with a water/ethanol mixture (typically 40 wt% water and 60 wt% ethanol) around 200 °C works well for deciduous and herbaceous biomass, but needs more severe conditions for coniferous biomass, probably because the coniferous lignin is less easy to hydrolyze.[69] The lignin that is solubilized during organosolv fractionation with ethanol is very similar to native lignin in wood, although part of the β-O-4 ether bonds are hydrolyzed as well.[70] An unexplored possibility is the combination of aquathermolysis as the first step to dissolve and convert the hemicellulose, followed by an organosolv fractionation to delignify the resulting lignin–cellulose complex.[70] Hereby, a full fractionation of the biomass in hemicellulose (derivatives), cellulose, and lignin is achieved. Both aquathermolysis and organosolv can be conducted in batch and in continuous mode. For small-scale (<10 kton/year) batch processes, industrial-scale autoclaves can be used. Continuous processing on an industrial scale in, for example, auger (screw) reactors can be challenging because of the need to handle biomass slurries under elevated pressures and temperatures.

4.3 (Thermo) Chemical and Biochemical Conversions

The aqueous fractions from the aquathermolysis and organosolv process mainly contain hemicellulose derivatives such as acetic acid, single and oligomeric sugars, sugar breakdown products such as furfural and hydroxymethylfurfural and humic substances from secondary reactions. Although the innate organic acids (e.g., acetic acid) that are formed from the hemicellulose during the aquathermolysis catalyze the hydrolysis and

subsequent dehydration of xylose to furfural, the yield of furfural can be enhanced by adding a mineral acid catalyst such as sulfuric acid. Sulfuric acid not only catalyzes the dehydration of xylose to furfural but it also speeds up the hydrolysis of the (oligomeric) hemicellulose fractions. Recent developments[71] indicate that the resulting C5-sugars are fermentable to bioethanol. A consecutive acid hydrolysis can be conducted in the state-of-the-art continuous stirred tank reactors. Alternatively, the solid cellulose and cellulose lignin-containing fractions from, respectively, the organosolv and the aquathermolysis can be pyrolyzed to obtain a biooil that is enriched in cellulose-derived anhydrosugars of which levoglucosan is the main component. In general, fast pyrolysis using fluidized bed technology is the preferred method because it is well known and can be scaled up relatively easily. Prior to the pyrolysis, the biomass should be dried to approximately 10–15 wt% of moisture. Typical pyrolysis conditions for the production of maximum biooil yields (typically up to 70 wt% (dry feedstock base)) are a reactor temperature around 500 °C, with a pyrolysis vapor residence time of seconds. Depending on the type of lignocellulosic biomass and the pyrolysis conditions, levoglucosan yields up to 15 wt% of the solid dry feed are achievable. The fact that most of the water-soluble ash elements (potassium and other alkali and alkaline-earth metals) are leached out from the solid during the aquathermolysis and organosolv treatment is beneficial for the subsequent pyrolytic conversion into anhydrosugars, because these metals tend to catalytically crack the sugar moieties during pyrolysis. Also, the fact that the cellulose in the aquathermolysis residue is probably more crystalline than in the original material is an advantage for the subsequent pyrolysis, because the desired levoglucosan is preferentially formed from crystalline cellulose. Also, the biooil might contain less lignin-degradation products because of recondensation reactions during the aquathermolysis, rendering the lignin thermally more stable than in the original material. As a consequence, most of the lignin will end up in the biochar. The solubilized lignin from the organosolv process is precipitated from the solution, washed, and dried. The resulting pure lignin can be pyrolyzed to biochar and a biooil (~50–60 wt% of the dry lignin feedstock) that is enriched with phenolic compounds (typically up to 60 wt% of the whole oil). Alternatively, the lignin can be burned for heat and power in a recovery boiler. Also here the preferred pyrolysis technology is fast pyrolysis. An overview of available fast pyrolysis reactors is given in Ref. 72.

The solid cellulose fraction from the organosolv process and the solid cellulose–lignin complex from the aquathermolysis can be hydrolyzed to glucose by using enzymes or acid catalysts. The glucose is subsequently fermented into a broth from which the bioethanol is recovered by distillation. This is a standard procedure in new second-generation lignocellulosic biomass-based biorefineries for bioethanol.

4.4 Product Recovery

The aqueous effluent from the aquathermolysis contains furfural that can be recovered as a valuable chemical. This is done by proven technology such as steam distillation or

solvent extraction. An example is the treatment of the aqueous condensate from the pulp and paper plant of Lenzing in Austria.[73] Lenzing produces yearly about 23,000 tons of acetic acid and 5400 tons of furfural out of the aqueous condensate. Both products are of a high quality and sold on the market with profit. The spent sulfite cooking liquor condensate is treated in an extraction plant. Most of the organic components of the condensate are separated from water by liquid–liquid extraction to obtain reusable process water and salable by-products. The economic efficiency of the extraction plant is provided by the reduction of the organic effluents as well as waste water combined with reduced investment and operating costs of a waste water treatment plant, reduction of the water consumption of the pulp mill due to closed loops, and earnings from the sales of the by-products acetic acid and furfural. Figure 8.12 presents a simplified scheme of the furfural/acetic acid extraction plant.

In the extractor (E) acetic acid, furfural, formic acid, and methanol are extracted from the organics through a polar organic solvent mix. The extractant is a mixture of tri-n-octylphosphineoxide (CAS 78-50-2) and undecane (CAS 1120-21-4), which does not dissolve in the condensate. The solvent extraction step is able to remove 85–90% of the organic compounds. The aqueous raffinate is purified and can be used as a fresh water substitute in the pulp mill. The solvent extract is transferred into a flash vessel where most of the water is removed. Afterward, the raw product is removed from the solvent extract by a stripping distillation (S). While the solvent is supplied to the extractor again, the acetic acid and furfural-rich overhead stream (raw product) is forwarded to a number of rectifying columns in which by-products are removed and the final product is purified to the required quality.[73]

The product from the fermentation of the sugar-containing solution after the hydrolysis of the (hemi)cellulose is an aqueous broth that contains ethanol, lignin, and various residues from the hydrolysis/fermentation process such as salts and microbial remnants. The ethanol–water azeotrope is distilled from this broth and further purified. The remaining aqueous distillation residue—the so-called stillage—is dried. The resulting

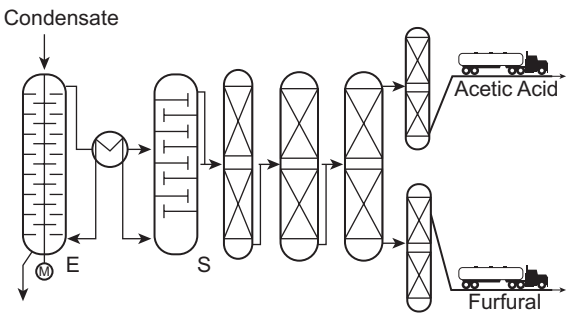

Figure 8.12 Furfural/acetic acid extraction plant to treat the condensate from Lenzing's sulfite pulping process (extraction efficiency ~80–90%).[73]

"dried distilled biomass" can serve as a fuel or as a cattle-feed additive. Alternatively, lignin can be extracted from the liquid stillage. Lignin is separated by means of a caustic wash, in which pH is increased to dissolve lignin. Then an S/L separation takes place to separate dissolved lignin, which is afterward precipitated by acid addition.[74]

The biooil from the pyrolysis of lignin contains monomeric phenols, oligomeric phenols, reaction water, and minor quantities of low-boiling components such as methanol and acetic acid. Separation of the lower boiling monomeric phenols from the oligomeric fraction can be achieved by evaporation, (fractional) steam distillation, vacuum distillation, liquid–liquid extraction, or combinations of these. Steam distillation is usually applied to separate a small amount of a volatile fraction from either a large amount of nonvolatile or heat-sensitive material. To separate the light monomeric fraction from the larger oligomeric fragments, steam distillation at low temperatures seems to be an appropriate method.[75–77] Subsequently, individual phenols can be recovered from the monomeric phenol mixture by vacuum distillation.[76]

Pyrolysis of the alkali metal-free lignin–cellulose solid from the aquathermolysis or the cellulose from the organosolv yields a biooil that is enriched in monomeric and oligomeric anhydrosugars. The major individual anhydrosugar is levoglucosan. Both the individual anhydrosugars and the oligomerics can be catalytically hydrolyzed with sulfuric acid to yield glucose. According to Radlein,[78] an important obstacle for the production of levoglucosan lies in the difficulty to purify it, for example, by crystallization. Although several procedures are available, they all suffer from low yields, cost ineffectiveness, and technical complexity.

5. CONCLUSION

Pyrolysis is a thermochemical conversion option that can play an important role in hybrid biorefinery concepts because it offers a flexible way to convert biomass and/or biomass residues into (a precursor for) value-added chemicals and products that enhance the profitability of the biorefinery. Separation/purification/upgrading of pyrolysis oil into biofuels and/or individual chemicals is challenging and poses a broad area of research that may require the development of a whole new type of chemistry, specifically devoted to the physicochemical characteristics of biomass pyrolysis oils.

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