Biomass pyrolysis for chemicals

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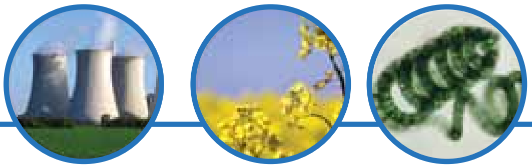

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The problems that are associated with the use of fossil fuels demand a transition to renewable sources for energy and materials. Biomass is a natural treasure for chemicals that, to date, have been made from fossil resources. Unfortunately, the heterogeneiety and complexity of biomass still precludes exploitation of its full potential. New technologies for economical valorization of biomass are under development, but cannot yet compete with petrochemical processes. However, rising prices of fossil resources will inevitably lead to replacement of oil refineries with biorefineries. A biorefinery uses various 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. Thermochemical processes such as fast pyrolysis can play an important role in biorefineries and this article presents a review of some pyrolysis-based technologies.

Introduction to the pyrolytic valorization of biomass

The bio-based society & the importance of biomass for chemicals

Before the onset of the petrochemical era, renewable feedstocks supplied a significant portion of the global chemical and energy needs. In the 1920–1930s the chemurgy movement in the USA promoted the use of biomass as a source of chemicals, with the belief that ‘anything that can be made from a hydrocarbon could be made from a carbohydrate’. The incentive was to find an economic way to use farm surpluses [1]. It was only in the relatively short period between 1920 and 1950 that we witnessed the transition to a nonrenewable-based economy that heavily depends on fossil resources. However, since the first oil crisis in the 1970s, decreasing resources, global warming and environmental pollution associated with the use of fossil fuels are growing incentives for the transition to renewable energy such as solar, wind, hydro and biomass. Among the renewable resources, **lignocellulosic biomass** is particularly suited as an abundant, low-cost feedstock for the production of bio-based chemicals, fuels and energy to substitute fossil resources. A drawback of the growing consumption of biomass for energy is the increase in price for the biomass feedstock. This conflicts with the **biorefinery** requirement for low-cost raw materials. Biomass alone is probably not able to solve the world’s power needs, but can satisfy the need for the synthesis of carbon-containing raw materials because its unique composition makes it especially suitable for the extraction of value-added chemicals and materials, which can replace petrochemicals [2,3]. The production of such chemicals from lignocellulosic biomass has a greater added value compared with the use of biomass as fuel. Therefore, the production of chemicals from biomass can contribute a great deal to the economy of a society that uses sun and wind for power. The added value from biomass-derived chemicals can be used to improve the economic feasibility of biorefineries.

Structure & composition of lignocellulosic biomass

Lignocellulosic biomass is a composite material in which the main constituents are cellulose (~50% of weight [wt%] dry base [d.b.]), hemicellulose (~25 wt% d.b.) and lignin

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Key terms

Lignocellulosic biomass: Plants and plant-derived organic material that contains hemicellulose, cellulose and lignin as major components.

Biorefinery: Sustainable processing of biomass into a spectrum of marketable bio-based products and bioenergy.

Pyrolysis: Thermal degradation in the absence of air or other molecular oxygen containing gases.

(~25 wt% d.b.). These components are linked together to obtain structural strength in combination with flexibility. In addition, biomass also contains water and minor amounts of extractives and inorganic compounds ('ash'). Cellulose is a long-chain linear polymer that contains predominantly crystalline arrangements with smaller amorphous regions. The cellulose polymers are arranged in microfibrils that are organized in fibrils, and these are combined into cellulose fibers, which are responsible for the fibrous nature of lignocellulosic biomass cell walls. Hemicelluloses are shorter; they are branched amorphous polymers of five- or six-carbon sugars. Together with lignin, hemicellulose forms the matrix in which the cellulose fibrils are embedded. The hemicellulose acts as a connector between cellulose and lignin [4]. Lastly, lignin, the third cell-wall component, is a 3D polymer formed from phenylpropane units with many different types of linkages between the building blocks. An impression of the structure of lignocellulosic biomass in wood, illustrating its complexity, is presented in **Figure 1** [5].

Depending on the plant species, lignocellulose biomass typically contains 30–50 wt% cellulose (consisting of D-glucose units), 15–30 wt% hemicellulose, 10–30 wt% lignin and smaller amounts of organic extractives and inorganic compounds. In general, herbaceous biomass typically contains significant amounts of inorganics (<15 wt%) and extractives (<20 wt%) when compared with woods (~0.3–0.4 wt% inorganics, ~2–3 wt% extractives). The hemicelluloses in deciduous woods (hardwoods) and agricultural herbaceous products, such as wheat straw, corn stover and switch grass, predominantly consist of D-xylose units, whereas coniferous (softwood) hemicellulose is mainly made up of D-mannose, D-xylose and D-galactose. The main building blocks in the biosynthesis of hardwood and herbaceous lignin are the phenolic alcohols sinapyl alcohol, coniferyl alcohol and coumaryl alcohol. Softwood lignin is almost exclusively made of coniferyl alcohol.

Pyrolysis-based thermal fractionation of biomass

The fact that the main biomass fractions, hemicellulose, cellulose and lignin, react differently at various temperatures to yield unique spectra of products [6–9], can be exploited to extract value-added chemicals by thermal processing, for example, via **pyrolysis**. Pyrolysis is the thermal degradation of organic material in the absence of (molecular) oxygen. It is a versatile thermal-conversion technology that comes in several varieties, depending on the desired products. **Table 1** summarizes the main pyrolysis technologies and their major products [10].

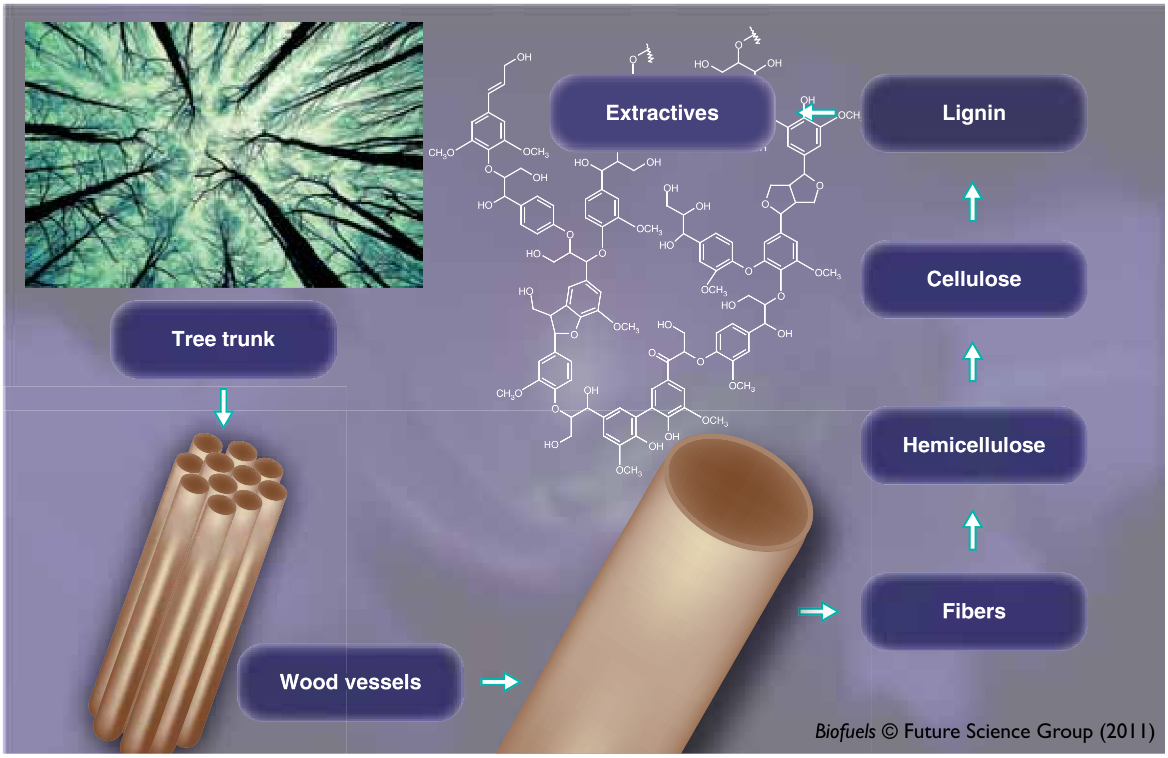

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Figure 1. The composition of wood, illustrating the structure of lignocellulosic biomass.

Table 1. Modes of pyrolysis and major products.

Mode	Conditions	Liquid (%)	Solid (%)	Gas (%)
Fast	Reactor temperature: 500°C Heating rates: >1000°C/s Hot vapour residence: ~1 s	75	12 char	13
Intermediate	Reactor temperature: 400–500°C Heating rate: 1–1000°C/c Hot vapour residence: ~10–30 s	50	25 char	25
Slow–torrefaction	Reactor temperature: ~290°C Heating rate: >1°C/c Solid residence: ~30 min	0–5	77 solid	23
Slow–carbonization	Reactor temperature: 400–500°C Heating rate: >1°C/c Solid residence: hours–days	30	33 char	35

Adapted from [10].

Table 1 shows that several temperature and heating-rate (HR) regimes are used, depending on the desired product slate (i.e., product mixture or product composition). Characterization of biomass pyrolysis is usually by temperature and HR. Unfortunately, these parameters are poorly defined in processing reactors, as well as in laboratory devices (e.g., see [11]). Therefore, the data in Table 1 should be considered as indicative.

In general, carbonization is conducted to produce charcoal and, when appropriate, by-products such as acetic acid and wood tars [12].

Torrefaction is 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 [13]. The purpose is to generate an enhanced fuel for generating heat and power. Lastly, fast and intermediate pyrolysis are thermal-conversion technologies, developed to generate high-liquid yields from biomass [10]. The liquid products, termed pyrolysis-oils or bio-oils, can be used for heat and power generation, but also as a feedstock for chemicals [14]. Since the late 1970s, fast-pyrolysis technology has been developed as a thermochemical-conversion technology to produce high yields of bio-oil from biomass [14–17]. During fast pyrolysis the usually finely ground and dry biomass (typically 10 wt% of moisture) is rapidly heated to temperatures of approximately 500°C, causing an almost instantaneous release of a multitude of thermal degradation products that are quickly quenched to produce a so-called ‘pyrolysis-oil’ or ‘bio-oil’; a mixture of condensed organic compounds and water. In addition, sizable fractions of char and permanent gases are formed. Table 2 gives an example of the average chemical composition of bio-oils from hard- and soft-wood.

Value-added chemicals from staged pyrolysis of chemicals

The different thermal stabilities of hemicellulose, cellulose and lignin provide an opportunity to use pyrolysis for the thermal fractionation of biomass into products that can substitute petrochemicals [18,19]. Figure 2 presents a schematic overview of the different thermal-stability regimes of each of the main biomass fractions [20]. The height of the thermal stability 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 measured by thermogravimetric analysis [21].

Figure 2 indicates the potential for the thermal fractionation of biomass. The rate of thermal breakdown and the product slate (i.e., product mixture or product composition) is determined by the order of thermochemical stability of the individual biomass constituents, which ranges from hemicellulose as the least stable polymer (fast degassing/decomposition from 200–300°C), to the more stable cellulose (fast degassing/decomposition from 300–400°C). Lignin exhibits intermediate thermal degradation behavior (gradual degassing/decomposition from 250–500°C).

Table 2. Compound classes in bio-oil.

Compound class	Composition range (wt% based on the organic fraction of bio-oil)
C1 compounds (e.g., formic acid, methanol and formaldehyde)	5–10
C2–C4 linear hydroxyl and oxo-substituted aldehydes and ketones	15–35
Hydroxyl, hydroxymethyl and/or oxo-substituted furans, furanoses and pyranones (C5–C6)	10–20
Anhydrosugars including anhydro-oligosaccharides (C6)	6–10
Water-soluble oligomeric and polymeric carbohydrate fragments of uncertain composition	5–10
Monomeric methoxyl substituted phenols	6–15
Pyrolytic lignin	15–30

Data from [20].

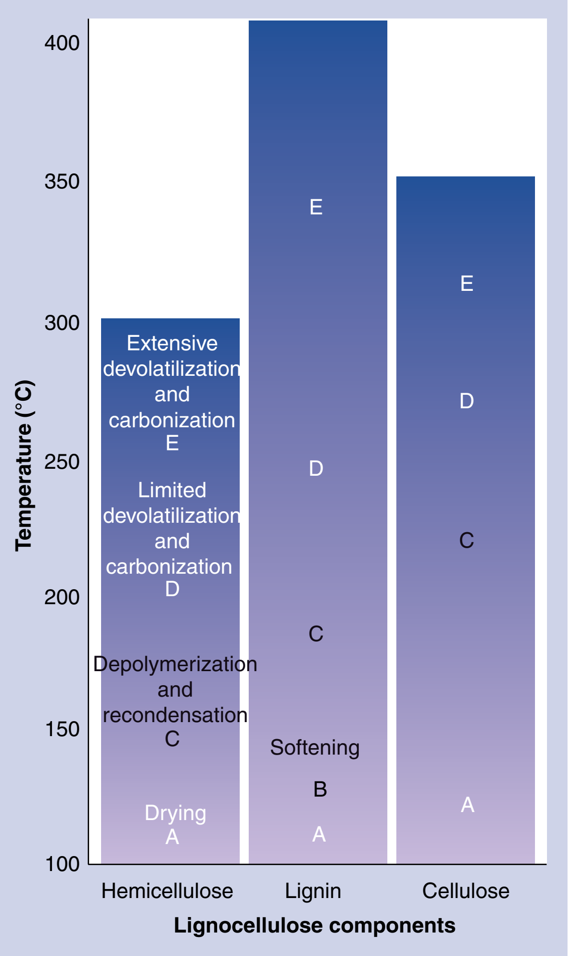

Figure 2. Thermal stability regimes for hemicellulose lignin and cellulose.
Adapted with permission from [20].

The concept of a step-wise pyrolysis to extract valuable chemicals from lignocellulosic biomass is graphically illustrated in Figure 3. Table 3 presents a more detailed overview of some important value-added chemicals that can be obtained from each of the main biomass fractions via pyrolysis [3,12,22].

The application examples of the major chemicals in Table 3 provides only a limited picture of their full potential. To illustrate the wealth of applications for furfural (from hemicellulose) and levoglucosan (from cellulose), Figures 4 & 5, respectively, present products that can be obtained from these chemicals [15,23,24]. For furfural these are mostly commercial. The situation for levoglucosan is different. Although recognized as a potentially valuable chemical, the existing market is very small and very highly priced. The is partly due to the low yields and the absence of a large-scale production capacity of the traditional method of vacuum pyrolysis of starch. Another barrier is the difficulty of purifying levoglucosan at low cost. In the next section of this paper an example of another possible application for levoglucosan as a pyrolytic precursor for bio-ethanol is described.

This article presents a review of innovative pyrolysis-based options that are potential candidates for the thermochemical conversion of lignocellulosic biomass to value-added chemicals.

Thermochemical biorefineries

Biorefinery is the sustainable processing of biomass into a spectrum of marketable products [25]. This definition encompasses a multitude of possibilities to convert biomass into bioproducts via (combinations of) different processing technologies including (bio)chemical and thermochemical processes. Biorefinery concepts can be classified according to platforms, products, feedstocks and processes.

Platforms may be defined based on:

- Intermediate products during the processing of the raw materials to the final biorefinery products. For example, fractionation of the biomass into lignin, cellulose- and hemicellulose-sugars provides the intermediates 'lignin' and sugar that can be further processed to final biorefinery products such as phenols (from lignin), sorbitol (from cellulosic glucose) and xylitol (from hemicellulosix xylose);
- Linkages between different biorefinery concepts;
- Final products of a biorefinery.

Combined platforms are possible, for example a biorefinary that fractionates biomass into lignin and sugars may further process the lignin and the sugars. 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, such as fuels, chemicals and (performance) materials. Figure 6 presents a detailed overview of the many possible combinations for biorefinery concepts.

In a (thermochemical) biorefinery, biomass is converted into energy carriers such as transportation fuels (e.g., ethanol), energy and/or chemicals. In terms of energy content, the amount of biomass for (transportation) fuels and combined heat and power (e.g., by combustion) is much higher than the amount used for the production of chemicals. However, the conversion of lignin into valuable chemicals generates much more added value than the use of the lignin as a fuel. The extra income from the sales of the lignin-derived chemicals can be used to improve/invest in the biorefinery. For instance, when the main product of a biorefinery is (hemi)cellulose bio-ethanol as a renewable transportation fuel, the lignin ends up in a residue that is mostly used as a fuel to generate heat. The economics

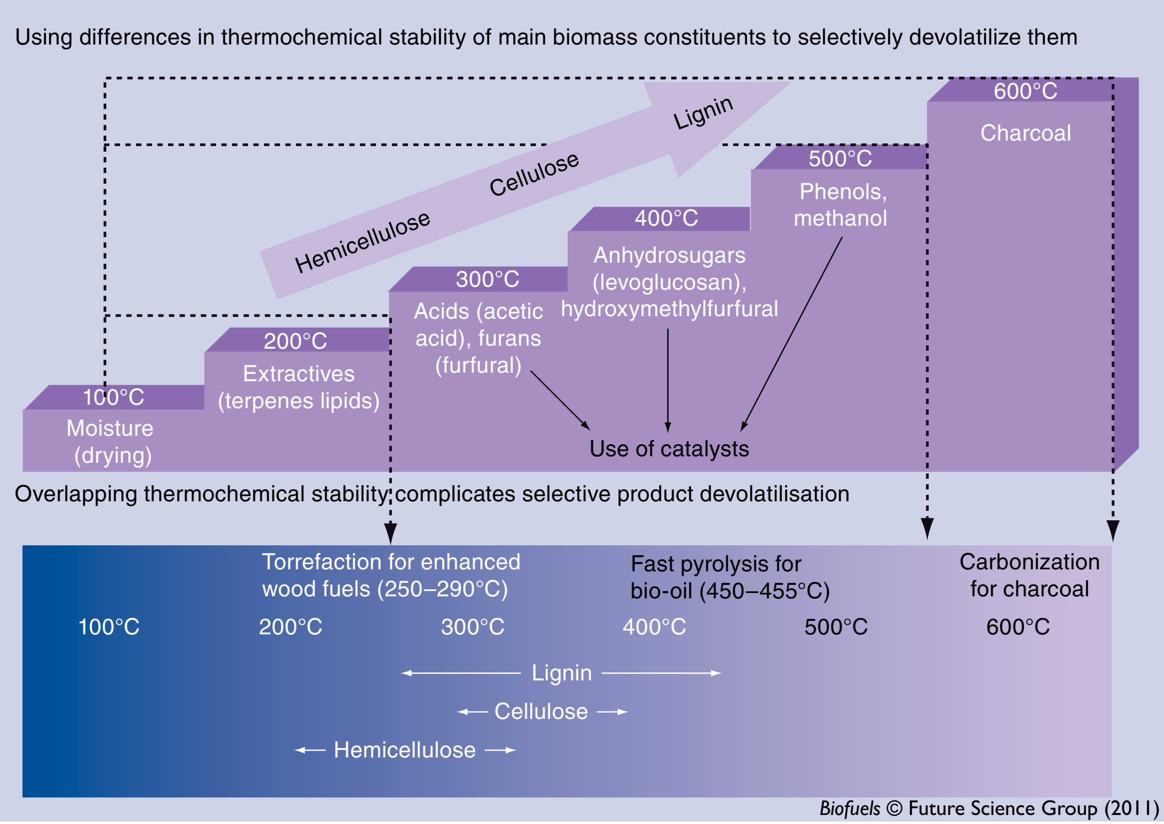

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Figure 3. Staged-degasification concept as an example of the thermal fractionation of biomass by a step-wise pyrolysis approach.

of the biorefinery will benefit much from the **valorization** of this lignin-rich residue to value-added aromatic chemicals instead of combustion of the residue for heat.

From **Table 3** and **Figure 3** it is obvious that pyrolysis of lignocellulosic biomass leads to an array of useful products, including liquid and solid derivatives and fuel gases. In the 1950s more than 200 chemical compounds had already been identified from the pyrolysis of wood [22]. Before the onset of the petrochemical era in the beginning of the 20th Century, pyrolysis processes were utilized for the commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstocks [26–28]. At the time, the dry distillation of wood for the production of charcoal was the mainstay of the chemical industry.

Many variations exist on the concept of thermochemical biorefineries [25,29], 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 [27]. This plant was erected to use the 400 tons per day of waste wood from the automobile plant.

It was designed not to make acetic acid (among charcoal and other products), but ethyl acetate (via esterification with bio-ethanol), which the company required in its lacquer and artificial leather departments. An interesting detail is the fact that the first T-Fords used bioethanol as their transportation fuel. Henry Ford strongly stimulated the use of renewable crops for fuels [1]. **Figure 7** gives a schematic overview of the plant, which was completely self-sufficient with regard to its heat demand.

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 producing renewable fuels from biomass [13,30]. **Figure 8** presents a view from the Energy Research Centre of The Netherlands on the potential layout of a future thermochemical biomass refinery [31]. As can be seen from the figure, torrefaction and gasification play an important role, and the valorization of several side-streams is important here too.

It is evident that the extraction of value-added chemicals from the complex bio-oil mixture is a challenge. Other challenges for further development of pyrolysis include the improvement of the reliability of reactors and processes and the demonstration of the suitability of the oil as a fuel for

Key term

Valorization: To add value by processing.

Table 3. Major chemicals from the pyrolysis of lignocellulosic biomass.

Pyrolysis products (major value-added chemicals underlined)	Market application examples
Biomass constituent: hemicellulose; thermal degradation range: 150–300°C	
Acetic acid	Bulk-chemicals, vinegar (food), cleansing agent, vinyl acetate, acetic anhydride, esters, solvent and road de-icer (as calcium acetate)
Furfural	Intermediate commodity chemical, solvent, resins, adhesives, food-flavouring agent and precursor for specialty chemicals
Furan, furanone, methanol, other C_1–C_4 oxygenates (e.g., formaldehyde, hydroxyacetaldehyde, acetone, acetol and lactones), C_5 and C_6-anhydrosugars and humic substances	
Biomass constituent: cellulose; thermal degradation range: 200–400°C	
Levoglucosan	Glucose, polymers and antibiotics
Hydroxyacetaldehyde	Food browning agent in 'liquid smoke'
1,6 anhydro-β-D-glucofuranose, furfural, hydroxymethylfurfural, furan and other C_1–C_4 oxygenates (e.g., methanol, formaldehyde, formic acid, acetone, acetol and lactones)	
Biomass constituent: lignin; thermal degradation range: 150–600°C	
2-methoxyphenols (e.g., guaiacol), 2,6-dimethoxyphenols (e.g., syringol) and catechols	Fine chemicals, pharmaceticals, food-flavouring agents in 'liquid smoke' and fragrance industry
Phenol	Bulk-chemicals, wood-adhesives, resins and plastics
Alkyl-phenols	Fuel additives
Methanol	Bulk-chemicals, solvent, fuel, antifreeze, ethanol denaturant, secondary-energy carrier for H_2 and bio-diesel
Other oxygenated aromatics (e.g., coumaran), furfural, acetic acid and other C_1–C_4 oxygenates (e.g., formaldehyde, formic acid, acetone, acetol and lactones)	
Pyrolytic lignin	
Biomass constituent: all fractions; thermal degradation range: 100–600°C	
Extractives (e.g., terpenes)	Fine chemicals, pharmaceuticals and turpentine
Charcoal	Fuel, soil improver, active carbon, metallurgy and BBQs
Pyrolysis-oil	Liquid fuel, feedstock for chemicals such as organic acids and phenolic compounds
Gases (e.g., CO, CO_2 and CH_4)	Fuel

Data from [3,12,22].

boilers, engines and turbines. From a more fundamental point of view, knowledge and control of the variety of different types of oxygen molecules in bio-oil (i.e., aldehyde, ketone, alcohol, ether, ester and acid) is needed in order to design pyrolysis processes for the production of specific types of bio-oil for desired applications (e.g., fuel and feedstock for chemicals) [17].

The vision of the Dutch Biomass Technology Group on a thermochemical biorefinery provides a good example of a pyrolysis-based biorefinery concept [201]. The concept uses fast pyrolysis as the primary process to convert biomass into bio-oil, which is subsequently fractionated in a secondary processing step. Finally, a tertiary upgrading step produces the final marketable products. Figure 9 gives a schematic overview of the bioliquids refinery concept.

Synopsis

Within the framework of historical research, technology development and the current state-of-the-art, this article highlights our work on some new thermochemical-conversion technologies in which pyrolysis plays a central role.

The following section focuses on staged-thermochemical processing of biomass by a step-wise pyrolysis approach and by a combination of a hot pressurized water treatment followed by pyrolysis. While these two-stage approaches are predominantly targeted at the carbohydrates in the biomass, the third thermal-conversion technology that is discussed focuses on the thermal cracking of lignin by (catalytic) pyrolysis. Finally, the described thermal-conversion technologies are integrated in a scheme that provides a roadmap of thermal fractionation and transformation possibilities for lignocellulosic biomass that may eventually find a place in a thermochemical biorefinery.

Innovative pyrolytic-conversion concepts Staged degasification for the thermal valorisation of biomass

Introduction, background & previous work

The intrinsic heterogeneity and complexity of lignocellulose calls for a biorefinery approach that is adapted to the feedstock and is difficult or impossible to match with current petrochemical technology. A direct conversion of the whole biomass by, for example, fast pyrolysis, leads to a complex mixture of many components.

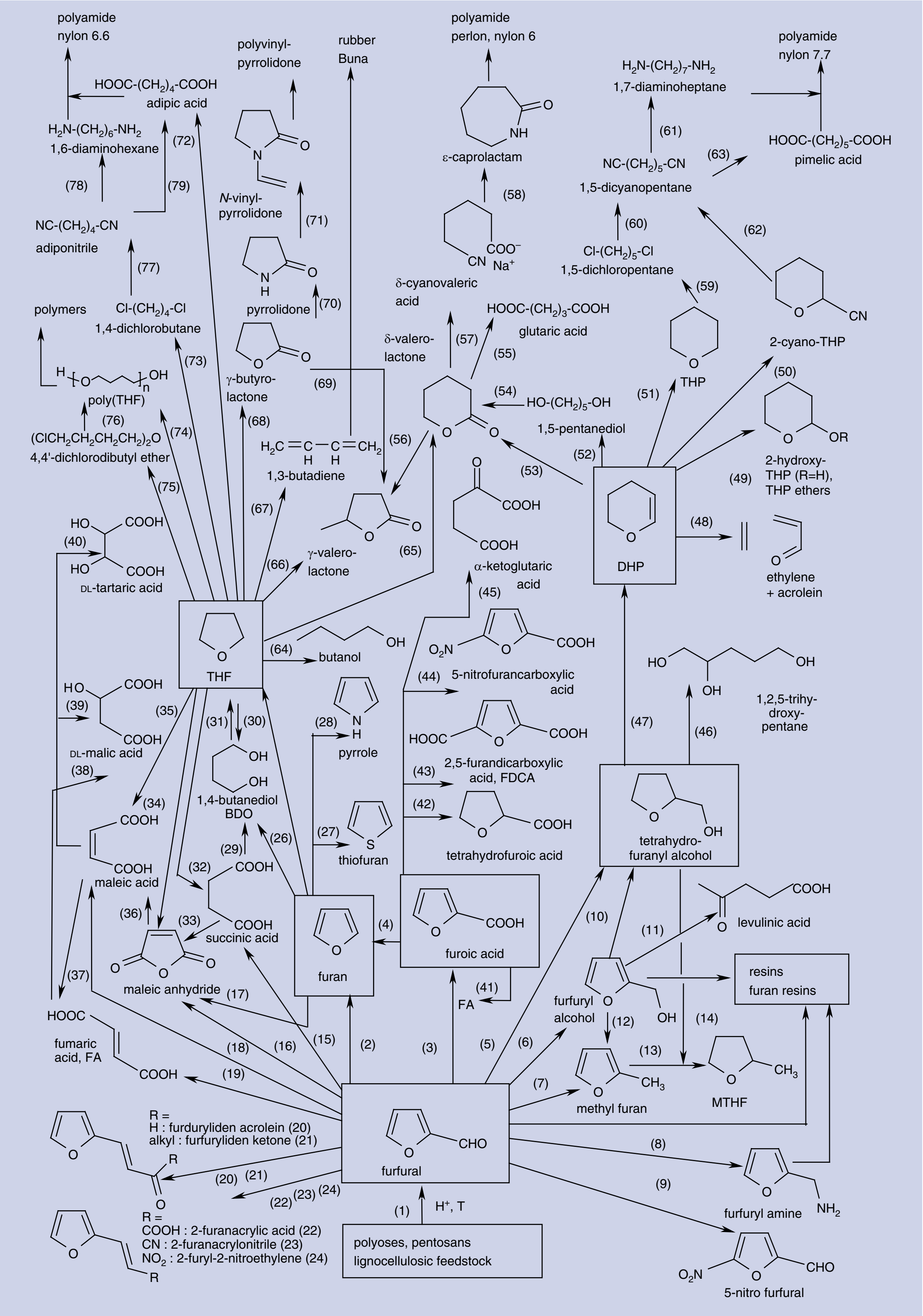


Figure 4. Products from furfural. Reproduced with permission from [23].

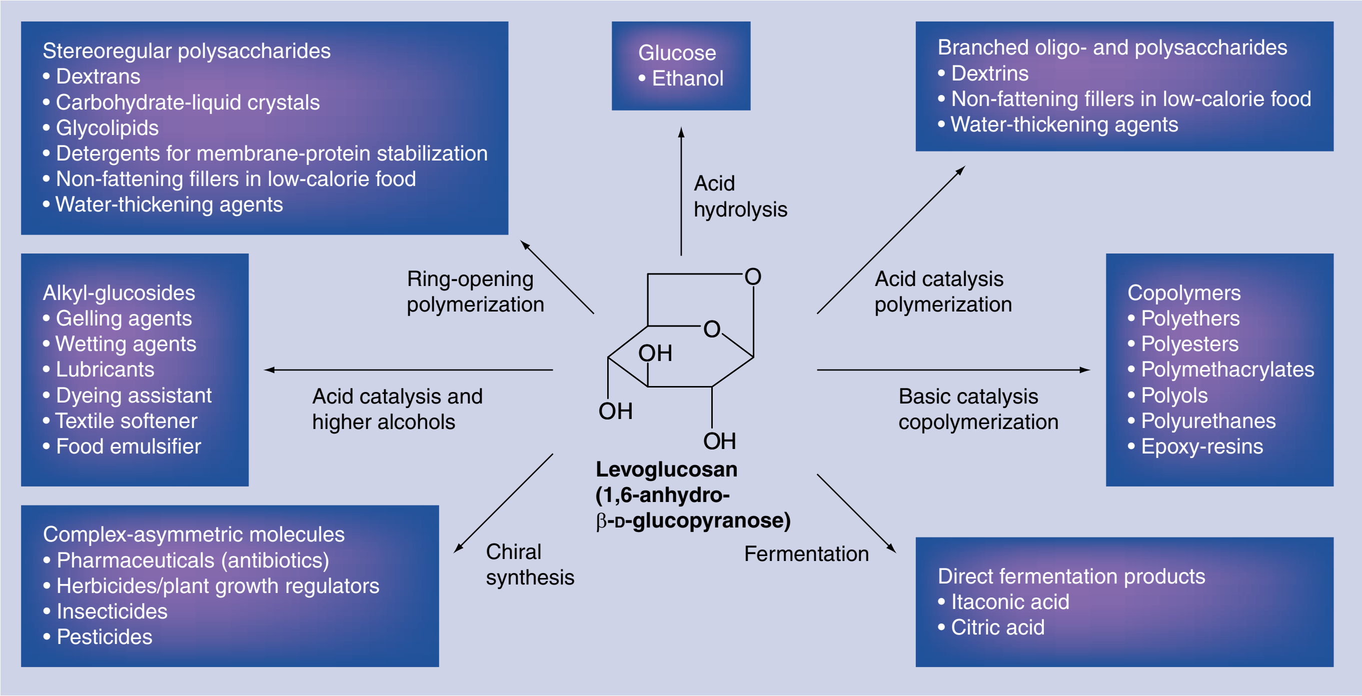


Figure 5. Products from levoglucosan.
Data from [16,24].

Isolation of individual substances from this soup is an expensive challenge. Unconventional solutions are needed.

It has been recognized for some time that an important prerequisite for the successful valorization of biomass to chemicals is an efficient fractionation into the main fractions; hemicellulose, cellulose and lignin. The main benefit of fractionation is that each of the major components are less heterogeneous than the original material and can be further processed into less complex product mixtures with higher concentrations of the desired chemicals.

An example of a group of fractionation technologies is the biomass-pulping processes, which are common practice in the pulp and paper industry (e.g., kraft pulping, sulphite 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 of this black liquor is combustion for heat. Another example of a fractionation technology is the production of bioethanol by fermentation of glucose, which 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 only one or two biomass fractions (e.g., organosolv pulping focussing on cellulose pulp and precipitated lignin).

Key term

Staged degasification: Step-wise thermal processing.

Recently, fast pyrolysis (rapid thermal conversion in the absence of air) has been developed to fractionate biomass into high yields of bio-oil (typically up to 80 wt% of the dry feedstock), gas and char. This is not a fractionation into the main constituents, celluslose, hemicellulose and lignin, but merely an efficient liquefaction of the solid biomass into 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 a real challenge.

Hemicellulose, cellulose and lignin react in different ways at different temperatures to yield different product slates (i.e., product mixture or product composition). In the **staged degasification** concept it is assumed that type, yield and selectivity of the formed products can be influenced by tuning the process conditions to the thermal stability of the main biomass constituents. It is expected that, due to the relatively mild conditions, each product fraction is less complex, more stable and less prone to unwanted secondary reactions than the 'one-pot' bio-oil from the harsher fast-pyrolysis process, where all three biomass components are degraded simultaneously and at the same temperature.

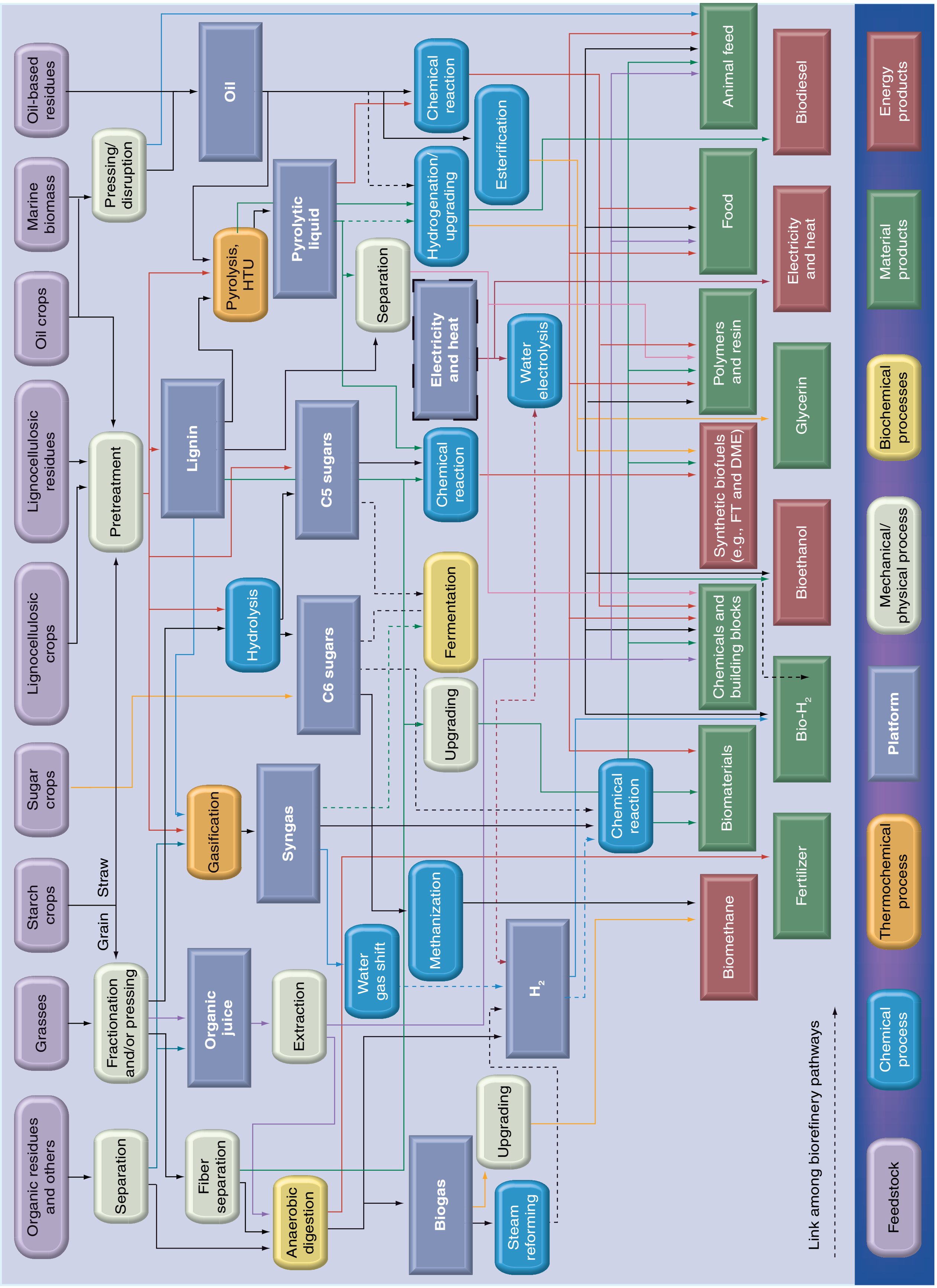
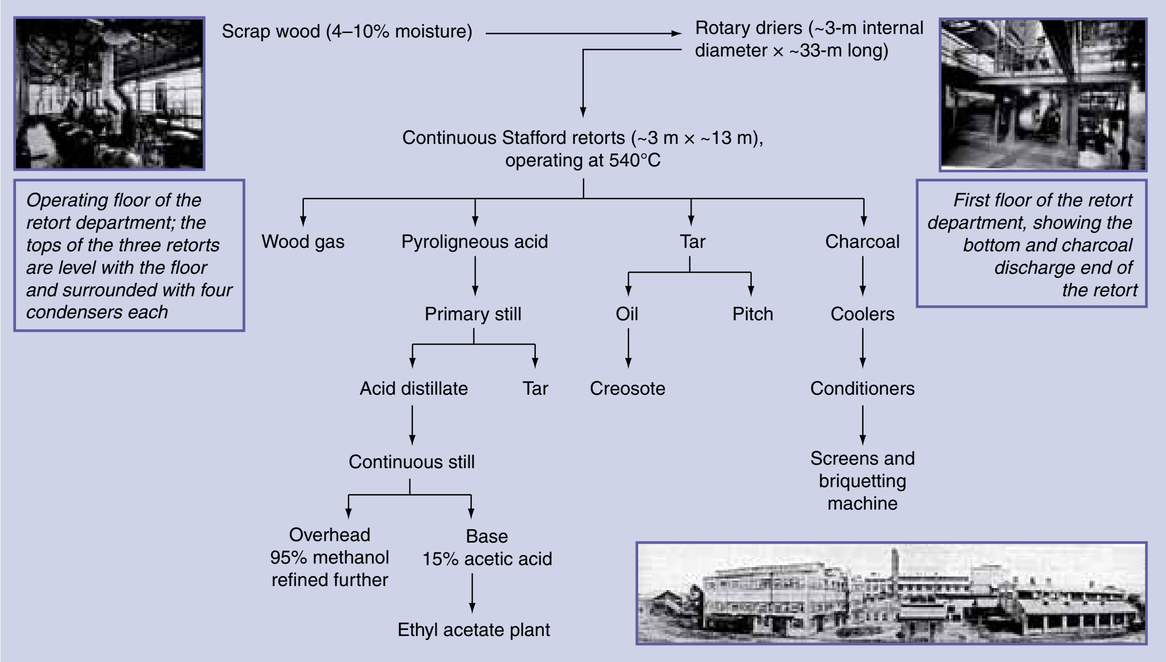


Figure 6. Classification of biorefinery systems.
DME: Dimethylether; FT: Fischer-Tropsch; HTU: Hydro thermal upgrading. Reproduced with permission from [25].



Operating floor of the retort department; the tops of the three retorts are level with the floor and surrounded with four condensers each

First floor of the retort department, showing the bottom and charcoal discharge end of the retort

Figure 7. Example from the 1920s of a thermochemical biorefinery; the flow sheet for the Ford continuous wood-distillation plant, Iron Mountain, Michigan, USA.
Reproduced with permission from [27].

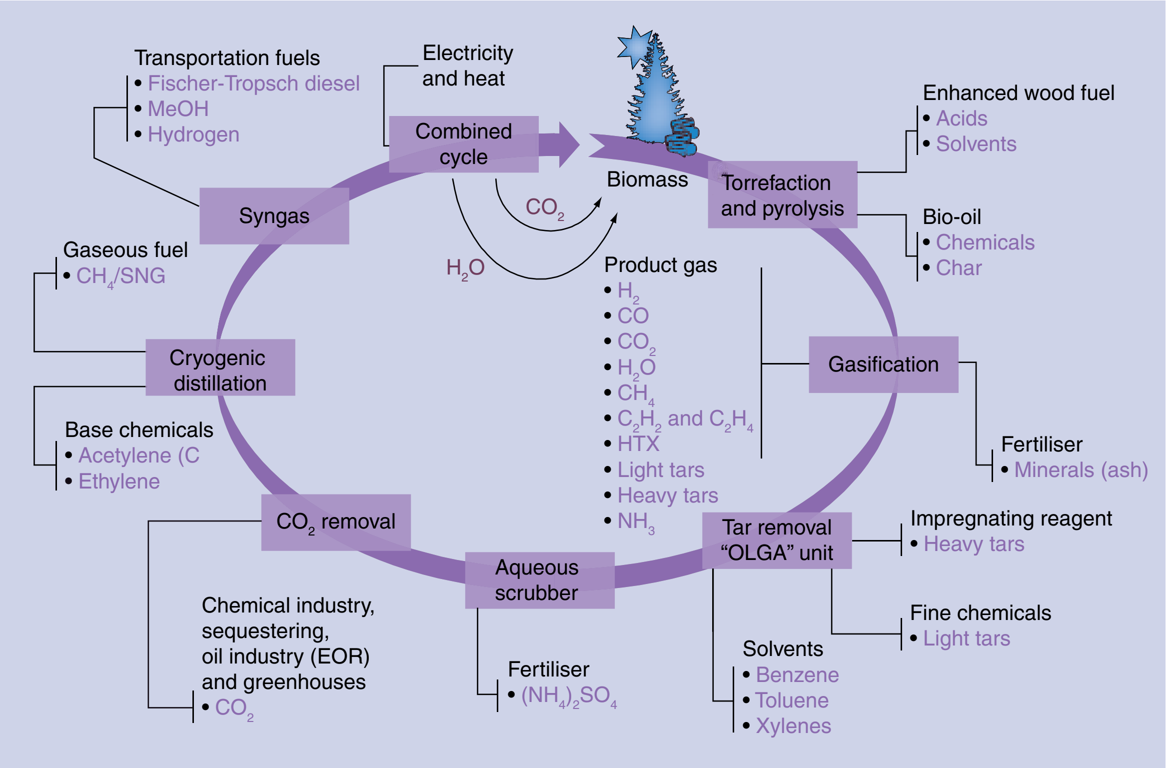


Figure 8. Thermochemical biorefinery concept from the Energy research Centre of The Netherlands.
EOR: Enhanced oil recovery.
Reproduced with permission from [31].

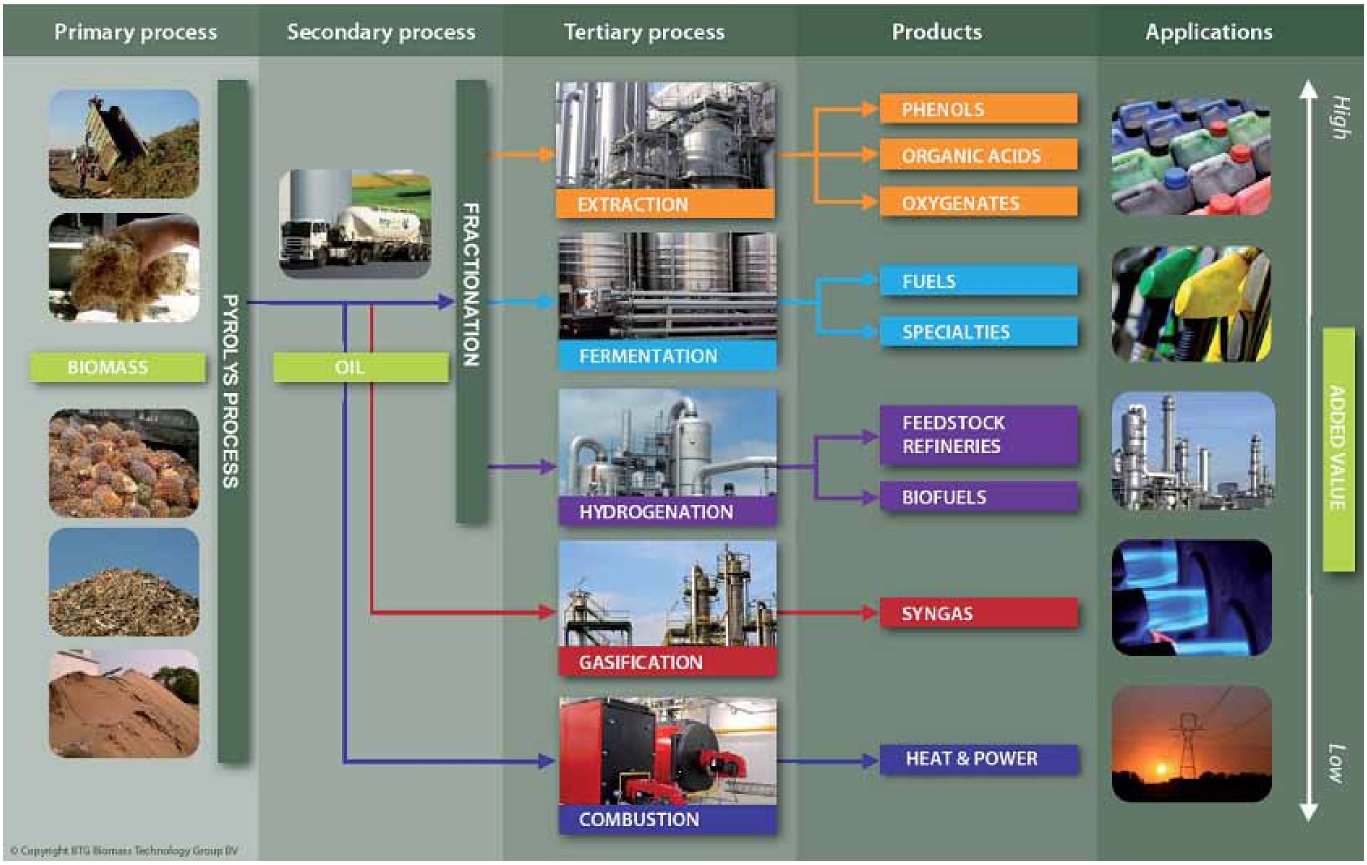


Figure 9. Biomass Technology Group's vision of a pyrolysis-based thermochemical biorefinery.
Reproduced with permission [201].

In an early example of a staged-pyrolysis approach, Roy and co-workers used a multiple-hearth vacuum pyrolysis reactor to process air-dry wood as feedstock [9]. Six pyrolysis oil fractions were collected at reactor hearth temperatures of 200, 263, 327, 363, 401 and 448°C, respectively. Overall bio-oil yield amounted to 65.8 wt%. Approximately half of the oil was collected in a primary condensation unit. Chemical analysis revealed the presence of several valuable chemicals such as acetic and formic acid (3.2 wt%), methyl-cyclopentene-ol-one (1.2 wt%), acetol (0.7 wt%), iso-eugenol (4.3 wt%), glucose (after hydrolysis) (5.4 wt%) and phenol (3 wt%). Unfortunately, the yields of chemicals from the secondary condensation unit are not given by the authors except for the carboxylic acids (5.8 wt%). Although the attained yields and selectivities for individual chemicals are rather limited, the approach clearly shows the potential of temperature staging to obtain pyrolysis oils that are enriched with certain chemicals.

Recent developments in our laboratory

We have further exploited temperature staging in the concept of staged degasification as a low-temperature thermochemical-conversion route to generate value-added chemicals from lignocellulosic biomass [32]. Figure 10 presents a schematic overview of the concept that is basically a step-wise pyrolysis approach. Thermal degradation products of each process step are collected separately.

Among the valuable chemicals that can be derived from the carbohydrate fraction of biomass [33], furfural [34] and levoglucosan [24,35] are interesting value-added chemicals, which could potentially be produced by thermochemical conversion. The pyrolytic formation of furfural and levoglucosan from lignocellulose has been investigated for decades [12,15,22,36], but no integrated pyrolysis-based production process for these two chemicals exist today. Although typical fast-pyrolysis oils can contain significant amounts of furfural, levoglucosan and other components, their separation is a big challenge because of the overall complexity of the oil [14]. To date, modern commercial processes to produce furfural involve mostly aqueous-phase hydrolysis/dehydration processes operating at relatively low temperatures (~200°C) and often using catalysts such as sulfuric acid [34].

The potential of the staged-degasification approach to produce furfural, levoglucosan and/or other chemicals has been assessed for beech, poplar, spruce and

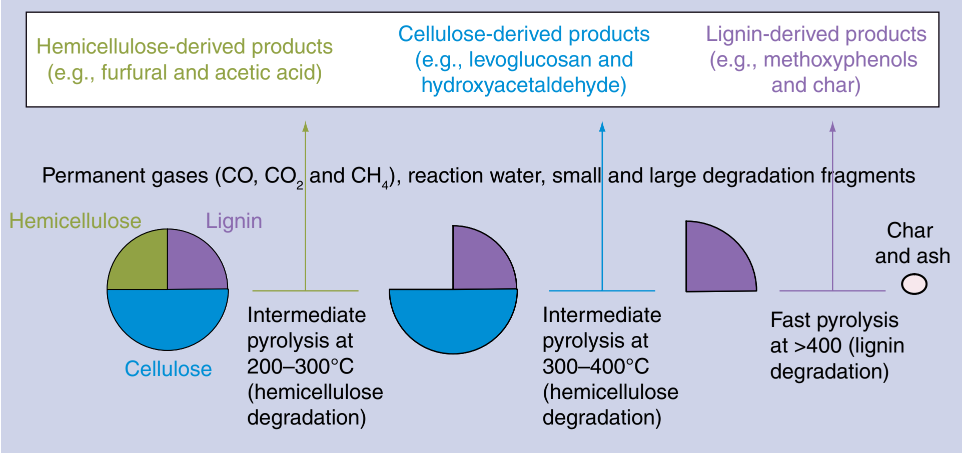


Figure 10. Staged degasification, a step-wise pyrolysis approach to selectively degrade biomass.

wheat straw as representative examples of deciduous, coniferous and herbaceous types of biomass. Two reactor types were tested, an auger reactor (a single-screw moving-bed type reactor) and a bubbling fluidized bed (BFB) reactor [32]. Degasification of the feedstock during a discontinuous step-wise temperature ramp leads to complex mixtures of degradation products. Step 1 at 200–300°C (HR ~1 < HR < 100°C/sec) is a slow-to-intermediate pyrolysis that is targeted at the conversion of hemicellulose. Step 2 at 300–400°C is an intermediate pyrolysis (HR < 1000°C/sec) targeted at the conversion of cellulose. Finally, the last step above 400°C is a typical fast pyrolysis (HR > 1000°C/sec) to degrade the lignin. Each mixture that is produced at the different steps consists of small amounts of degradation products that originate from all three main biomass constituents. Except for acetic acid, the yields of individual chemicals were generally below 1 wt% (d.b.). However, certain groups of thermal degradation products, such as C_2-C_4 oxygenates and phenols, are formed in higher yields, up to 3 wt%. Fluidized bed pyrolysis with beech typically yields more water, less permanent gases and char, less methanol and phenols and more levoglucosan, when compared with conventional pyrolysis in the screw reactor. The main reasons for these differences are the longer solid-residence time and the large temperature gradients in the screw reactor when compared with the fluidized bed. Results are presented in **Figure 11**, which compares the combined pyrolysis product yields obtained at 280 and 350°C for both reactor approaches.

Although the yields of valuable chemicals and/or groups of chemicals from a two-stage low-temperature degasification process in the fluidized bed are in some cases higher than the corresponding yields from the auger approach, they are below 3 wt% of the dry feedstock (except for carboxylic acids).

When compared with a one-step pyrolysis, the staged approach in the BFB offers a better selectivity for carboxylic acids at 280°C, as was also the case for the auger reactor [32]. It is envisioned that a limited yield is not necessarily a drawback for a cost-effective process, provided that product selectivity is sufficient for effective separation and upgrading. Higher yields and better selectivities can be obtained by further optimization of reactor conditions, catalysts and specific biomass pretreatments.

As described above, we explored the staged-degasification concept using a discontinuous pyrolysis approach. In stage 1, the biomass is degasified at 280°C, products are collected and, after the evolution of volatiles has decreased to a low level, the partially degraded biomass is removed from the reactor to cool down. Subsequently, the partially degraded biomass is subjected to stage-2 pyrolysis at 350°C. This sequence is probably not optimal for an effective devolatilization during stage 2 because of the recondensation phenomena during the cooldown after stage 1, causing the formation of thermally stable intra-lignin and lignin–cellulose bonds. An improved approach would be a fast and continuous rise to the stage 2 temperature. In general, a fast HR enhances the liberation of volatiles [37] with the wanted products among them. A staged-degasification process using interconnected (fluidized bed) reactors at different temperatures might lead to higher product yields and/or better selectivities. In this approach the partially reacted biomass is mechanically (e.g., by a feeding screw and/or conveyor belt) conveyed under an oxygen (air) free gas atmosphere (e.g., nitrogen) from one reactor compartment to the other.

Hybrid-staged processing of biomass for furfural & levoglucosan

▪ Introduction, background & previous work

Degasification of biomass during a step-wise temperature rise in multiple hearth, auger and fluidized bed reactors has been studied to explore the production of chemicals as is described in the previous section.

Owing to the limited product yields, alternative approaches are needed to obtain higher yields, for example, by the optimization of reactor conditions, application of catalysts and application of specific biomass pretreatment procedures. As described in the introduction section, the main constituents (hemicellulose, cellulose and lignin) are strongly interconnected by a variety of physicochemical bonds that makes it difficult to separate them as individual constituents in high yields. Consequently, efficient and cost-effective fractionation technology is a clear asset to open up the possibility to treat each constituent separately, using dedicated conversion technologies to obtain specific target chemicals. A biorefinery in which the fractionation is combined/integrated with subsequent processing steps offers a solution for a cost-effective and environmentally sound valorization of biomass.

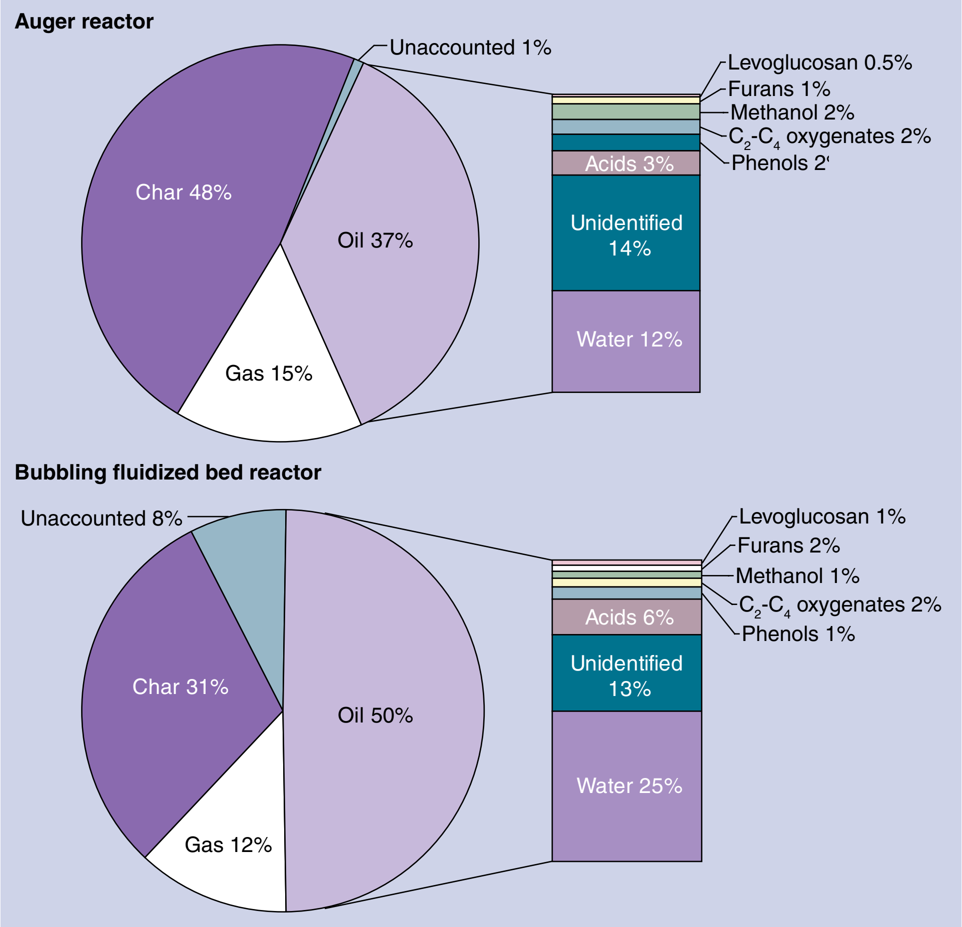


Figure 11. Staged degasification of beech wood chips: comparison of the total product yields from the sequential pyrolysis at 280–350°C in two reactor types.
Reproduced with permission from [32].

Hemicellulose can be removed from biomass by treatment with hot pressurized water [38–45]. This results in the formation of water-soluble oligomeric and monomeric sugars and their degradation products such as furfural and hydroxymethyl furfural [34,46,47]. The formation of these products is catalyzed by acetic acid, originating from the acetyl groups of hemicellulose. Water-soluble components such as alkali metal ions are leached out from the solid biomass. In the absence of the cracking activity of alkali metals (e.g., potassium [48]), cellulose can be depolymerised to levoglucosan in good yields [49,50]. Cellulose and lignin are relatively unaffected by the hot water treatment, although lignin can be solubilised as well, especially when the reaction products are continuously removed from the solid biomass [51]. 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 [40,52]. The recondensed structures could be more thermally stable than the parent material and less prone to thermal degradation under conditions where cellulose does degrade. This implies that in a subsequent pyrolysis step a more selective depolymerization of cellulose is possible, resulting in enhanced yields of levoglucosan and fewer lignin-derived degradation fragments when compared with direct pyrolysis of the original feedstock.

In the 1980s, Shafizadeh had already envisioned a hybrid process in which the fast pyrolysis of biomass for levoglucosan is preceded by the removal of the hemicellulose via a mild sulfuric acid hydrolysis [7].

The acid hydrolysis transforms the hemicellulose into water-soluble carbohydrates while the subsequent fast-pyrolysis step converts the resulting lignocellulose complex into a high levoglucosan-containing bio-oil. Shafizadeh developed the process as a hybrid pyrolytic route to fermentable sugars, that is, C_6 sugars. The highest yields of this process were found from softwoods, since their hemicelluloses contain a large fraction of (fermentable) C_6 sugars (mannose and galactose). The process includes some interesting features that are still worth investigating. For instance, Shafizadeh anticipated the existence of anhydro-polysaccharides in the tar and he obtained a significant increase in the yield of glucose by a mild acid hydrolysis of the pyrolysis tar. On a 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 12 presents a conceptual design of Shafizadeh's process as a pyrolytic route to fermentable sugars from softwood.

Key term

Hybrid thermochemical approach: Combination of two thermochemical processes in which the reaction media differ (i.e., liquid-phase treatment in water and gas-phase pyrolysis).

The importance of Shafidazeh's groundbreaking work was recognized by workers from the University of Waterloo, who 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 [14]. In 1999 So and Brown compared the cost of producing ethanol from cellulosic biomass via a biorefinery **hybrid thermochemical approach** [53,54], analogous to Shafizadeh's concept, to acid hydrolysis and enzymatic-hydrolysis technologies [7]. 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.

In the 1980s the relative ease of hemicellulose hydrolysis was exploited by the New Zealand Convertech process that used a series of five continuously operated modules, in which the main hydrolysis, chemical extraction and drying operations took place [55]. The process used steam hydrolysis to break down the biomass into its chemical constituents, such as cellulose, lignin, volatiles and sugars derived from hemicellulose. The main emphasis was on the separation of hemicellulose from the lignin–cellulose complex and the production of a low-moisture product termed 'Cellulig'. Although patented in 1995 [101], no commercial follow up took place as far as we know. The reviewers of the Convertech system believe that the main reason is the diversity of potential products [55]. Commercialization depends on focusing on relatively short-term goals, not on the entire spectrum.

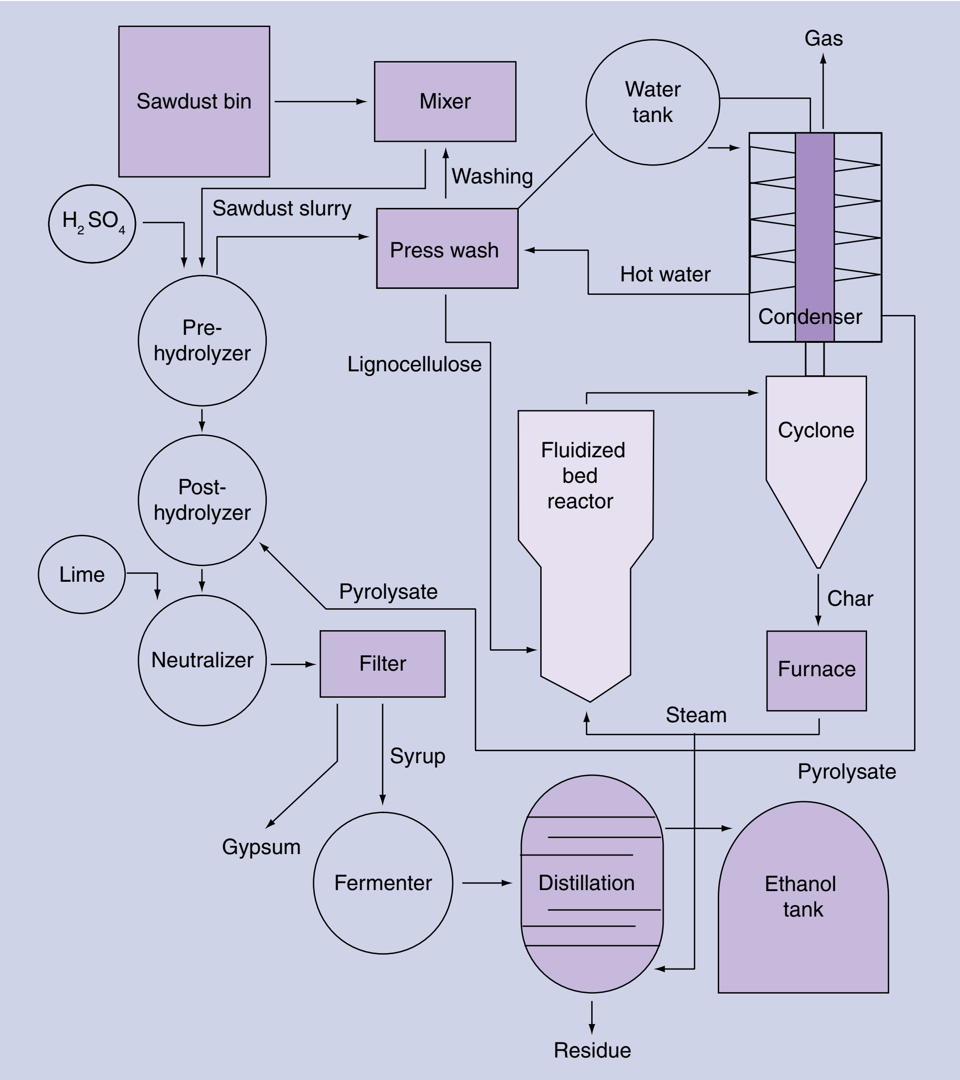


Figure 12. Combined acid hydrolysis and pyrolysis for the production of fermentable sugars. Reproduced with permission from [7].

As an alternative to the conventional dilute sulfuric acid-catalyzed production of furfural from biomass, workers from the Latvian State Institute of Wood Chemistry (Gravitis *et al.*) developed an approach that uses small amounts of catalysts such as concentrated sulfuric acid [56]. The process is able to obtain a furfural yield of 75% of the theoretical maximum (~73 wt% of the pentosan content). Given the 55% yield of conventional processes, this is a significant improvement. In addition, the integration of the furfural production with the production of levoglucosan and/or lignin was addressed [56]. A possible drawback of the integrated process is the fact that, prior to the fast pyrolysis step for the production of levoglucosan, a certain amount of the catalyst should be removed from the biomass by a water wash. Otherwise the yield of levoglucosan will probably be negatively affected.

Recent developments in our laboratory

Along similar lines, we are working on a novel hybrid staged-thermolysis concept for the production of furfural and levoglucosan from lignocellulosic biomass [57]. Compared with the catalyzed processes for furfural, our approach uses the autocatalyses by the innate acids (mainly acetic acid) that are liberated from the hemicellulose upon treatment with hot pressurized water. An advantage of this approach is the simultaneous leaching of the water-soluble inorganics, like the alkali metals, that would otherwise act as cracking catalysts in the levoglucosan-producing pyrolysis step. This hybrid concept is presented in **Figure 13** and involves a synergistic combination of hot pressurized water treatment (aquathermolysis) and (fast) pyrolysis, in which the fractionation of the lignocellulosic biomass is integrated with the production of valuable chemicals. The aquathermolysis step leads primarily to the production of furfural from the hemicellulose, while a subsequent fast pyrolysis step of the dried lignocellulose residue (enriched in cellulose and lignin) selectively converts cellulose into levoglucosan. Important byproducts are acetic acid from the aquathermolysis and residual bio-oil and char from the pyrolysis step. To ensure a successful fast pyrolysis, the wet lignocellulose residue (typically >50 wt% of moisture) from the aquathermolysis should be dried to approximately 90 wt% dry matter. This can be accomplished by, for example, a combination of a heated filter press, followed by a standard belt-drying procedure. The heat for drying can be generated by combustion of (part of) the pyrolysis products, that is, the gases. Part of the removed water can be condensed and recycled for the aquathermolysis step. Various options for heat integration are available, but a detailed discussion of these possibilities falls outside the scope of this article.

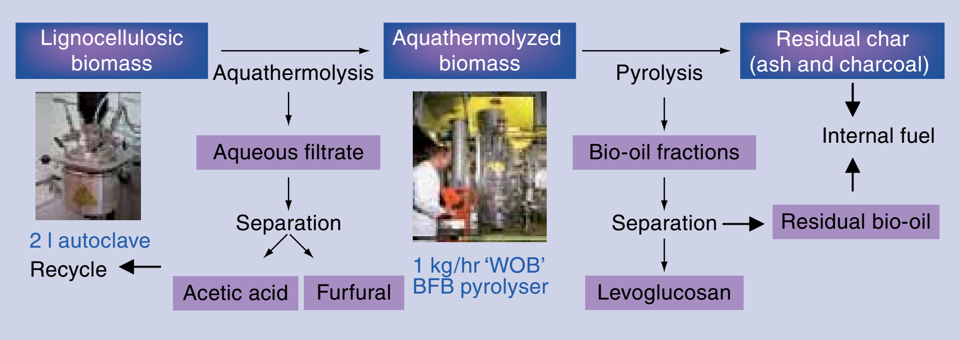


Figure 13. Hybrid-staged degasification concept.
BFB: Bubbling fluidized bed; WOB: Wervelbed Opstelling Biomassa.

Experimental studies with beech, poplar and spruce wood and wheat straw explored the potential of a hybrid thermolysis option to valorize lignocellulosic biomass. Aquathermolysis in an autoclave at 200°C predominantly yields furfural and/or hydroxymethylfurfural, mainly from the hemicellulose fraction of the biomass. In a subsequent BFB pyrolysis of the aquathermolyzed residue at 350°C, the cellulose fraction is selectively depolymerised to levoglucosan. Up to 8 wt% (d.b.) of furfural, 3 wt% (d.b.) of hydroxymethylfurfural (from spruce) and 11 wt% (d.b.) of levoglucosan were obtained in the hybrid-thermolysis concept. Detailed results of our work are given in **Table 4**, which compares the results of the hybrid concept for beech, poplar, spruce and straw with the results of a direct one-step pyrolysis. It is clear that the hybrid concept results in higher yields for the target chemicals furfural and levoglucosan when compared with a direct pyrolysis. The hybrid approach also leads to higher yields and selectivities compared with the staged-degasification concept, as can be seen in **Figure 14**, which compares the yields of some major products from staged degasification and hybrid staged-degasification of wheat straw.

Lignin pyrolysis for phenolics

▪ Introduction, background & previous work

The previous sections on staged-thermochemical processing mainly dealt with the thermochemical conversion of the carbohydrate fraction of lignocellulosic biomass. The lignin is merely converted to low amounts of phenolics and char. As the second most abundant natural polymer next to cellulose, lignin is the major aromatic biopolymer and a valuable renewable source for aromatics that could replace aromatic petrochemicals in a variety of products [58,59]. In addition, lignin and lignin-containing residues are large waste streams from the pulp and paper industry and from biorefineries that use the carbohydrate fraction of the biomass, for example for the production of bio-ethanol [60,61].

Globally, approximately 50 Mt per year of lignin originates from the pulp and paper industry, predominantly from kraft-, soda- and sulphite-pulping of softwood, hardwood and agricultural residues such as straw, flax and grasses). Only 1 Mt is used for commercial purposes including lignosulphonates from sulfite pulping and 0.1 Mt as (chemically modified) kraft lignins from kraft pulping [62].

At present, most of these sulfur-containing lignin-streams are combusted for generating power and/or heat, an application with very limited value. These sizable amounts of lignin are, in principle, available for valorization into chemicals and performance products. New developments in soda-pulping technology have resulted in sulfur-free lignins from herbaceous types of biomass such as straw and grass. Furthermore, large amounts of (hydrolytic) lignin will be produced from future bio-ethanol-based biorefineries by processes such as steam explosion and organosolv-pulping. The first is a thermomechanical treatment that uses sulfuric acid

Table 4. Breakdown of the product composition from aquathermolysis and pyrolysis experiments.

Thermolysis products†	Beech				Poplar				Spruce				Straw			
	A	P	A + P	DP	A	P	A + P	DP	A	P	A + P	DP	A	P	A + P	DP
Furfural	5.5	0.3	5.8	0.3	3.5	0.3	3.8	0.2	1.9	0.3	2.2	0.2	7.5	0.3	7.8	0.3
HMF	1.2	0.7	1.9	0.2	0.3	0.6	1.0	-	3.0	0.6	3.6	0.3	0.5	0.7	1.2	0.1
Levoglucosan	-	9.7	9.7	1.1	-	9.5	9.5	0.4	-	11	11	2.7	0.8	7.5	8.3	-

†All yields are in wt% (dry base).
A: Aquathermolysis; DP: Direct pyrolysis of the fresh, dried feedstock; HMF: Hydroxymethylfurfural; P: Pyrolysis of the aquathermolysed residue.

for the hydrolysis and steam explosion for breaking up the fibrous biomass structure. Organosolv-pulping of hardwood, grasses and straw leads to a high-quality lignin that is essentially sulfur-free. Organosolv-pulping refers to a thermal and pressurized treatment of the lignocellulosic biomass with water and organic solvents such as ethanol and carboxylic acids. The biomass is fractionated into lignin, cellulose and a hemicellulose-containing side stream. Generally, the hydrolytic lignins are the main fraction in the side-stream that originates from the processing of wood and agricultural residues for transportation fuels and chemical building blocks.

Only recently, with the upcoming focus on biorefineries, has lignin gained new interest as a chemical resource, as again the supply of fossil feedstocks is becoming more and more insecure and expensive.

However, economic and technological considerations still preclude a large-scale mass production of low molecular weight chemicals from lignin in competition with petrochemicals. This is inherent to the specific nature of the complex and stable lignin polymer, which makes it difficult to convert it into valuable monomeric chemicals.

Lignin pyrolysis has been studied for almost 100 years with a focus on unraveling the structure of the aromatic biopolymer, and on the production of monomeric phenols [63,64]. In the past 25 years little attention has been paid to the use of lignin as a chemical resource. Lignin has instead been used for fundamental studies on degradation mechanisms by (advanced) pyrolysis methods combined with sophisticated separation and detection systems (including GC–MS).

In the literature on the (gaseous phase) pyrolysis of lignin for the production of chemicals, limited yields of monophenolic compounds are commonly reported, rarely exceeding 5–6 wt%, based on dry lignin. To enhance the yield of monomeric phenols, several pyrolysis approaches have been pursued [65], such as pyrolysis of lignin in the presence of a hydrogen-donor agent (e.g.,1,2,3,4-tetrahydronaphthalene [tetralin]), Fe_2O_3 catalyzed lignin liquefaction in the presence of solvents and, in a hydrogen atmosphere, pyrolysis of lignin with tetralin and phenol, Cu(II) acetate-catalyzed lignin degradation, pyrolysis of lignin with cresol in a hydrogen atmosphere, $ZnCl_2$-catalyzed pyrolysis of lignin with and without tetralin, lignin pyrolysis with basic salts such as NaOH, K_2CO_3 and Na_2CO_3, and lignin pyrolysis with neutral salts such as NaCl and KCl.

In a recent international collaboration the fast pyrolysis of several lignin samples and the analysis of the products was attempted in order to, first, establish the potential for this method of lignin processing and, second, to compare procedures and results [66]. The research was carried out in the International Energy Agency Bioenergy Agreement Pyrolysis Task 34 – PyNe. A total of 14 laboratories in eight different countries contributed to the project. Two lignin samples were distributed to the laboratories for analysis and bench-scale process testing via fast pyrolysis. The first sample was a sulfur-free lignin obtained from annually harvested nonwoody plants (wheat straw and Sarkanda grass [*Saccharum munja*]). The pulping method was the soda-pulping process (aqueous NaOH). The material was a highly purified lignin recovered by precipitation,

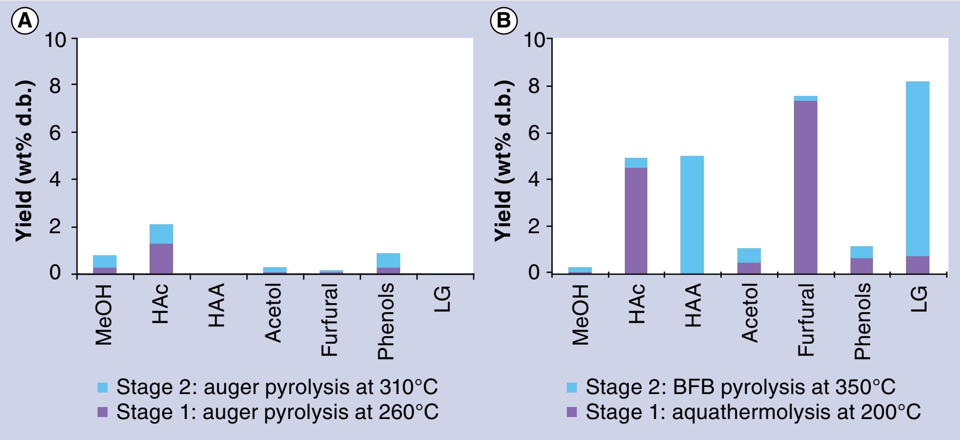


Figure 14. Thermal valorization of wheat straw by staged degasification and hybrid-staged degasification.
BFB: Bubbling fluidized bed; d.b.: Dry base; HAA: Hydroxyacetaldehyde; HAc: Acetic acid; LG: Levoglucosan; MeOH: Methanol; wt: Weight.

followed by washing and drying. The second sample was a concentrated lignin material, which was a residue from ethanol production by weak-acid hydrolysis of softwood. This lignin contained a significant fraction of cellulose- and hemicellulose-degradation products and was not purified. **Figure 15** presents photographs of both lignins.

Analyses included proximate and ultimate analysis, thermogravimetric analysis, and analytical pyrolysis. The bench-scale test included BFB Reactors and entrained flow systems. Based on the results of the various analyses and tests it was concluded that a concentrated lignin (estimated at ~50% lignin and 50% cellulose) behaved like a typical biomass, producing a slightly reduced amount of a fairly typical bio-oil, while a purified lignin material was difficult to process in the fast pyrolysis reactors and produced a much lower amount of a different kind of bio-oil. It turned out that lignin can not be effectively fast pyrolyzed in reactor systems designed for whole biomass materials. However, less purified lignin products, as derived from some hydrolysis-based systems, may be suitable feedstock in conventional fast pyrolysis with minor adjustments for temperature control in feeding and product collection methods [66]. Owing to the physicochemical characteristics of lignin as a thermoplastic, thermally stable and often powder-like material, and due to the nonspecific nature of the pyrolysis process itself, industrial lignin-pyrolysis processes are rare. Since lignin is considered a potentially very attractive source for biofuels and bio-based performance chemicals, new-upgrading technology will be required for this purpose. A possible route is hydrotreatment using a heterogeneous catalyst and hydrogen as reactant. Desired reactions include **hydrodeoxygenation** (HDO), the removal of oxygen in the form of water and depolymerization. Typically, high pressures (100–200 bar) and temperatures (300–450°C) are required to convert lignin into low molecular weight compounds in good yield [67,68].

The thermochemical valorization of lignin-rich waste streams from, for example, biorefineries is a challenge, because generally the lignin is not in a pure form but mixed with residual (unconverted) carbohydrates, microbial biomass from fermentation, minerals and so forth. Pyrolysis of this residual material thus leads to an impure pyrolytic lignin oil (PLO) that contains – as well as the lignin-derived phenolics – the thermal degradation products from the nonlignin constituents. As a consequence, separation and purification of this oil is very challenging.

Fractional catalytic pyrolysis is an elegant one-step process that has been applied successfully in the conversion of a hybrid poplar wood into a bio-oil that contains high concentrations of cresols and phenols, while the carbohydrate fraction was selectively converted into gaseous products [69]. Here, specific catalysts are used to selectively convert the impurities in the lignin-rich waste stream (predominantly the residual carbohydrates), while the lignin is merely thermally cracked to phenolic substances.

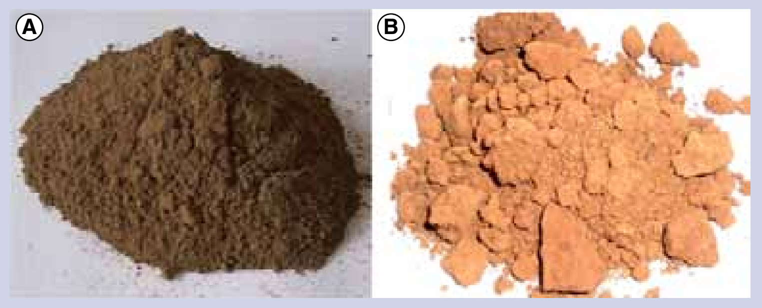


Figure 15. (A) Straw/grass soda-pulping lignin and (B) softwood weak acid hydrolysis lignin.

Fractional catalytic pyrolysis can be regarded as a form of 'extractive pyrolysis' through which the separation problems, related to the fast pyrolysis of impure lignin-rich (biorefinery) residues, can probably be tackled. An effective conversion of the carbohydrate impurities leads to a mixture of permanent gases that do not condense with the phenolics from the lignin. As a result, a bio-oil is obtained that consists mainly of phenolic material.

Recent developments in our laboratory

Recently, we have developed a novel-BFB pyrolysis technology to generate PLOs from technical (i.e., pure) lignins, for example, for subsequent hydrotreating trials [70]. A schematic drawing of the laboratory-scale pyrolysis test rig (lignin feed rate up to 1 kg/h) is presented in **Figure 16**.

The process features a specific protocol for lignin pretreatment, feeding and intermediate pyrolysis. The liquefied lignin was subsequently hydrodeoxygenated using a ruthenium-based catalyst. The PLO has a decreased molecular weight when compared with the original lignin, thus making the conversion to low molecular weight derivatives easier.

The continuous fast pyrolysis of the lignin resulted in a PLO containing approximately 13–20 wt% of a phenolic fraction. The amount of low molecular weight phenolic compounds in the oil was approximately 7–9 wt%. Approximately half of this amount was identified as (predominantly) guaiacols, syringols, alkyl phenols and catechols. These results are graphically presented in **Figure 17** for two tested lignins.

Both as individual chemicals and as mixtures, these compounds have the economic potential to replace

Key term

Hydrodeoxygenation: Catalytic treatment of the biomass or bio-oil with pressurized hydrogen at temperatures in the range of 200–400°C with the aim to reduce the bound oxygen content of the feed.

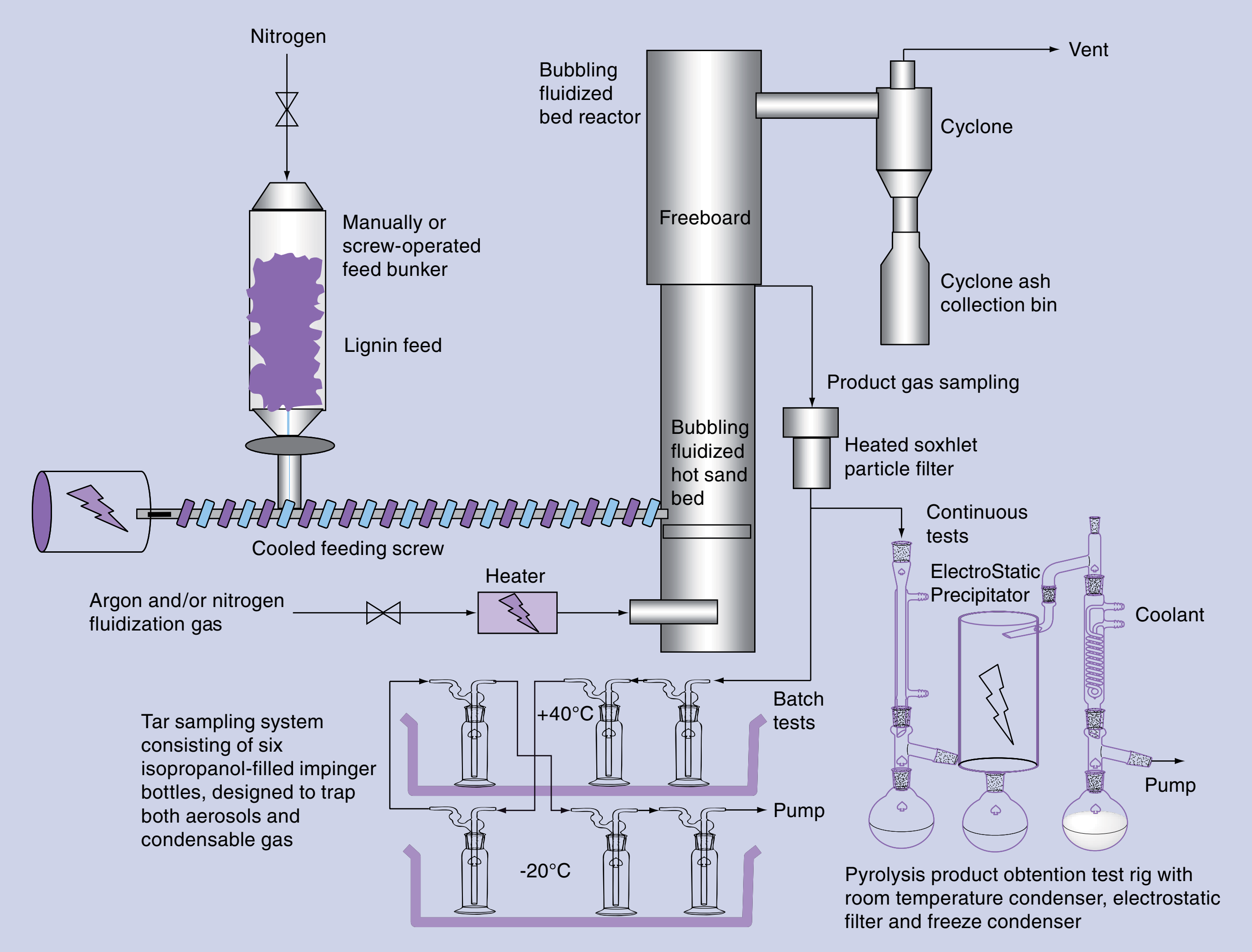


Figure 16. Laboratory-scale bubbling fluidized bed test rig for the pyrolysis of lignin.
Reproduced with permission from [71].

a variety of petrochemical substitution options for a variety of products, for example, in wood adhesives, bioplastics, pharmaceuticals, fragrances, octane enhancers for transportation fuels and so forth. Considering the standard pyrolysis process that was used, the obtained yields are a promising result and clearly indicate the potential for fast pyrolysis to valorize lignin. Further, it was shown that the PLO can be converted by a short HDO (catalytic treatment with pressurized hydrogen) reaction with ruthenium on activated carbon catalyst as a catalyst into cycloalkanes, alkyl-substituted cyclohexanols, cyclohexanol and linear alkanes [70]. This shows that the catalytic activity of ruthenium on carbon is too high for the hydrogenation of PLO towards low molecular weight phenolics. However, the products formed are still interesting and the HDO oil is useful as an oxygenated fuel additive for internal combustion engines.

Thermochemical biorefineries

In the previous sections an overview is presented of some new thermochemical conversion approaches for lignocellulosic biomass to produce value-added chemicals from each of the main biomass fractions; hemicellulose, cellulose and lignin. An efficient method for the (thermal) fractionation of biomass into a specific combination of its main constituents is a key issue in a biorefinery [71].

The addressed technologies are presented in Figure 18, which provides a pyrolysis-based roadmap for thermal fractionation and degradation of biomass. Figure 18 can also be viewed as an example of a (part of a) thermochemical biorefinery, that is, a biorefinery in which (various types of) lignocellulosic biomass can be converted to various products by a mix of various (pyrolysis-based) thermochemical processing options. The (enzymatic) hydrolysis of cellulose falls outside the scope of the roadmap, but is incorporated as an example of an important valorization route to glucose, as feedstock for the production of bio-ethanol via fermentation.

Much attention is presently focused on the production, application and upgrading of bio-oil from fast-pyrolysis of whole biomass for fuels and chemicals [72,73]. 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. However, recent developments show encouraging results [74–77], although yields are often limited. Given the complexity of the bio-oil, it is promising that some chemicals can be separated at all. It is debatable whether the yields of valuable chemicals in the bio-oil are high enough to merit their extraction, purification and finally their sale. This depends on many variables such as oil price, market situation (price and volume) for the specific chemical and a full techno-economic evaluation of the separation procedure, including a lifecycle analysis. This discussion falls outside the scope of the paper.

Pyrolysis can also play an important peripheral role in various types of hybrid biorefineries [78]. An example of a development that is currently going on in our

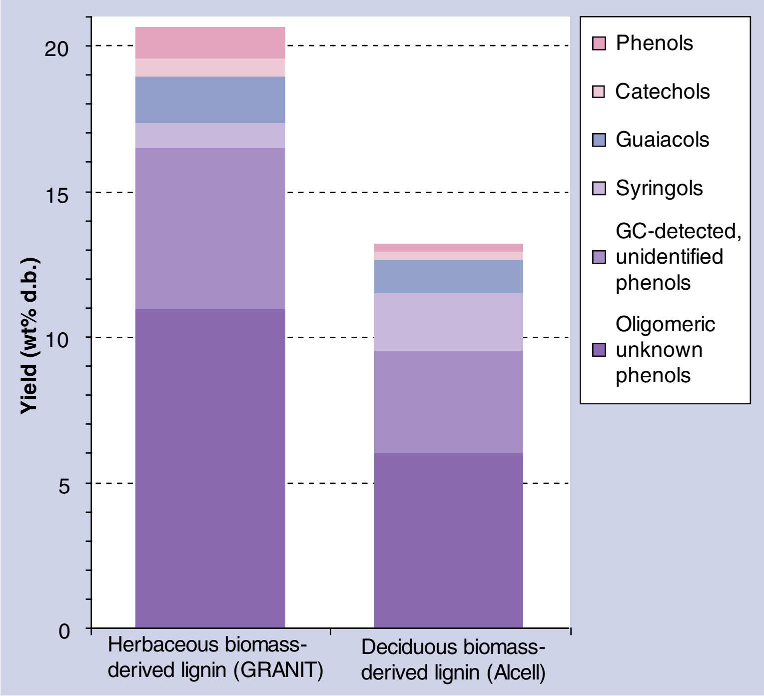


Figure 17. Product distribution of the pyrolytic lignin oil from a deciduous and a herbaceous biomass.
d.b.: Dry base; wt: Weight.
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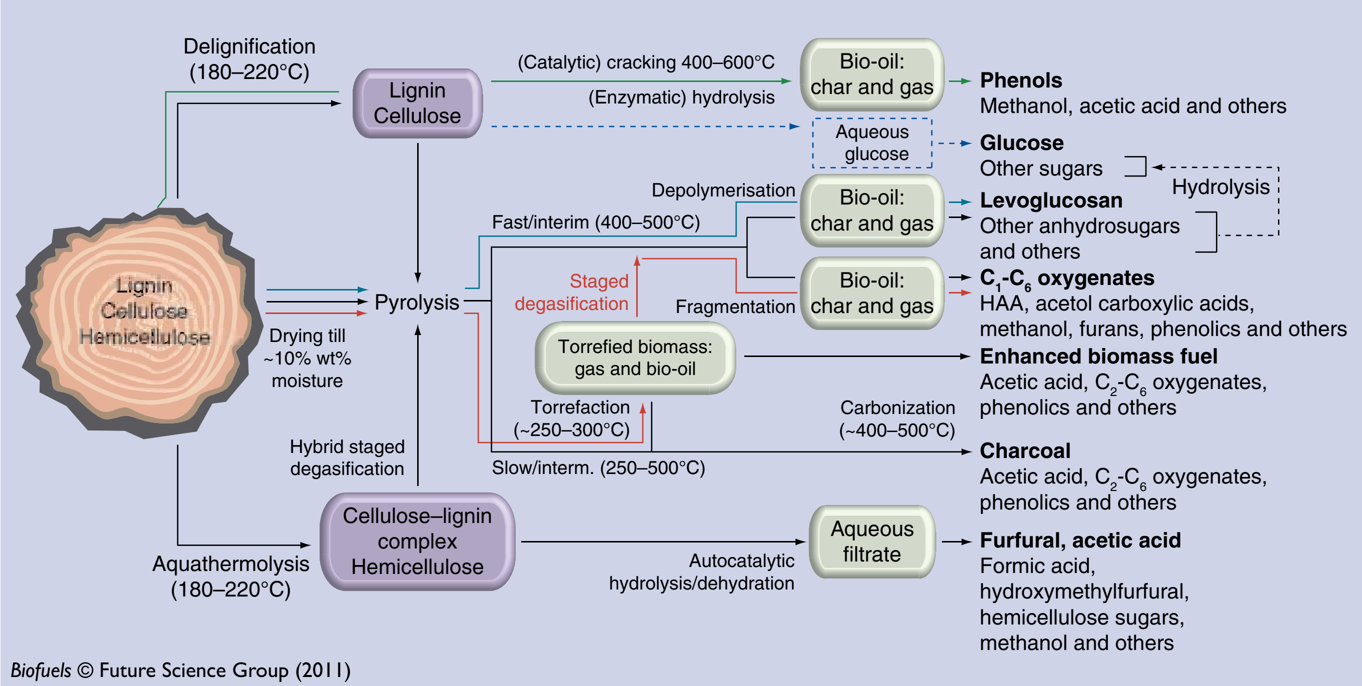

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Figure 18. Thermal fractionation and degradation routes for thermochemical valorization of biomass. The red, blue and green lines denote the routes that are highlighted in this article, respectively: staged degasification, hybrid-staged degasification and lignin pyrolysis.
HAA: Hydroxyacetaldehyde.

laboratories is the thermochemical conversion of the lignin-containing residual stream from a typical second generation bio-ethanol biorefinery, which is illustrated in **Figure 19** [79]. Integration of the lignin-pyrolysis section with the rest of the biorefinery enables the optimal use of material and heat within the refinery. This is an important aspect in several European and Dutch projects, for example, the sixth framework EU-integrated project BIOSYNERGY (2007–2010) [202] and the Dutch national Energy Research Subsidy – LongTerm project LIGNOVALUE (2007–2010) [203].

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 product that permits economies of scale [80].

Future perspective

The main parameters that govern the thermal degradation of lignocellulosic biomass are temperature, HR, gas- and solid-residence times and the reaction environment. The three major biomass polymers; hemicellulose, cellulose and lignin, possess dissimilar thermal stabilities and produce diverse degradation products when subjected to different temperatures. Owing to the overlapping thermal stabilities of the main biomass polymers, a selective thermal degradation of the whole biomass into a limited number of chemicals with high specificity and yield, is a challenge. In general, product mixtures from the thermal degradation of biomass contain a variety of degradation products from all three main biomass polymers. However, the fact that the thermal stabilities of the biomass polymers are affected by heat treatments can be exploited to decrease the overlap between them, enabling better selectivity to specific products through staged-thermal processing. It will offer the possibility of using dedicated thermal-processing technology for each of the fractions to enhance selectivity and yield of desired chemicals.

It is anticipated that fast pyrolysis will play an increasingly important role in the field of biomass conversion in the (near) future. In biorefineries, fast pyrolysis will either be the central processing unit or a peripheral unit for the conversion of residues. Here, a key issue is the valorization of lignin. The pyrolytic conversion of lignin into valuable chemicals is a challenge and, to determine the added value of lignin utilization other than its use as a fuel for power, application research and techno-economic analysis is required and should be a driving force guiding research efforts.

Carbonization is the oldest pyrolysis technology and is (still) mainly used for the production of charcoal, although other products can be generated as well (e.g., wood-vinegar and wood-tar). Torrefaction is a well known pyrolysis technology too. A slow-pyrolysis product option that is gaining much attention now, is the production of bio-char which may be used as a soil improver and crop-growth enhancer in agricultural applications [81]. Major R&D efforts will be needed to elucidate the relationships between slow-pyrolysis technology, the resulting charcoal quality and the applicability of the bio-char for soil improvement. Undoubtedly, this will lead to a further revival/new developments of charcoal-producing technologies.

Finally, the use of catalysts suppresses or promotes the devolatilization of combustible substances from the biomass. These materials are typically applied by impregnating the biomass. Other catalytically active materials may be used as an external aid, for example, in the form of fluidization material in a fluidized bed reactor or in the form of a catalytically active fluidization gas (e.g., steam, hydrogen, oxygen and CO_2). Downstream treatment of the primary product vapors in a fixed catalyst bed is another possibility. The use of catalysts in biomass pyrolysis is gaining more interest today [82–84] since it is a rather unexplored field. To date, positive results are scarce because of unwanted gas production and rapid deactivation of the catalyst. This clearly indicates the need for low-cost, effective and robust catalysts.

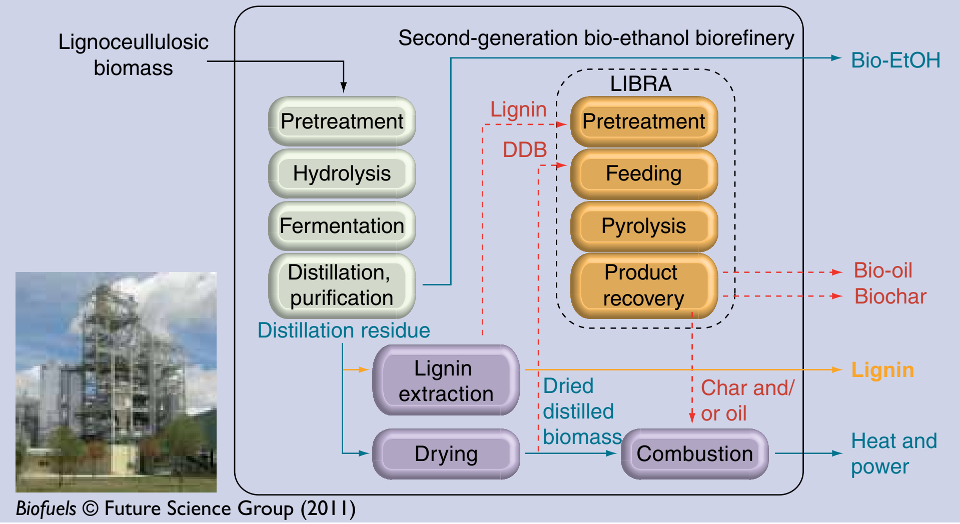

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Figure 19. Lignin biorefinery approach, under development by the Energy Research Centre of The Netherlands. The process set up is an example of the thermochemical valorization of the lignin-enriched residue from a cellulose ethanol-based biorefinery.

Executive summary

- Decreasing resources, global warming and environmental pollution associated with the use of fossil fuels are strong incentives for a transition to renewable energy, such as solar, wind, hydro and biomass. Among these renewable resources, lignocellulosic biomass is particularly suited as an abundant, low-cost feedstock for production of bio-based chemicals, fuels and energy to substitute for fossil resources.
- An important prerequisite for the successful valorization of biomass to chemicals is to establish an efficient method for the fractionation of lignocellulose into its main fractions; hemicellulose, cellulose and lignin. The intrinsic heterogeneiety and complexity of lignocellulose calls for a biorefinery approach that is adapted to the feedstock and is difficult or impossible to match with current petrochemical technology. Unconventional solutions are needed.
- The fact that hemicellulose, cellulose and lignin react differently at various temperatures and yield a dissimilar spectra of products can be exploited to extract value-added chemicals from biomass. The differential thermal behavior of the biomass components can be exploited via staged-thermal processing.
- Among the valuable chemicals that can be derived from the carbohydrate fraction of biomass, carboxylic acids, such as acetic acid, in addition to furfural and levoglucosan, are interesting value-added chemicals. The lignin fraction is an interesting feedstock for production of phenolics and derived chemicals.
- Staged degasification is a low-temperature thermochemical conversion route that generates value-added chemicals from lignocellulose in a step-wise pyrolysis approach. Due to the overlapping thermal stabilities of the main biomass fractions, staged degasification leads to complex mixtures of degradation products that occur in limited yields, typically below 5 wt%. It is anticipated that higher yields and better selectivities can be obtained by further optimization of reactor conditions, application of catalysts and/or specific biomass pretreatments, such as washing-out the water-soluble ash minerals.
- A hybrid staged-degasification concept that involves a synergistic combination of hot-pressurized water treatment (aquathermolysis) and (fast) pyrolysis shows substantial improvements in the yields for target products furfural and levoglucosan. Alternatively, the pyrolysis step can be replaced by a second aquathermolysis step (at higher temperatures than the first aquathermolysis), focusing on the extraction of phenols.
- As the second most abundant natural polymer next to cellulose, lignin is the major aromatic biopolymer and a valuable renewable source for aromatics, which can replace aromatic petrochemicals in a variety of products. With novel (fast) pyrolysis technology, significant yields of pyrolytic lignin oil can be produced from lignin and lignin-containing material for further upgrading, for example, by hydrotreating.
- An efficient (thermal) fractionation of biomass into a specific combination of its main constituents is a key issue in a biorefinery. Fast pyrolysis is expected to play an important role in future biorefineries, either as a central unit or as a peripheral unit to process biorefinery residues including lignin.

Financial & competing interests disclosure

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