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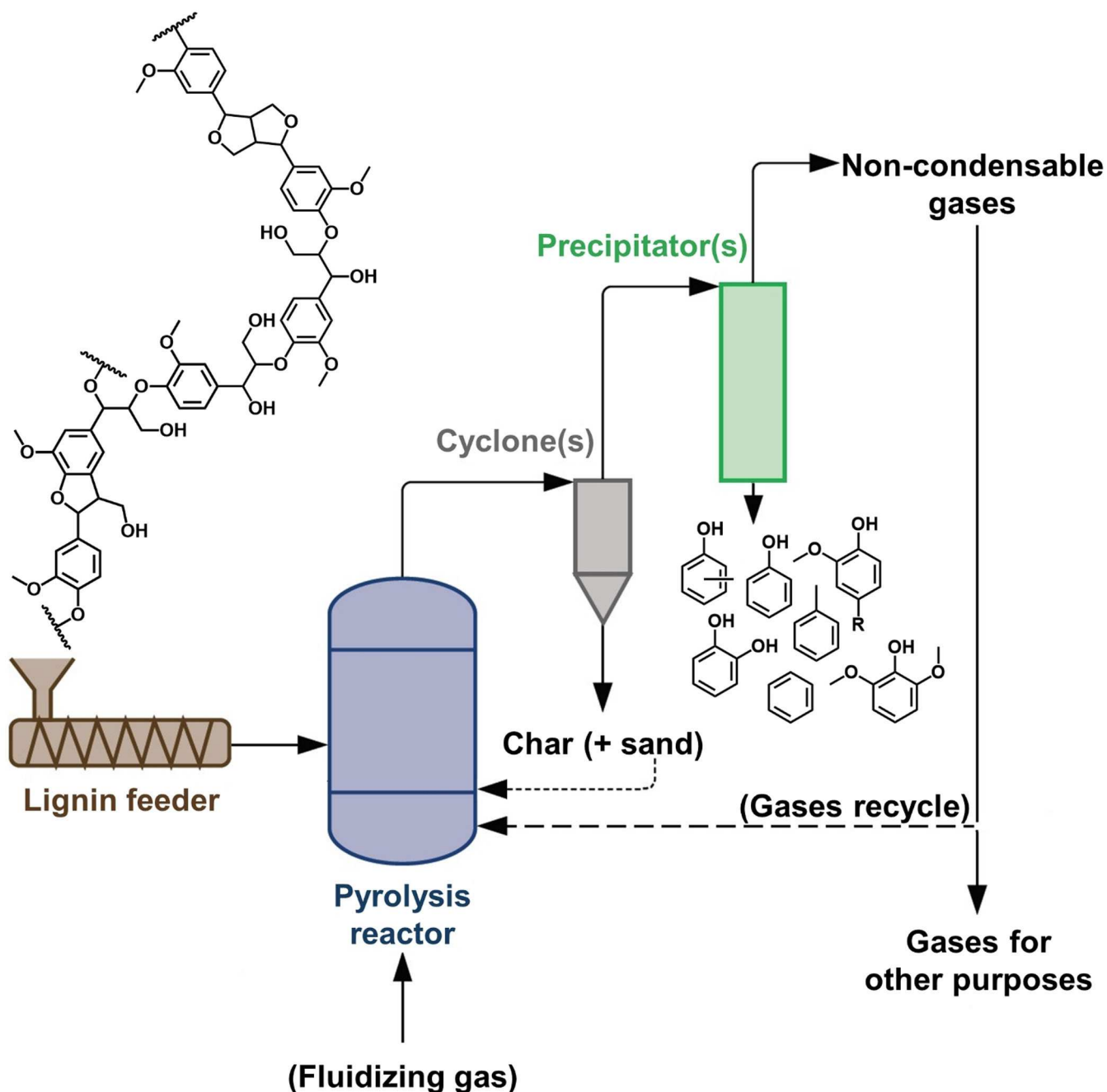European Chemical Societies Publishing

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Technology Overview of Fast Pyrolysis of Lignin: Current State and Potential for Scale-Up

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Lignin is an abundant natural polymer obtained from lignocellulosic biomass and rich in aromatic substructures. When efficiently depolymerized, it has great potential in the production of value-added chemicals. Fast pyrolysis is a promising depolymerization method, but current studies focus mainly on small quantities of lignin. In this Review, to determine the potential for upscaling, systems used in the most relevant unit operations of fast pyrolysis of lignin are evaluated. Fluidized-bed reactors have the most potential. It would be beneficial to combine them with the following: slug injectors for feeding, hot particle filters, cyclones, and fractional condensation for product separation and recovery. Moreover, upgrading lignin pyrolysis oil would allow the necessary quality parameters for particular applications to be reached.

1. Introduction

The growing demand for energy, chemicals, and materials is met mainly by fossil resources.[1] To tackle the intrinsic problems of these feedstocks, such as their limited supply and effects on the environment, the use of sustainable resources is of great importance.[2] In particular, lignocellulosic biomass is a widely available feedstock from which valuable products can be obtained with a low carbon footprint.[3]

Lignocellulosic biomass is composed mainly of cellulose, hemicellulose, and lignin. It also contains small amounts of inorganic components and extractives, the latter being chemicals that solvents can extract.[4] The different building blocks of lignocellulosic biomass make it a versatile feedstock. The carbohydrate fraction (i.e., cellulose and hemicellulose) has enabled the production of the biofuels ethanol and butanol, platform chemicals such as 5-hydroxymethyl-furfural and lactic acid, and other commodities such as citric acid.[5] In the case of lignin, it has not been exploited to a similar extent.[6]

Lignin is a complex material rich in aromatic substructures and has the potential to become a source of valuable compounds, provided that it is efficiently depolymerized.[7] The resulting compounds have a wide range of applications, including their use as chemical feedstocks, fuels, polymers, and solvents.[8] Nonetheless, industries still regard lignin as a low-value by-product. The pulp and paper industry extracts over 50 million tons of lignin annually to improve fiber flexibility and to prevent paper from turning yellow.[9] In bioethanol production, lignin is removed to enable the fermentation of the carbohydrate fraction.[10] In both cases, lignin is mainly combusted for heat and power, with only a few other commercially viable products.[11,5a] Furthermore, a significant amount of residual lignin is expected to be a by-product of emerging lignocellulosic biorefineries.[12] Apart from these industries, which consider lignin to be a side product, lignin can be primarily targeted trying to prevent structural degradation that could hamper further use.[13] The exploitation of lignin through depolymerization could increase the efficiency of biomass conversion, enhancing economic and environmental benefits.[14]

Successful valorization of lignin depends on biomass fractionation, the depolymerization method applied, and the upgrading of the products.[15] Depolymerization can be achieved by chemical, thermochemical, and biological methods.[14a,16] Among the thermochemical approaches, fast pyrolysis stands out as one of the most promising, but its large-scale implementation remains challenging. Comprehensive reviews have been published about the pyrolysis of lignocellulosic biomass.[17] However, there is a lack of critical analysis of different reports about the fast pyrolysis of isolated lignin.

Here, we evaluate the systems used in the most relevant unit operations of fast pyrolysis of lignin to assess their suitability and potential for upscaling. We start discussing lignin as a feedstock and its processing by fast pyrolysis. We continue analyzing the strengths and weaknesses of systems for feeding, reaction, and product collection. Finally, we summarize the current technological state and opportunities to consolidate large-scale processes for fast pyrolysis of lignin.

2. Lignin and Its Processing by Fast Pyrolysis

The characteristics and properties of lignin depend to a great extent on the source of the biomass and the fractionation strategy applied to obtain lignin that is separated from cellulose, hemicellulose, and other biomass components.[18] Such aspects are essential concerning further processing towards aromatics.[19]

2.1. Lignin structure

Lignin is a polymer composed mainly of three phenylpropanoid units, namely *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), derived from oxidative combinatorial coupling of the monolignols *p*-coumaryl, coniferyl, and sinapyl alcohols (Figure 1).[20] The structure of lignin depends on the type of biomass and the conditions under which it grows.[20e] In general, herbaceous biomass contains 8–15% lignin, which consists mainly of H, G, and S units; hardwoods have 20–30% lignin consisting primarily of G and S units, while softwoods have 25–38% lignin with mainly G units and smaller amounts of H units.[14a,21] Nonethe-

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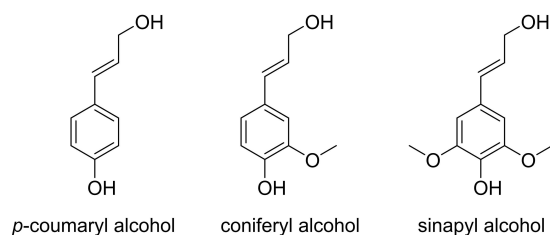   OSUA 201, Forschungsstrasse 111, 5232 Villigen (Switzerland)

Figure 1. Main monolignols used to produce lignin by oxidative combinatorial coupling.

less, a large number of other substructures, incorporated during lignin biosynthesis, may also be present.[20a–c,e] These moieties are linked by different types of connections (e.g., β-O-4, β-5, β-β, 5-5, 5-O-4, and β-1) and may have various types of functional groups, thus resulting in intricate structures.[22]

Fractionation to procure lignin can irreversibly alter the native state of the lignin[23] as well as affect other biopolymers[24] present in the biomass. Lignin can be obtained by delignification, by which it is liberated from the biomass in the form of a solid precipitate or a depolymerized oil, and a carbohydrate-rich pulp is produced (e.g., by Kraft pulping, sulfite pulping, and soda pulping).[25,15] These procedures can be performed under a wide range of conditions, including alkaline, acidic, reductive, oxidative, or others (e.g., in the presence of ionic liquids for solubilization of the entire biomass, extracting lignin and hemicellulose by means of ionosolv pulping, or by mechanical pretreatment followed by solvent extraction).[15] Other methods convert and solubilize carbohydrates by acid-catalyzed hydrolysis (e.g., the Klason method), enzyme-catalyzed hydrolysis, or thermal processes.[25,15]

In a fractionation process, the operating conditions and the type of reactor strongly influence the characteristics of the resulting lignin. Consequently, they determine the reactivity and the possibilities for valorization of the lignin. For example, Kraft lignin is obtained by means of the common process that utilizes sodium hydroxide and sodium sulfide, which provide an alkaline environment that promotes biomass delignification and lignin solubilization under harsh conditions. The lignin is degraded by cleavage of the ether bonds and the formation of more carbon-carbon linkages, which cause the structure to condense, a disadvantage for further processing.[25b] In addition, the presence of bisulfide ions promotes the incorporation of sulfur in the form of thiol groups, which hinders downstream processing.[25b,15] Some methods preserve the structure of the native lignin to a greater extent, as is the case with the extraction of lignin by means of γ-valerolactone-based solvent systems.[18b,26] Similarly, processes based on active stabilization mechanisms prevent lignin condensation.[13] Schutyser et al.[15] described different fractionation methods and their influence on lignin characteristics.

2.2. Fast pyrolysis of lignin

Fast pyrolysis is a depolymerization method in which the processed material is rapidly heated (using heating rates

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between 20 and 20 000 °C s⁻¹) to temperatures between 400 and 800 °C in the absence of oxygen. Figure 2 shows a conceptual flow diagram of a fast pyrolysis process, including its most relevant stages and some alternative features. Lignin begins to decompose as the moieties of the polymer are removed, thus generating oligomers.[27] Further decomposition leads to gases, liquids (lignin pyrolysis oil), and char.[17f] Gaseous products are formed due to decomposition to low-molecular-weight compounds, while char forms during repolymerization processes. There are a number of interesting applications for these solids and gases, but other thermochemical processes are better suited for obtaining them (i.e., gasification and carbonization, respectively).[28] The liquids compose the most valuable product, containing compounds such as phenols and hydrocarbons with a large variety of substituents and functional groups. The product distribution depends on the lignin used as well as on the pyrolysis conditions.[29]

Decades of research have been devoted to finding the best conditions for fast pyrolysis in order to maximize the yield of pyrolysis oil and improve product selectivity. The main focus of these studies has been lignocellulosic biomass. However, lignin represents an attractive raw material. It is abundant and has the potential to produce a wide variety of chemicals. Fan et al.[30] reviewed the conditions of lignin fast pyrolysis, including temperature, feeding rate, residence time of the pyrolysis vapors in the hot zone, types of catalysts, the reactor, and the lignin structure.

3. Feeding

The development of large-scale biorefineries is complicated by the heterogeneity of the feedstocks and deficiencies in their logistics.[31] Lignin as a feedstock could solve several of these problems; some lignins can be produced in large amounts at specific locations. However, the characteristics of the lignin

must be considered in order to determine the appropriate feeding strategy.

3.1. Obstacles to lignin feeding

The pyrolysis process begins with feeding the lignin into the reactor. This initial step is of great importance, not only to ensure proper operation (e.g., in continuous flow), but also to acquire the appropriate feeding rate relative to the energy input. If the feeding rate is too high or too low for the energy input into the reactor, the heating rate will be affected, changing the yield and chemical profile of the products.[32]

Feeding lignin is problematic when using feeders designed for the pyrolysis of whole biomass. This is due primarily to the low-temperature softening and melting point of lignin, as determined by its structure, and which can cause it to melt and cause blockages before it reaches the reactor.[33] Such blockages are one of the major barriers to the implementation of lignin pyrolysis,[34] inhibiting both continuous flow and control of the feeding rate.

3.2. Pretreatment of lignin before feeding

In contrast to previous theories that linked the melting point of lignin to the cellulose content[33c] or the concentration of oxygenated functional groups,[35] Han et al.[33a] indicated that the degree of crosslinking and condensation in the lignin structure are the main factors affecting the melting point. To approach this, modification of the lignin feed was explored. Pretreatment with reagents, such as calcium formate,[36] or pelletizing with a natural clay mineral[34,37] have been shown to alleviate the problem. Thring et al.[38] dissolved lignin in acetone (1:2 weight ratio) and injected the liquid feed with a syringe pump to eliminate melting.

Lignin pretreatment may also improve the selectivity of the process. Using calcium hydroxide, a relatively low-cost, low-hazard, readily available reagent, Zhou et al.[35] achieved continuous feeding, while at the same time improving selectivity to phenols and aromatics. Lee et al.[39] obtained similar results with calcined waste seashells, which decreased the temperature at which lignin decomposition occurred.

Despite the benefits, some pretreatment (e.g., with clay additives) may cause an increase in the amount of ash (the solid inorganic component) that is produced. Ash contains metals, such as magnesium, aluminum, and calcium, which can act as vapor cracking catalysts and increase the amount of non-condensable gases.[40] Insufficient separation of the ash from the vapor stream will leave traces in the oil. The inorganic content in oil appears to catalyze polymerization reactions, which increase viscosity and the apparent diameter of the suspended char, that is, submicron char particles that form during pyrolysis and are suspended in the pyrolysis oil.[41] If the oil is used for energy, it can also have undesirable effects, such as high-temperature corrosion and the formation of deposits.[17c,k] Similarly, ash in the char by-product is undesirable
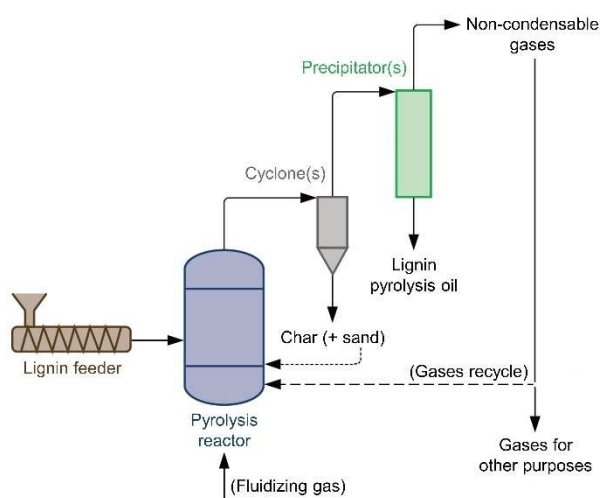

Figure 2. Conceptual flow diagram of a fast pyrolysis process (with alternative features in parentheses).

if it is combusted for heat and power;[40] other applications with the char (e.g., to improve soil) might also be impacted. Aside from the ash content, pretreatment may be costly or require nonrenewable feedstocks.

3.3. Reactor feeders: screw and slug injectors

Screw feeders are often used in biomass handling and can transfer lignin to the reactor by positive displacement.[42] Although screw feeders may function successfully,[32] in most cases melting of the lignin obstructs continuous operation. Such feeders have been modified, for example, by using a cooling water system; however, in some cases, there was only a slight decrease in the melting of lignin.[33c,43] A collaborative effort involving 14 laboratories across Europe and the USA also used liquid nitrogen, dry ice, and polyethylene glycol for cooling and had more success.[33c] Beis et al.[44] passed a high flow of nitrogen gas through a screw feeder at a lignin feeding rate of 0.4 g min^{-1} to minimize plugging. However, such adaptations are likely to be impractical and more costly for upscaling the process.

In some cases, lignin is fed into the reactor by an intermittent slug injection system,[45] which may prevent highly cohesive material from blocking the system and undergoing undesirable reactions during feeding. A pneumatically activated pinch valve releases small amounts of lignin into a horizontal tube; the lignin accumulates to form a slug. Intermittent pulses of an inert gas, controlled by a solenoid valve, propel the slug into the reactor, preventing the feed from settling in the tube. A continuous gas flow is used to prevent back-flow, and an additional cooling jacket may be used in the feeding line to prevent melting. With the slug injection system, continuous feeding at rates of up to 600 g h^{-1} have been achieved,[45a] meaning that there is potential for upscaling the system while enabling feeding without altering the lignin structure. Furthermore, the rubber pinch valve sleeve, which is easily replaced, is the only component subject to wear, so operating costs are low. Berruti et al.[46] reported details of the system and its optimization. Based on the above information, a slug injection system is the system of choice for unmodified lignin. However, further studies are required to analyze the effects of this type of feeding on the fast pyrolysis process itself.

4. Reactors

The reactor can also affect lignin fast pyrolysis, but it has received relatively little attention. Its importance stems from its effect on the heating rate, which strongly affects yield and selectivity. For instance, a low heating rate (below 20 °C s^{-1}) will lead to slow pyrolysis and result in a higher yield of solid char.[47] The reactor is a crucial aspect when considering the upscaling and commercialization of the process. Reactors work either in continuous or in batch mode (see below, Tables 1–8), and their potential for upscaling differs.

4.1. Continuous-flow reactors

4.1.1. Fixed-bed reactor (FBR)

The fixed-bed reactor (FBR; Table 1) comprises a static reaction bed, a feeding unit, and a gas flow to ensure inert conditions and to carry the products to the outlet.[30] Fixed-bed reactors have been used for the pyrolysis of lignin; they work well with catalysts, which can be incorporated into the bed in the form of pellets or the catalyst can also form the bed. Contact of the primary products of pyrolysis with the catalyst can be maximized as the vapors pass over the bed,[38] thus improving the selectivity of the process.

Shafaghat et al.[48] pyrolyzed lignin under different conditions (temperature, catalyst, type of lignin, carrier-gas flow rate) using a bench-scale fixed-bed reactor. They achieved their highest yield (36 wt%) of lignin pyrolysis oil with Kraft lignin (100 g) at 500 °C and a carrier-gas flow rate of 600 ml min^{-1}. Strong acidic and basic catalysts, such as H-beta and HY zeolites, reduced the liquid yield but enhanced selectivity towards phenols and monomeric aromatic hydrocarbons.[48] Lee et al.[49] also increased the selectivity for aromatics, particularly towards alkylphenols and pyrocatechols, by using a tandem fixed-bed reactor with both an in situ and ex situ catalyst (natural zeolite and HZSM-5, respectively). Thring et al.[38] pyrolyzed 3 g of organosolv lignin using an HZSM-5 catalyst and achieved a 43 wt% liquid yield with 88.8 wt% of the liquid product being aromatic, mainly toluene (36.7 wt%), xylenes (33.0 wt%), and benzene (9.4 wt%).

Despite promising results for fixed-bed reactors, several critical aspects must be considered. Only small amounts of lignin have been tested, so their suitability for larger scales is questionable. A disadvantage that may play an essential role is that the bed is usually heated from its periphery, resulting in uneven temperature in the reactor and relatively low heating efficiency.[30] As product yield and selectivity are highly dependent on temperature, this results in a lower yield and inhomogeneity of the products. The production of char is also a major problem. Lignin produces a larger amount of char compared to the whole biomass,[17h] which would affect the bed and represent operational complications. These aspects indicate that the fixed-bed reactor would be unsuitable for lignin pyrolysis on a large scale.

4.1.2. Bubbling fluidized-bed reactor (BFBR)

Within a bubbling fluidized-bed reactor (BFBR; Table 2), a preheated fluid is forced upwards through a porous distributor into a bed of solid particles (e.g., sand). Such particles will later transfer heat to lignin. When the velocity of the fluid is sufficiently high, the solid bed begins to expand and move, causing it to behave like a fluid.[50] The raw material (lignin) can be injected into the reactor, where it decomposes to form the pyrolysis products. Such a system maximizes the interaction between the lignin particles and the hot fluid, allowing efficient temperature control and homogeneous heat transfer.[30] It also

Table 1. Fast pyrolysis of lignin using fixed-bed reactors (FBR).

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%] Organic	Aqueous	Notable details	Feeding	Product collection	Ref.
Alcell® lignin (from hardwoods)	3.3 (10 g lignin dissolved in acetone, 1:2 weight ratio)	43		Pressure: atmospheric pressure; Catalyst: HZSM-5; Optimal: pyrolysis temperature of 550°C and weight hourly space velocity of 5 h⁻¹; Major products of lignin pyrolysis oil: toluene, benzene, and xylene	Lignin particle size: 20–40 μm; Lignin weight-average molar mass: <2000 g mol⁻¹; Lignin was dissolved in acetone (1:2 weight ratio) and the mixture was fed using a syringe pump Time: 30 min	Lignin pyrolysis oil: using a water condenser	[38]
Kraft lignin	0.5–3 (lignin/seashells)	ca. 34		Pyrolysis temperature: 500°C; Major products of lignin pyrolysis oil: alkyl phenols and methoxy phenols	Batch; Lignin pretreated by addition of seashells	Lignin pyrolysis oil: using two water condensers at −20°C	[39]
Kraft lignin	3	ca.34 (noncatalyzed pyrolysis and pyrolysis catalyzed by natural zeolite)		Catalyst: natural zeolite; Pyrolysis temperature: 500°C; Sweep gas: N₂; Major products of lignin pyrolysis oil: guaiacols (noncatalyzed and catalyzed by natural zeolite)	Batch	Using a condenser at −20°C	[49]
Kraft lignin, dealkaline lignin, organosolv lignin, and Klason lignin	100	21.01 (noncatalyzed pyrolysis)	14.94 (noncatalyzed pyrolysis)	Noncatalyzed and catalyzed (using silica sand, lignin char, alumina, spent FCC, HZSM-5, H-beta, HY, and MgO) pyrolysis; Optimal: pyrolysis temperature of 500°C and a carrier gas flow rate of 600 ml min⁻¹; Sweep gas in the reactor: N₂ (99.9%)	Batch	Char: keeping it inside the reactor; Lignin pyrolysis oil: using four condensers (the first cooled by the surrounding air and the other working at −30°C)	[48]

ensures the homogeneous distribution of heat, which influences pyrolysis kinetics; reaction rates are limited by the heat transfer through the particles and the rate of particle heating is usually the rate-limiting step in the reaction.[17c]

Despite the above advantages, results of collaborative international research showed that the typical fluidized-bed reactor systems are insufficient for feeds with a high concentration of lignin.[33c] This was due to melted lignin blocking the feeding system and bed defluidization caused by agglomeration. Defluidization reduces the effectiveness of heat transfer to the lignin, leading to slow pyrolysis.

Several mechanical features have been added to combat agglomeration, including adjustments to the feeder and the introduction of a mechanical stirrer in the bed.[52,45a,c] Using a slug injection system and a mechanical stirrer, Gooty et al.[45c] pyrolyzed up to 200 g of lignin in a BFBR at feeding rates of up to 600 g h⁻¹. They obtained a phenolic-rich lignin pyrolysis oil with a dry oil yield of 23.5 wt%. De Wild et al.[51] and Nowakowski et al.[33c] obtained notable oil yields of 54.7 and 49.7 wt %, respectively. However, none of these studies resulted in the elimination of agglomeration and the continuous pyrolysis of lignin over extended periods of time.

As highlighted in section 3.2, pretreatment can combat agglomeration and, thus, defluidization of the bed. Using calcium hydroxide, Zhou et al.[35] successfully pyrolyzed 300 g of lignin for three hours in a BFBR and postulated that this would have been possible for an even more extended period of time. Except for fine char powder, there were no agglomerates, and they achieved a yield of 38 wt%, 55–60% of which were phenolic compounds.

Variations in the material of the bed affect the yield and quality of the oil resulting from lignin pyrolysis. Li et al.[45b] tested five different bed materials (silica sand, lignin char, activated lignin char, birch bark char, and foamed glass beads) in the pyrolysis of Kraft lignin at a pyrolysis temperature of 550°C. Activated lignin char performs better than silica sand. There was a relative increase in the yield of lignin pyrolysis oil (43%), and the properties of the product improved (lower average molecular weight, more phenolics, less tar, and lower acidity). This is attributed in part to the better capacity of char to absorb the liquifying lignin and maintain adequate bed fluidity, unlike silica sand, which agglomerates and defluidizes when it comes into contact with liquefying lignin.[45b]

Despite the success in overcoming agglomeration, there are very few BFBR pilot-scale systems for the pyrolysis of lignin. More effort needs to be made in combining alterations to the system and scale-up.

4.1.3. Circulating fluidized-bed reactor (CFBR)

Circulating fluidized-bed reactors (CFBR; Table 3) are similar to BFBR, but the residence time of the char is similar to that of the vapors and the gas; the char is attritted due to the higher velocity of the gas, and its removal requires an extensive process.[17d] The reactor is heated by recirculation of heated sand from a secondary char combustor.[17d] It is suitable for large

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Table 2. Fast pyrolysis of lignin using bubbling fluidized-bed reactors (BFBR).

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%] Organic	Aqueous	Notable details	Feeding	Product collection	Ref.
Acetosolv lignin (from corn stover)	300	38.0		Bed: silica sand; Sweep gas in the reactor: N$_2$ at 9 SLPM; Major products of lignin pyrolysis oil: phenolics	Rate: 100 g h⁻¹; Sweep gas in the feeder: N$_2$ at 1 SLPM; Lignin pretreated by adding 5 wt% of Ca(OH)$_2$	Using two stages of gas cyclones, an electrostatic precipitator at 90°C, and a condenser at −10°C	[35]
ALM lignin (sulfur-free soda lignin from annually harvested nonwoody plants)	100	49.7		Bed: silica sand; Residence time in the bed: 1–2 s; Pyrolysis temperature: 450°C	Rate: 240 g h⁻¹; Particle size: 1–2 mm; Feeder: water-cooled screw	Using cooling traps and electrofilters operated at 8–10 kV and 4 kV	[33c]
Organosolv (from wheat straw, poplar, and spruce), Kraft and soda lignins	200 (30 wt% clay)	34 (Kraft lignin), 42 (soda lignin), 40–42 (organosolv lignins)		Major products of lignin pyrolysis oil: guaiacols, catechols, alkylphenols, and syringols.	Lignin fed as 2 mm extrudates containing ca. 30 wt% of a clay	Using two cyclones, a water-cooled 4°C tar knock-out pot, a room-temperature electrostatic precipitator, and a −25°C freeze condenser	[34]
Kraft lignin	450 (30 wt% clay)	48		Bed: silica sand; Pyrolysis temperature: 550°C	Feeder: water-cooled screw; Lignin fed as 2 mm extrudates containing ca. 30 wt% of a clay	Using 2 cyclones, a water-cooled 4°C tar knock-out pot, a room-temperature electrostatic precipitator, and a −25°C freeze condenser	[34]
Alcell lignin (from hardwoods) and ALM lignin (sulfur-free soda lignin from annual nonwoody plants)	Continuous mode: 200; Batch mode: 50	Continuous mode: 21 (ALM), 13 (Alcell lignin)	21 (ALM), 24 (Alcell lignin)	Pressure: atmospheric pressure; Pyrolysis temperature: 400°C; Bed: silica sand; Sweep gas in the reactor: Ar at 20 Nl min⁻¹ (preheated at 300°C); Residence time: ca. 1 s; Major products of lignin pyrolysis oil in continuous mode: phenols, catechols, guaiacols, and syringols; Major products of lignin pyrolysis oil in batch mode: guaiacols, syringols, alkyl phenols, and catechols	Lignins used as pellets (size 1–3 mm); Continuous mode: Feeder: cooled screw; Sweep gas in the feeder: N$_2$ at 1 Nl min⁻¹; Rate: 100 g h⁻¹; Time: 2 h; Batch mode: 50 g of lignin quickly fed into the preheated reactor	Continuous mode: Char: using a cyclone; Lignin pyrolysis oil: using a room temperature condenser, a room temperature electrostatic precipitation filter, and a −20°C freeze condenser; Batch mode: Char: using a cyclone; Lignin pyrolysis oil: using six impingers containing isopropanol (three at 40°C and three at −20°C)	[43]
Kraft lignins (Indulin AT and Lignoboost™) and organosolv lignin (Acetocell)	ca. 100	23 (Indulin AT), 22 (Lignoboost™), 16 (Acetocell)		Pyrolysis temperature: 550°C; Sweep gas in the reactor: N$_2$ (total nitrogen flow rates through the feeder and reactor: 10 LPM); Residence time: 1–2 s	Lignin particle size: <425 μm; Feeder: screw; Sweep gas in the feeder: N$_2$; Rate: 0.4 g min⁻¹	Char: using a hot gas filter at 450°C; Lignin pyrolysis oil: using a condenser at 4°C and an electrostatic precipitator	[44]
Kraft lignin	200	21.3, 24.5, 30.4, 19.8, 22.9	16.0 (Silica sand), 12.8 (Lignin char), 12.5 (Activated lignin char), 12.5 (Birch bark char), 10.8 (Foamed glass beads)	Pyrolysis temperature: (550±5)°C; Bed: silica sand, lignin char, activated lignin char, birch bark char, and foamed glass beads; Sweep gas in the reactor: N$_2$ (preheated at 300°C); Residence time: 1.7 s; Mechanical stirring in the reactor: 60 rpm	Feeder: slug injector; Carrier and pulse gas for the injection of lignin powder slugs: N$_2$; Rate: 600 g h⁻¹; Time: 20 min	Char: filtering the vapors going out of the reactor through a hot filter using a 10 μm wire mesh and a ceramic fiber layer; Lignin pyrolysis oil: using two cyclonic condensers (working with an oil bath at 80°C and an ice bath) with an electrostatic precipitator-cum-condenser (at 70°C and 14 kV) in between, and a cotton wool demister	[45b]
Kraft lignin	200	ca. 36 (water content of ca. 30%, but fractional condensation allows to have a water content of <1 wt% in organic fraction)		Pyrolysis temperature: 550°C; Bed: silica sand (Sauter-mean diameter of 180 μm); Sweep gas in the reactor: N$_2$ (preheated); Residence time: 1.5 s; Mechanical stirring in the reactor: 40 rpm	Feeder: slug injector; Carrier and pulse gas for the injection of lignin powder slugs: N$_2$; Time: 20–30 min	Char: filtering the vapors going out of the reactor through a hot filter using a stainless steel 40 μm screen and a ceramic fiber insulation layer; Lignin pyrolysis oil: using two cyclonic condensers (working with an oil bath at 80°C and an ice bath) with an electrostatic precipitator-cum-condenser (at 40–70°C and 14 kV) in between, and a cotton wool demister	[45c]
Organosolv lignins (from wheat straw), Alcell lignin (organosolv lignin from hardwoods), and Granit lignin (soda lignin from annual nonwoody plants produced by ALM)	40	30.8	23.9 (wheat straw lignin A)	Pyrolysis temperature: 500°C; Pressure: atmospheric; Bed: sand; Sweep gas in the reactor: Ar (pre-	Feeder: water-cooled screw; Sweep gas in the feeder: N$_2$	Char: using a cyclone and a hot particle filter for gas sampling, and a hot particle filter for lignin pyrolysis oil sampling; Lignin pyrolysis oil: using seven impingers containing isopropanol (one at 0°C, three at 40°C, and three at −20°C)	[51]

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Table 2. continued

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%] Organic	Aqueous	Notable details	Feeding	Product collection	Ref.
		32.0	19.9 (wheat straw lignin B)	heated, at five times the minimum fluidization velocity) Residence time: 1–3 s Major products of lignin pyrolysis oil: guaiacols, syringols, alkylphenols, and catechols	Rate: 500 g h⁻¹ Lignins were co-fed with a proprietary catalyst as 1–3 mm particles Time: 20–40 min		
		24.4 30.5	14.5 Alcell 17.1 Granit				
Hydrolysis lignins (from the lignocellulosic ethanol production process St1 Cellunolix, variable carbohydrates content)	1500	32–51	4–16	Pyrolysis temperature: 500, 550, and 600 ($\pm$5) °C Pressure: atmospheric Superficial gas phase residence time in the reactor: <1 s Bed: 300 g sample of white aluminum oxide (0.56–0.71 mm, $\rho = 4000$ kg dm⁻³) Nitrogen is used as the main gas for fluidization Clogging and bed agglomeration are more pronounced for lignin having lower carbohydrate content Bed agglomeration is overcome by adding a rapidly rotating mixer in the reactor Utilization of steam and ethanol as hydrogen sources tested, but hydrogen ended up mostly in the gas phase	Feeder: cooled screw Rate: 500 g h⁻¹ Time: 3 h	Char: using two cyclones after the reactor Lignin pyrolysis oil: using a water-cooled heat exchanger at 40°C and an electrostatic precipitator at 20°C Non-condensed water and light after the electrostatic precipitator: two glycol coolers at −10°C (one tube heat exchanger and a second smaller tube heat exchanger filled with additional glass packing)	[52]

throughputs but would require careful control to satisfy the requirements of successful pyrolysis. Little is known about the application of this type of reactor to lignin fast pyrolysis. However, it has been tested at a pilot scale using lignin obtained from the production of lignocellulosic ethanol.[52a,b,53] Using a screw feeder, 15 kg h⁻¹ of lignin (particle size of 0.25–3 mm) were fed into the cold part at the bottom of a reactor to avoid melting.[52a] The reactor was operated under atmospheric pressure at 511 to 538°C and a superficial fluidization gas velocity of 7 m s⁻¹. The temperature was controlled by adjusting the flow rate of the hot quartz sand (0.1–0.6 mm, $\rho = 2600$ kg dm⁻³) fed by a screw feeder. Bed agglomeration was avoided because of the high gas velocity and the forces applied to the particles of sand and lignin. Product separation was done with two cyclones, two scrubbers working at 40°C, and one cooler. A mass balance revealed the production of 37 wt% of lignin pyrolysis oil, 43 wt% of char, 11 wt% of water, and 11 wt% of noncondensable gases. The heat requirements were met mainly by the combustion of the char and some of the noncondensable gases in a combustor that was stable at 700°C.[52a] The rest of the gas was used for fluidization. Additional fuel was required only at start-up and shutdown. A main drawback was the deposits in the cyclones and gas lines of the product, which resulted in a build-up of pressure and shorter operational periods.[52a]

CFBR systems are promising due to the large throughput, the use of side products (char and noncondensable gases) for heat as well as operation without significant agglomeration. Nonetheless, the processing of pyrolysis products after the reactor must be improved in order to increase the duration of the operation.

4.1.4. Pyrolysis centrifuge reactor (PCR)

Pyrolysis centrifuge reactors (PCR; Table 4) differ from the fixed- and fluidized-bed reactors. Instead of a bed material, the heat transfer medium is the reactor itself. The reactor rotates and centrifugal forces drive the raw material particles onto the hot surface of the reactor wall, which is usually heated electrically to around 500–600°C.[17g] The heated surface of the lignin melts and when the material moves away from the wall, the molten layer decomposes to form the pyrolysis products.[32] Advantages over other reactors include compatibility with large particles and efficient pyrolysis oil collection by cause of higher partial pressure of condensable vapors due to the lack of a carrier gas.[17g] The rotation causes the lignin and any char that is produced to be moved along the length of the reactor to an outlet, which ensures a continuous process and inhibits agglomeration.[54] However, the cooling nozzle became plugged after approximately one hour of operation in multiple cases. To increase the duration of operation, Trinh et al.[32] suggested an increase in the diameter of the nozzle. They obtained a total oil yield of 43 wt% and a dry oil yield of 34 wt%; 204–481 g of lignin fed at 5.6 g min⁻¹ were pyrolyzed in each run.[32] Guaiacols and syringols (phenolics) were the most abundant components of the oil (27.4 and 18.3%, respectively). To improve selectivity,

Table 3. Fast pyrolysis of lignin using circulating fluidized-bed reactors (CFBR).

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%]		Notable details	Feeding	Product collection	Ref.
		Organic	Aqueous				
Hydrolysis lignin (from the lignocellulosic ethanol production process St1 Cellunolix)	Pilot-plant scale (15 kg h^{-1} of lignin)	37	11	Pyrolysis temperature: 511–538 °C Pressure: atmospheric Superficial fluidization gas velocity: 7 m s^{-1} Bed: quartz sand (0.1–0.6 mm, $\rho = 2600$ kg dm^{-3}) fed using a screw feeder Heat supply: combustor working stable at 700 °C (fuels: char, part of noncondensable gases, and pellets)	Feeder: screw Lignin: 15 kg h^{-1} of lignin (particle size of 0.25–3 mm) fed into the bottom of a reactor (cold part) to avoid melting problems	Char: using two cyclones after the reactor Lignin pyrolysis oil: using two scrubbers working at 40 °C and one cooler	[52]

Zhou et al.[54] directly upgraded the pyrolysis vapors in situ using a downstream HZSM-5-based catalytic fixed-bed. Although a dry-liquid containing 70 wt% of oxygen-free aromatics (mainly benzene and toluene) was obtained, the yield decreased from 27.6 to 5.7 wt% after adding the catalyst. More research needs to be undertaken to determine whether catalysts can be effectively incorporated into the PCR or whether other upgrading methods should be considered.

In addition to the relatively poor compatibility with catalysts, because the process is surface-area dependent, scale-up of the PCR may lead to other problems. It may be challenging to reach the rotational speeds required to ensure high centrifugal forces and the temperature needed for adequate heat transfer.

4.1.5. Entrained-flow reactor (EFR)

Based on gasification technologies, the entrained-flow reactor (EFR; Table 5) heats its processed material by means of a preheated inert gas stream.[17m] The vapor products are collected by the carrier gas and passed through a condensing system.

A nitrogen-entraining gas at 700 °C was used at the Energy Research Centre of The Netherlands to process two types of lignin, a purified soda lignin and a concentrated lignin from lignocellulosic ethanol production.[33c] Continuous processing at a feeding rate of 40 g h^{-1} successfully achieved a lignin pyrolysis oil yield of 36.6 wt%.[33c] Mukkamala et al.[36] tested the feeding of 1 kg of lignin/calcium formate (1:1) at a feeding rate of 1–2 g min^{-1} over 6 h. They obtained a liquid yield of 33 wt% with no agglomeration. Both studies resulted in a high proportion of deoxygenated aromatic and phenolic products and a reduction of typical guaiacyl and syringyl products.

The entrained-flow reactor is generally less popular for the fast pyrolysis of lignocellulosic biomass than other reactors, such as those with a fluidized bed. This is probably due to the inefficient heat transfer between the hot gas and the solid particles, which leads to the requirement for small particles (< 2 mm) and high gas flows, both of which would limit scale-up.[17m] The lignin feed is usually in the form of a powder; thus, heat transfer may be less problematic than with the whole biomass. However, the use of carrier gas results in low partial pressures of the vapor products, thus affecting product collection and gas recycling.[17a] For lignin, the lack of agglomeration in the system may outweigh this disadvantage.

4.2. Batch reactors

4.2.1. Milligram-scale pyrolyzer

A pyrolyzer working with milligrams of sample in a batch process (mg-scale pyrolyzer; Table 6) is generally used in studies of fast pyrolysis of lignin. Small quantities enable easy heating and cooling as well as the coupling of analytical instruments to allow efficient online separation and analysis of the products. For example, products can be separated by gas chromatography (GC) and subsequently analyzed by mass spectrometry (MS).[56] There can also be parallel separations followed by analyses by means of MS and a thermal conductivity detector (TCD), to determine high-molecular-weight condensable products and noncondensable gases, respectively.[26c] Alternatively, Fourier-transform infrared (FTIR) spectroscopy[57] or molecular beam mass spectrometry (MBMS)[58] can be used to analyze the products directly. Some configurations yield products in amounts that are large enough to be analyzed offline.[59]

Another important advantage of milligram-scale pyrolyzers is that they can be used for kinetic studies. Thermogravimetric analysis (TGA) is widely used in such research.[60] However, the heating rates are insufficient for fast pyrolysis, and information about the specific compounds produced is limited (unless a complementary technique such as MS or FTIR is used). Reactor setups such as pyrolysis-GC/MS do not have these shortcomings. They can achieve fast pyrolysis processes and accurately separate and identify the species that compose the product mixture. This offers the additional advantage of giving access to information that provides insights into reaction mechanisms.[61]

In pyrolysis-GC/MS setups, the lignin is initially immobilized (e.g., using quartz wool). A platinum coil is commonly used to

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Table 4. Fast pyrolysis of lignin using pyrolysis centrifuge reactors (PCR).

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%] Organic	Aqueous	Notable details	Feeding	Product collection	Ref.
Straw lignin (hydrolysis process)	28–45	27.6	17.4	Pyrolysis temperature: 500°C; Sweep gas in the reactor: N_2 at 4 Nl min^{-1} (preheated at 450°C); Residence time: 1.8 s	Rate: 1.1–1.8 g min^{-1}; Lignin particles of 0.35–1.4 mm were fed tangentially into the horizontally oriented pyrolysis reactor cylinder; Time: 25 min	Char: using a change in the flow direction separator (at 460°C), a cyclone (at 440°C), and a hot gas filter (at 300°C, with a pore size of 1 μm); Lignin pyrolysis oil: using a cooling bath (at −20°C) and a dry ice/ethanol bath (at −71°C)	[54]
Lignin from wheat-straw (residue of an ethanol process with a lignin content of 79 wt%)	204–481	34	9	Rotor speed: 18000 rpm; Optimal: pyrolysis temperature of 550°C, gas residence time of 0.8 s, and a feed rate of 5.6 g min^{-1}; Major products of lignin pyrolysis oil: acetic acid, levoglucosan, guaiacol, syringols, and p-vinylguaiacol	Rates: 4.1–10.4 g min^{-1}; Times: 50–62 min	Char: using cyclones heated to 500°C; Lignin pyrolysis oil: using a bubble chamber at 30–50°C filled with isopropyl alcohol, a coalescer, and a water condenser	[32]
Residual lignin from a straw ethanol process	350–750	ca. 33	ca. 10	Rotor speed: 8870 rpm; Pyrolysis conditions: pyrolysis at 550°C with a residence time of 0.8 s	Rates: 340–990 g h^{-1}; Times: 60 min	Char: using cyclones; Lignin pyrolysis oil: using a bubble chamber at 30–40°C filled with isopropyl alcohol, a coalescer, and a water condenser	[55]

achieve heating rates of up to $20°C\,ms^{-1}$ and an inert gas carries the vapor pyrolysis products. These systems are suitable to study noncatalyzed and catalyzed lignin pyrolysis, the latter with catalysts such as zeolites, aluminosilicates, transition metal oxides, and zeolite-supported transition metals.[26c,59a,62] Ma et al.[63] achieved 74.9 wt% liquid yield and high selectivity for aromatic hydrocarbons using an H-USY catalyst. The catalyst has a pore size, grain size, and acid sites that are appropriate for deoxygenation reactions. Such results are consistent with equivalent observations using other types of zeolites.[64]

Milligram-scale pyrolyzers are not adequate for large-scale applications. Nonetheless, they provide valuable insights into fast pyrolysis processes, which might be relevant for adjusting the operation of pyrolysis reactors with better potential for scale-up.

4.2.2. Microwave reactor (MWR)

The heat transfer in microwave pyrolysis reactors (MWR; Table 7) differs from that in other pyrolysis reactors. Microwave radiation penetrates the feedstock, causing molecules to vibrate. The heat is generated from the interior of the sample and spread to the outer regions.[65]

The method has been applied with and without catalysts. Farag and co-workers[66] achieved 15–20 wt% of lignin pyrolysis oil with guaiacols, phenols, and catechols as the main products. Additional work permitted kinetic modeling and successful extraction of phenols.[66,67] Bu et al.[68] heated 20 g lignin in a microwave generator with different amounts of activated carbon as a catalyst and achieved lignin pyrolysis oil yields of 15–41 wt%, 13–45% of which was phenol and up to 78% were total phenolics. Using an HZSM-5 catalyst, Fan et al.[69] also produced a phenolic-rich lignin pyrolysis oil with 31.9% selectivity to alkyl phenols at a catalyst-to-lignin ratio of 0.2. Yields of 29.0 and 23.3 wt%, respectively, were obtained for in situ and ex situ catalytic upgrading. Without HZSM-5, high selectivity for methoxy phenols (73.7%) was observed, and at 450°C the lignin pyrolysis oil yield was 34.11 wt%.

Potential problems include the presence of hot spots, which poses the threat of nonuniform heating and may alter the yields and the selectivity of pyrolysis.[70] This is particularly relevant when upscaling the reactor. More research needs to be undertaken to determine whether such problems would be significant and whether they can be overcome by methods such as stirring and cavity design.[71] Challenges to scale-up may also be posed by the range of microwave penetration, which is typically only 1–2 cm.[17g]

4.2.3. Vacuum reactor (VR)

In vacuum reactors (VR; Table 8), lignin pyrolysis takes place under vacuum, limiting further depolymerization and secondary reactions (e.g., repolymerization). Zhou et al.[72] pyrolyzed 50 mg of organosolv lignin in a vacuum pyrolyzer and achieved an

Table 5. Fast pyrolysis of lignin using entrained-flow reactors (EFR).

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%]		Notable details	Feeding	Product collection	Ref.
		Organic	Aqueous				
Kraft lignin	300 (lignin/calcium formate)	32.5		Pyrolysis temperature: 500 °C Residence time: ca. 3 s Major products of lignin pyrolysis oil: alkylated phenols	Rate: 1–2 g min^{-1} Sweep gas: 6 L min^{-1} Lignin pretreated by adding Ca(HCOO)$_2$	Char: using a hot-gas filter immediately after the reactor at 500 °C Lignin pyrolysis oil: using a condenser at 4 °C and an electrostatic precipitator	[36]

outstanding liquid yield of 90%. Oligomers were the main component of the oil.

It is possible to scale-up the reactor for a continuous process. A 3000 kg h^{-1} vacuum reactor for lignocellulosic biomass pyrolysis was set up by Pyrovac Inc. in Canada.[74] However, the project was abandoned in 2002; the large vessels and piping required for an effective vacuum made the process complex and costly.[17g] This means that, at present, such a reactor is not feasible.

5. Product Collection

The separation and collection of products in fast pyrolysis of lignin are vital to ensure a high yield and high-quality lignin pyrolysis oil, which is solid-free, has a low water content, and a high concentration of monomers. A high water content means that pyrolysis oil has a low heating value, is highly corrosive, and is very acidic; as a result, it is unsuitable for fuel applications.[75] Minimizing the water content during product collection may make subsequent upgrading unnecessary. In addition, the oil quality can be increased by limiting secondary reactions, such as vapor cracking and repolymerization. Therefore, condensation of the product vapors must be rapid and balanced with the necessity to remove solid particulates before that happens. In terms of these criteria, separation systems after the lignin pyrolysis reactor will be reviewed, including an assessment of their suitability for upscaling.

5.1. Char removal

Removing the char is important to achieve a homogeneous product and to limit secondary reactions because the char can act as a catalyst. Collecting the char is also beneficial as it can be combusted for heat and power on-site, sold as an end-product for applications such as to improve soil, or used in construction.[76]

With reactors such as the centrifuge reactor, catch-pots have been used to remove large, coarse particles.[32] The solid particles fall into the pot, while the vapor stream is channeled in another direction. The mechanism is simple and effective for large solid particles. Alternatively, the cyclone system can remove solids with a wide range of particle sizes. The vapor stream enters the cyclone at a tangent, causing it to circulate downwards and form a vortex. The solid particles fall to the bottom while the clean vapors travel up the cyclone through the center of the vortex.[77] In a review of condensation systems for biomass pyrolysis, Papari et al.[78] found that the content of char decreased from 2.8 wt% to below 0.5 wt% when upgrading from one to two cyclones. Although increasing the number of cyclones may enhance char removal, it also extends the length of time that the vapor products are under high-temperature conditions, which can lead to secondary reactions. Therefore, one or two cyclones is the typical case. Cyclones are particularly favorable due to their low capital and running costs, reliability, and suitability for use at high temperature.[77]

Hot particle filters are used to remove fine solid particulates and have been shown to have a positive effect on the composition of the pyrolysis oil. Mei et al.[79] observed that changing the filter temperature at intervals between 350 and 500 °C caused a change in the chemical composition and structure of the pyrolysis oil produced from pine sawdust. Specifically, increasing the temperature increased the aromaticity of the pyrolysis oil. Further investigations should be carried out with a lignin feed to determine whether such results can be reproduced.

5.2. Collection of lignin pyrolysis oil

Condensation and collection of the final lignin pyrolysis oil are important to maximize yield and reduce water content. Several systems have been used in the pyrolysis of lignocellulosic biomass,[78] but only a few have been applied to lignin pyrolysis.

Bubbling the vapors through a quenching solvent at a low temperature causes them to condense. The vapor components are quickly and considerably diluted by the solvent, thus preventing secondary reactions. Isopropyl alcohol has been used on several occasions[32,51,55] due to its suitability for relatively nonpolar compounds. Trinh et al.[32] described the possibility of esters forming during the reaction of isopropanol with carboxylic acids; however, it is assumed that this is negligible at low temperature (< 50 °C) in the absence of a strong base or acid. The solvent can be extracted to produce the raw lignin pyrolysis oil, but the water fraction remains and, thus, lowers the quality of the oil. Overall, the method is probably impractical on a large scale; methods of producing oil with a lower water content and less solvent contamination are preferable.

Table 6. Fast pyrolysis of lignin using milligram-scale pyrolyzers.

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%] Organic	Aqueous	Notable details	Feeding	Product collection	Ref.
GVL-lignin	0.0015–0.0020	61.4		Optimal: heating up to 750°C at 20°C ms^{-1} and held 20 s Major products of lignin pyrolysis oil: phenols and alkoxy phenols	Batch	–	[26c]
Alkaline lignin (from softwood)	–	ca. 40 (noncatalyzed pyrolysis)		Temperature profile: heating up to 650°C at 20°C ms^{-1} and held 20 s Sweep gas: He Noncatalyzed and catalyzed (using high-surface-area mesoporous aluminosilicates) pyrolysis Major products of lignin pyrolysis oil: phenols alkoxy ketones (noncatalyzed pyrolysis)	Batch	–	[62b]
Kraft lignin (from softwood), dioxane lignin (from softwood and hardwood), Klason lignin (from softwood and hardwood), and organosolv lignin (from softwood and hardwood)	0.0010–0.0020	ca. 41 (noncatalyzed pyrolysis of Kraft lignin from softwood at 650°C) ca. 66 (noncatalyzed pyrolysis of dioxane lignin from softwood at 750°C) ca. 66 (noncatalyzed pyrolysis of dioxane lignin from hardwood at 650°C) ca. 56 (noncatalyzed pyrolysis of Klason lignin from softwood at 750°C) ca. 68 (noncatalyzed pyrolysis of Klason lignin from hardwood at 750°C) ca. 60 (noncatalyzed pyrolysis of organosolv lignin from softwood at 650°C) ca. 53 (noncatalyzed pyrolysis of organosolv lignin from hardwood at 750°C)		Temperature profile: heating up to 350–750°C at 20°C ms^{-1} and held 20 s Sweep gas: He Noncatalyzed and catalyzed (using H-USY) pyrolysis	Batch	–	[62d]
Dioxane lignin (from poplar)	0.001–0.002	ca. 32 (noncatalyzed pyrolysis)		Temperature profile: heating up to 550°C at 20°C ms^{-1} Sweep gas: He Noncatalyzed and catalyzed (using silica, silicalite, HZSM5, and HUSY) pyrolysis Study of the influence of catalysts on radical	Batch	–	[62c]

Table 6. continued

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%] Organic / Aqueous	Notable details	Feeding	Product collection	Ref.
Kraft lignin	–	37.4 (noncatalyzed pyrolysis of untreated lignin) 30.4 (noncatalyzed pyrolysis of lignin pretreated with NaOH) 34.2 (noncatalyzed pyrolysis of lignin pretreated with H_2O_2) 41.4 (noncatalyzed pyrolysis of lignin pretreated with NaOH and H_2O_2) 42.5 (noncatalyzed pyrolysis of lignin pretreated with HCl) 38.6 (noncatalyzed pyrolysis of lignin pretreated with HCl and H_2O_2)	formation during lignin pyrolysis Major products of lignin pyrolysis oil: alkoxy phenols (noncatalyzed pyrolysis) Temperature profile: heating up to 650 °C at 20 °C ms^{-1} and held 20 s Sweep gas: He Noncatalyzed and catalyzed (using the zeolites FAU, MOR, BEA, and MFI with similar Si/Al of ca. 40) pyrolysis Major products of lignin pyrolysis oil: alkoxy phenols (noncatalyzed pyrolysis)	Batch Pretreatments of lignin included stirring in aqueous solutions containing NaOH, H_2O_2, NaOH with H_2O_2, HCl, or HCl with H_2O_2 followed by grinding into fine powder	–	[62a]
Alkaline lignin	0.0015	ca. 40 (noncatalyzed pyrolysis)	Temperature profile: heating up to 650 °C at 20 °C ms^{-1} and held 60 s Sweep gas: He Noncatalyzed and catalyzed [using (non)acidic alumina silicates, transition metal oxides, and zeolite-supported transition metals] pyrolysis Major products of lignin pyrolysis oil: alkoxy phenols (noncatalyzed pyrolysis)	Batch	–	[62e]
Alkaline lignin	–	39.5 (noncatalyzed pyrolysis with pyrolysis times of 10 s and 20 s)	Temperature profile: heating up to 650 °C at 20 °C ms^{-1} and held 0.1–20 s Sweep gas: He Noncatalyzed and catalyzed (using H-USY zeolite) pyrolysis Study of deactivation and regeneration of H-USY zeolite during catalytic pyrolysis Major products of lignin pyrolysis oil: alkoxy phenols (noncatalyzed pyrolysis)	Batch Lignin particle size: <75 μm	–	[62f]
Alkaline lignin	0.0015	39.5 (noncatalyzed pyrolysis)	Temperature profile: heating up to 650 °C at 20000 °C s^{-1} and held 20 s Sweep gas: He Noncatalyzed and catalyzed (using H-ZSM5 with different Si/Al, Na-ZSM5, H-USY, H-beta, silicalite, SiC, and amorphous silica-alumina) pyrolysis Major products of lignin pyrolysis oil: alkoxy phenols (noncatalyzed pyrolysis)	Batch Lignin particle size: <75 μm	–	[63]
Organosolv lignins (from prairie cordgrass and Aspen) and Kraft lignin	ca. 0.0005	–	Temperature profile: 50 °C during 5 s, heating up to 600 °C at 1000 °C s^{-1}, and held for 1 min	Batch	–	[56c]

Table 6. continued

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%] Organic Aqueous	Notable details	Feeding	Product collection	Ref.
Alkaline lignin	0.0080 ± 0.0002	–	Major products of lignin pyrolysis oil: guaiacol-substituted compounds Temperature profile: quartz reactor containing the sample placed in a pyroprobe inside a Brill cell at 200°C was heated up to 400–700°C at 20000°C s⁻¹ and held 2–30 s Sweep gas: N₂ at 110 mL min⁻¹	Batch	–	[57]
Kraft lignin (from Lignoboost process)	0.040	38.09 (noncatalyzed pyrolysis)	Noncatalyzed and catalyzed pyrolysis (using HZSM-5, FCC, and olivine as packed bed placed after the sample, separated by quartz wool) Temperature profile: heating to 560°C during 40 s and held 80 s Sweep gas: N₂ at 50 mL min⁻¹ Major products of lignin pyrolysis oil: guaiacols	Batch	Char: using extraction by dimethyl sulfoxide Lignin pyrolysis oil: using condensation and dissolution with acetone	[59a]
Organosolv lignins (Alcell lignin and another organosolv lignin)	0.040	49.6 (Alcell lignin, noncatalyzed pyrolysis at 470°C) 52.1 (organosolv lignin, noncatalyzed pyrolysis at 560°C)	Noncatalyzed and catalyzed (using HZSM-5, FCC, and olivine as packed bed placed after the sample, separated by quartz wool) pyrolysis Temperature profile: heating to 470°C or 560°C during 40 s and held 80 s Sweep gas: N₂ at 50 mL min⁻¹ Major products of lignin pyrolysis oil: syringols and guaiacols	Batch	Char: using extraction by dimethyl sulfoxide Lignin pyrolysis oil: using condensation and dissolution with acetone	[59b]
Milled wood lignin	0.0003	–	Temperature profile: heating up to 600°C at 20°C ms⁻¹ and held for 20 s Study about intermolecular interaction mechanism of lignin pyrolysis studied by density functional theory methods and analytical pyrolysis-gas chromatography/mass spectrometry	Batch	–	[61a]
Organosolv lignin (from corn stover)	0.500 for online analysis 0.800 for lignin pyrolysis oil condensation	–	Temperature profile: heating up to 500°C at 2000°C s⁻¹ Sweep gas: He with a linear velocity 20.5 cm s⁻¹ Residence time: 15–20 ms Study about mechanistic insights on oligomer formation and the evolution of chemical species during lignin pyrolysis	Batch Lignin particle size: ≤ 75 μm	Lignin pyrolysis oil (if not analyzed online): using an ice-bath-surrounded tube containing methanol	[61b]
Alkaline lignin and Alcell lignin	–	–	Temperature profile: heating up to 400–800°C at 10°C ms⁻¹ and held 15 s Major products of lignin pyrolysis oil: phenols	Batch	–	[56a]
Black-liquor lignin (from an alkali pulping of mainly Chinese polar and reed)	0.0005	–	Temperature profile: heating up to 500–900°C at 20000°C s⁻¹ and held 30 s Major products of lignin pyrolysis oil: guaiacols Study of the influence of lignin characteristics on pyrolysis mechanism	Batch	–	[56b]
Alkaline lignin	–	–	Temperature profile: heating up to 400–800°C and held for 5 min Pressure: atmospheric Sweep gas: N₂ at 100 mL min⁻¹ Study about the effect of molecular weight on lignin pyrolysis	Batch	Lignin pyrolysis oil: using an ice-water condenser	[60a]

Table 7. Fast pyrolysis of lignin using microwave pyrolysis reactors (MWR).

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%]		Notable details	Feeding	Product collection	Ref.
		Organic	Aqueous				
Kraft lignin	300 (containing 20–40 wt% of char)	15–20	17–21	Pyrolysis conditions: 20–40 wt% of microwave absorber (char), nominal setting power of 1.5–2.7 kW (heating up to 900–1240 K), and 800 s of pyrolysis. Sweep gas: N_2 at 500 mL min^{-1}. Major products of lignin pyrolysis oil: guaiacols, phenols, and catechols. Additional information about product kinetic modeling and extraction of phenols are reported by Farag et al.[67] and Fu et al.[73]	Batch. Lignin is mixed with char (a good microwave-to-heat convertor)	Char: retained in the reactor. Lignin pyrolysis oil: using three condensers at −18°C	[66]
Alkaline lignin	20	41.48 (highest lignin pyrolysis oil yield)	20.25 (highest amount of phenols and phenolics)	Conditions with the highest lignin pyrolysis oil yield: pyrolysis temperature of 450°C, weight hourly space velocity of 0.88 h^{-1}, retention time of 8 min, and system previously purged during 15 min using N_2 at 1000 mL min^{-1}. Conditions with the highest amount of phenols and phenolics: pyrolysis temperature of 550°C, weight hourly space velocity of 2.18 h^{-1}, retention time of 8 min, and system previously purged during 15 min using N_2 at 1000 mL min^{-1}. Catalyst: activated carbon. Major products of lignin pyrolysis oil: phenols, guaiacols, hydrocarbons, and esters	Batch	Lignin pyrolysis oil: using condensers with cooling water at 5°C	[68]
Alkaline lignin		34.11 (without catalytic upgrading) 28.95 (in situ) 21.75–29.24 (ex situ catalytic upgrading)		Pyrolysis conditions: oxygen-free environment reached by pumping down the system during 10 min, pyrolysis temperature of 550°C held until the end of production of pyrolysis vapors. Microwave absorber: SiC. Upgrading: in situ and ex situ using H-ZSM5 (in situ: catalyst-to-lignin ratio of 0.3; ex situ: catalyst-to-lignin ratio of 0.1–0.4 and catalytic temperatures of 250–550°C)	Batch	Lignin pyrolysis oil: using a condensing system	[69]

Designed to remove bulk liquids from gas streams through gravitational separation, cooled knock-out pots have been used to collect the lignin pyrolysis oil. As the product vapors condense, the liquid that forms accumulates at the bottom of the pot, while the noncondensable vapors pass to an outlet. De Wild et al.[34] used a water-cooled 4°C knock-out pot and obtained a liquid with two phases: water and an organic fraction. The condenser is effective on a large scale, but the quality of the oil is poor.

Fractional condensation requires successive condensers at different temperatures to collect fractions with different chemical properties. Unlike other methods, in fractional condensation the organic oil fraction can be collected separately, without water. Gooty et al.[45c] pyrolyzed Kraft lignin and optimized a subsequent fractional condensation system, which consisted of two cyclonic condensers with an electrostatic precipitator-cum-condenser in the middle and a cotton-wool filter. The first condenser and the electrostatic precipitator-cum-condenser were optimized to condense the components of the vapors with high molecular weight (with high boiling points) to produce the oil fraction. The third condenser was kept at a significantly lower temperature (<10°C) to recover water and any other light components of the vapor. The oil fraction contained 94% of the phenolic compounds found in the raw lignin pyrolysis oil and had a water content below 1 wt%. The quality of the oil produced by fractional condensation is much higher than that of any other system used in fast pyrolysis of lignin; fractional condensation should be used when systems are scaled-up. If particular properties of the lignin pyrolysis oil are required, then it can be upgraded.[30,80a,b,c]

6. Summary and Outlook

Fast pyrolysis of lignin has the potential to produce value-added chemicals. Such a process consists of the following operations: lignin feeding, lignin fast pyrolysis, and cleaning and collecting the product. These operations are important because they affect not only the product yield and selectivity, but also the potential of commercialization of the process.

The highest yields of lignin pyrolysis oil after fast pyrolysis have been achieved in batch reactors. These reactors are used to analyze and improve the yield and selectivity of the product, but more research must be conducted to determine how to reproduce such advances in continuous-flow systems. Several continuous-flow reactors have been tested, but not all of them are suitable for lignin pyrolysis. Fixed-bed reactors have a simple design and are suitable for use with a catalyst. However, poor heating efficiency and char agglomeration in the reactor are likely to interfere with continuous operation.

A number of reactors (BFBR, CFBR, PCR, and EFR) have been tested for their robustness and have successfully pyrolyzed large amounts of lignin. EFR and PCR reactors show no agglomeration without having to change the lignin in any way, and PCR generates a high partial pressure of condensable vapors, allowing efficient product recovery. However, difficulties may be encountered when upscaling EFR and PCR. PCR is likely

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Table 8. Fast pyrolysis of lignin using vacuum reactors (VR).

Type or source of lignin	Amount pyrolyzed [g]	Lignin pyrolysis oil yield [wt%]		Notable details	Feeding	Product collection	Ref.
		Organic	Aqueous				
Organosolv lignin	0.05	ca. 90		Optimal pyrolysis conditions: pyrolysis under vacuum (pressure down to 0.3 mbar reached after flushing the system with N$_2$) at 450 °C (reached using a heating rate of 8000 °C s^{-1}) during 3 s Major products of lignin pyrolysis oil: oligomers	Batch	Lignin pyrolysis oil: using fast cooling at −100 °C	[72]

to have problems with heat transfer. Similar issues have been reported for EFR processing lignocellulosic biomass, but these may be of lesser significance during scale-up when using lignin due to smaller particle size. Furthermore, with EFR systems, the low partial pressure of the condensable vapors hinders product recovery. BFBR has excellent heat transfer, achieving high lignin pyrolysis oil yields. In contrast to EFR and PCR, BFBR can be used with catalysts. The primary drawback of BFBR is that agglomeration within the reactor causes defluidization of the bed, but there are a number of strategies to deal with this. Agglomeration can be prevented by pretreating the lignin feed with reagents such as calcium hydroxide, a low-cost, low-hazard, readily available substance. Pretreatment can improve selectivity towards phenols and aromatics and promote the feeding of the lignin into the reactor, which is otherwise problematic due to melting of the lignin. Other approaches can also help combat agglomeration, including the use of unconventional bed materials, stirring, and a slug injector to improve the feeding system. In the CFBR system, lignin melting during feeding and agglomeration do not occur. However, further testing on larger scales and for longer operation times are required to evaluate the suitability of this system for scale-up.

Product collection is another vital part of the lignin pyrolysis process as it influences the characteristics of the resulting pyrolysis oil. The goal is to achieve the effective separation of solids, including char and ash, the latter being of particular importance with pretreated lignin, as well as effective product collection. Hot particle filters can be used to remove fine particulates and have had positive results with lignocellulosic biomass. It is also of interest to determine the effect of hot particle filters on the composition of the lignin pyrolysis oil. One or two cyclones can be used to separate solids from the vapor stream and to condense the vapors as quickly as possible, thus limiting secondary reactions. Fractional condensation results in the highest quality of lignin pyrolysis oil as the water fraction and the organic oil fraction can be collected separately. Further upgrading could be applied to reach specific desired properties of lignin pyrolysis oil. Catalysts could also improve the quality of lignin pyrolysis oils.[81]

The above reactors are conventionally heated by electricity or nonrenewable fuel combustion, with the known disadvantages of these types of energies. Other alternatives, such as the combustion of char, are frequently employed to meet heat requirements and to minimize the waste streams.[17m] An emerging technology is solar-assisted pyrolysis, whereby the required heat is supplied by concentrated solar rays. A renewable source of heat increases the sustainability of the process.[82]

Tables 1–8 list the differences in the fast pyrolysis of lignin, depending on the system used. Overall, more effort must be invested if commercialization is to be achieved, focusing on promising systems such as slug injectors, fluidized-bed reactors, cyclones, hot particle filters, and fractional condensation configurations.

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Conflict of Interest

The authors declare no conflict of interest.

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