1 Introduction

Despite major efforts in sustainability research, today's society still depends extensively on fossil resources. Energy and even more so chemicals are mainly generated from fossil feedstock. The disadvantage is not only that by using the resources massive amounts of greenhouse gases are emitted [1]. But also further detriments to the environment, human and animal health, like environmental mining issues or lung diseases from emissions, come along with their intensive use. Moreover, fossil fuel resources are limited. This limitation holds true despite the fact that due to increasing crude oil price and better exploitation technology the proven oil reserves have increased from 1980 to 2016 from about $640 \cdot 10^9$ barrels by the factor 2.5 [2]. The fossil fuel reserves-to-production ratio was estimated in 2015 to be about 50, 55, and 120 years for crude oil, natural gas, and coal, respectively [3]. Although the quantity of known resources has increased also the demand increases rapidly due to global population growth and rising living standards. In 2015 a global population of 7.3 billion people lived on earth. It is expected that with an annual growth of 1.18 % a population prospect of 8.5 billion people will be reached in 2030 [4]. Together with the growing population also living standards are rising. Thus, not only peak oil but also the peak of natural gas and coal are estimated within the next half-century [5]. A major share in the depletion of these resources has the production of petrochemicals. Approximately 5 % of annual oil and gas production is utilized in petrochemicals [6]. Moreover, the demand for and production of chemicals increases dramatically [7]. About $16.6 \cdot 10^6$ barrels of liquefied petroleum gas, ethane, and naphtha were utilized per day in 2015 and in prospect $21.2 \cdot 10^6$ barrels will be their daily demand for chemical production in 2040 [8]. The demand is further illustrated by the development of chemicals sales, which increased from $270 \cdot 10^6$ \$ in 1970 to $4200 \cdot 10^9$ \$ in 2010 and rise is estimated to accelerate to $6400 \cdot 10^9$ \$ in 2020 (not inflation-adjusted) [9].

Therefore, to meet the growing future demand, it is inevitable that the development of all regenerative energies, including bioenergy, are advanced to global prevalence. But, while the future energy demand might be met by regenerative energy technologies such as photovoltaic, thermal solar, hydrodynamic and wind power, only sustainable material cycles can be the solution to anthropogenic materials use. The future sustainable demand, replacing petrochemicals, can only be achieved by recycling, new products from biomass or possibly atmospheric CO_2. Unfortunately, already today the utilization of biofuels as an energy resource is expected to affect global food security [10]. Thus, to achieve the vision of regenerative materials cycles, while evading the competition with food production, other biomass sources than e.g. corn starch [11] or sugar cane [12] have to be evaluated [1].

This situation has of course not gone unnoticed by researchers, politicians and societies all over the world. Many countries have policies and roadmaps pushing the utilization and research of non-food-biomass for energy and chemicals. Intensive research is conducted on lignocellulosic biorefineries [1, 13–20]. Lignocellulosic biomass – a material composed of the carbohydrates cellulose and hemicellulose, and aromatic lignin – is the most abundant organic material on earth as it is the material grasses, straws, wood and other plant biomass are made of. Admitting that the technology of lignocellulosic biomass processing is of notably higher complexity [1], utilization of lignocellulosic biomass poses also a major chance as lignocellulose is abundant in huge amounts. For example, in the USA $400 \cdot 10^6$ t of straw (dry matter) remain unused, while in Germany $50 \cdot 10^6$ t could be used without diminishing natural field cultivation and organic fertilizing [15].

Pulping of lignocellulosic biomass is a well-established technology, while the production of bioethanol from the cellulose fraction is on the brink of commercial success. Regardless of the employed process, huge amounts of lignin are produced as a by-product. About 20 to 35 % of the utilized total biomass is comprised of lignin [21] and lignin amounts to approximately 20 % of the earth's land biosphere [22]. In industrial wood pulping about $80 \cdot 10^6$ t of lignin are produced [23] and with the increasing activity in lignocellulosic ethanol production, the available amount of lignin will further increase [22]. Common practice is the combustion of lignin for process energy, as its polyaromatic structure is very stable, and therefore, challenging to chemically modify [22]. But it is expected that modern biorefineries, will be energetically completely self-sufficient and thus have roughly 60 % of excess lignin [1].

Due to its interesting chemical structure, containing high fractions of aromatics, lignin could be a valuable source for aromatic products [20]. But due to the intrinsic natural resistance to microbial or enzymatic degradation (recalcitrance) it is tough to degrade biologically [1, 24]. Therefore, thermochemical conversion of lignin is an alternative as the harsh reaction conditions enable extensive degradation. Pyrolysis is such a process in which, under the absence of additional oxygen, the chemical structure is cleaved to form char, gas, and oil which is, in case of lignin, rich in aromatics. Possible products encompass biochar for soil enhancement, bio-bitumen, fuel additives, activated carbon, bio-resins, bioplastics, or specialty chemicals such as food additives and pharmaceuticals [20].

Many parameters influence the pyrolysis process performance. To achieve high liquid product yields, i.e. pyrolysis oil yield, a short oil vapor residence time in the hot reaction zone is necessary to prevent secondary cracking from oil to gas [25]. Furthermore, an excellent heat and mass transfer and high heating rates favor a high liquid product fraction. Circulating fluidized bed technology is characterized by exactly these attributes.

In a nutshell, circulating fluidized bed pyrolysis of lignin could be a promising process to reduce the humankind's profound dependence on fossil resources for the production of chemicals. CFB lignin pyrolysis does not only allow high yields of pyrolysis oil containing valuable chemical components, but also lignin is biosynthesized in large abundance.

2 State of art

This chapter provides an overview on the current technology for lignin pyrolysis. Because the biomass composition is directly impacting process performance as well as product composition, chemical composition and properties of lignocellulosic biomass are discussed, followed by a topical review on biomass pyrolysis technology with a particular emphasis on circulating fluidized bed reactors and lignin pyrolysis. Moreover, the parameters influencing pyrolysis performance are discussed and typical product yields, spectra, properties and applications of char, oil, and gas compared. The chapter is concluded with a discussion of the state of art in pyrolysis process modeling, including reaction pathways, kinetics, pyrolysis in fluidized bed reactors and pyrolysis refineries.

2.1 Lignocellulosic biomass

It is estimated that on annual basis about 1.7 to $2.0 \cdot 10^{11}$ t of terrestrial biomass is photosynthesized, with a fraction of $6 \cdot 10^{9}$ t used anthropogenically, mostly for food production and energy generation and only 3 to 3.5 % as material [15]. An additional sustainable biomass utilization potential of $1.3 \cdot 10^{9}$ t exists in the United States only [26, 27], of which roughly 95 % is lignocellulose. One example for lignocellulosic biomass is wheat straw, of which $529 \cdot 10^{6}$ t/a is generated worldwide. 43 %, 32 %, and 15 % are produced in Asia, Europe, and North America, respectively. [14] It is a very attractive resource for the production of bioethanol because of its fast growth, low cost and low lignin content [28, 29]. In Germany $50 \cdot 10^{6}$ t straw (dry matter) is available for production of chemicals and fuel without negatively affecting the agricultural nutrient cycles [15].

The cell wall of vascular plants mostly consists of the biopolymers: cellulose, hemicellulose (polyoses), and lignin [14, 30, 31], and is hence referred to as lignocellulosic biomass. The composition depends on biomass type and origin (cf. Table 2.1). Additional biopolymers in lignocellulosic biomass are polyhydroxy fatty acid esters, polyisopropenoids (e.g. terpenes and steroids), glycosidic pectins and energy storing carbohydrates (sugars and starch). Other minor constituents can be dyes, pigments, flavors, alkaloids, and inorganic matter, with their amount and composition depending on the biomass type. [14] The biopolymers are heavily intertwined with each other [30] but can be separated by pulping technologies [30–32]. Cellulose is a valuable resource for pulp and paper industry as well as for production of renewable ethanol [33], levoglucosan (potentially useful as polyol) [34] and others. From hemicellulose furfural based nylon can be produced [14]. Lignocellulosic biomass consists of 6 to 33 wt.-% lignin [14, 31], which is the largest renewable resource of aromatics on the planet [30]. In conclusion, lignocellulosic biomass such as straw and forest resources is available in great abundance and a renewable resource for both fuel and chemical production.

Table 2.1: Composition (wt.-% dry matter) of biomass types (data from [14, 31])

biomass type	cellulose	hemicellulose		lignin
		hexoses	pentoses	
hardwood	30-43	2-5	17-25	18-25
softwood	40-48	12-15	7-10	26-33
straw/ grasses	35-41	0-5	15-28	6-24

2.1.1 Cellulose and hemicellulose

Cellulose

Cellulose and hemicellulose fibers provide structural support to plant cells. Cellulose, as the main constituent of the cell wall, is the most prevalent biopolymer. [14] It is approximated that the annual biosynthesized yield of cellulose is $1.3 \cdot 10^9$ to $1 \cdot 10^{11}$ t/a [14, 35]. Cellulose is a non-branched water-insoluble polysaccharide built from glucose monomers linked by β–1,4–glycosidic bonds yielding a syndiotactic β–1,4–polyacetal of cellobiose (4–O–β–D–glucopyranosyl–D–glucose) (cf. Figure 2.1) [14, 33, 35]. The length of a cellulose chain ranges from several hundred to tens of thousands of β–glucose molecules [14]. Its basic structure can thus be expressed by multiples of cellulose $C_{6\,P}H_{10\,P+2}O_{5\,P+1} \approx (C_6H_{10}O_5)_P$, where P is the degree of polymerization (number of glucose units with $M_{\text{glucose}} = 162\,\text{g/mol}$) [14, 35]. The degree of polymerization for technical (treated) cellulose is in the range of about 1000 to 3000 [23] and for untreated cellulose in the range of 5000 to 10 000 [36]. The molar mass of a cellulose polymer depends on its degree of polymerization: $M_{\text{cell}} = M_{\text{glucose}} \cdot P + 18 \approx 162\,\text{g/mol} \cdot P$ [35]. Cellulose is a nonmelting polymer [35].

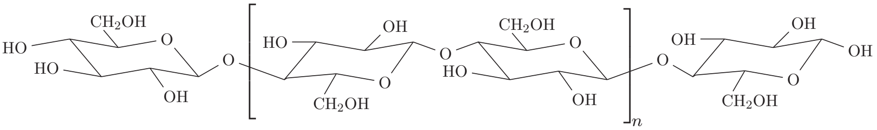


Figure 2.1: Model chain structure of cellulose

Hemicellulose

Hemicellulose (Greek: hemisys=half) is an amorphous polyose (cf. Figure 2.2) in the plant cell membrane and consists of hexose and pentose subunits, among them are D–glucose, D–galactose and D–mannose (hexoses) and D–xylose and L–arabinose (pentoses). [14, 33] Furthermore, hemicellulose can encompass sugar acids (uronic acids) such as D–glucuronic, D–galacturonic and methylgalacturonic acids. The bonding frequency and composition (amount of specific hexoses and pentoses) in hemicellulose depends on the biomass type and its source. The main linkages are xylan β–1,4–linkages. In hardwood, more xylans are found than in softwood, which contains more glucomannans than hardwood. [33] The degree of polymerization of technical hemicellulose is within 50 to 200, and thus considerably lower than that of cellulose [23, 36].

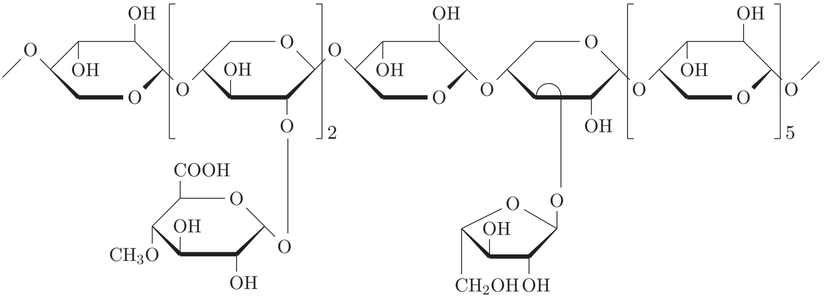


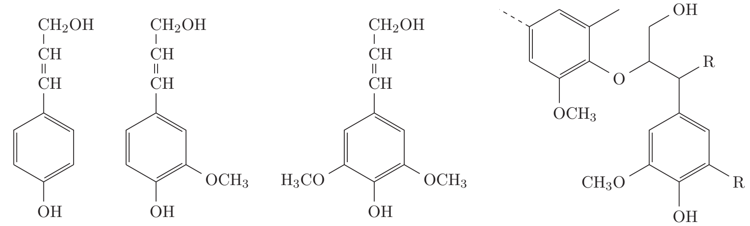
Figure 2.2: Model structure of hemicellulose (arabino–4–O–methyl–glucuronoxylan), as proposed by [37–39] in [14]

2.1.2 Lignin

Lignin, which comprises about 20 % of the planet's biosphere mass [22], is after cellulose the second most common organic substance in the world [14]. It was first named in 1813 by the Swiss botanist de Candolle, M. A. P. [40] after the Latin word lignum (wood). Together with hemicelluloses, lignin is a binding agent between adjacent cells and is heavily intertwined with hemicellulose and cellulose microfibrils in the cells itself, forming a composite structure with outstanding strength and elasticity. Furthermore, lipophilic lignin controls water permeation as well as nutrient and metabolite transport. Finally, lignin defends plants against microorganisms by inhibiting penetration of harmful enzymes into the cell walls. [30, 31]

Lignin is mostly obtained as a by-product of pulping processes. These processes are Kraft, sulfite, soda, organosolv, and aquasolve pulping and other processes of minor importance [13, 30–32, 41]. The most important process is Kraft pulping with an annual global production of 73 %, which relates to $170 \cdot 10^6$ t pulp [32]. The majority of lignin is burnt for pulping chemical recovery and supply of pulping process energy; less than 2 to 5 % is isolated and sold [22, 31]. Recent research interest in alternative pulping processes has increased due to intensified work on lignocellulosic biorefineries [6, 17]. The aim is to sustainably produce bioethanol as fuel and lignin as a by-product.

The content of lignin in biomass increases from grasses/straw over hardwood to softwood (Table 2.1). Lignin is an amorphous randomly cross-linked polyphenol, consisting of the phenylpropane (C_9) subunits coumaryl, coniferyl, and sinapyl alcohol, which have zero, one, and two methoxyl groups (Figure 2.3), respectively [14, 30, 31, 42]. Depending on plant type and species the contents of these primary monomer units vary (cf. Table 2.2) [30]. Softwood lignin is primarily built from coniferyl alcohol (guaiacyl structure) and thus called G-lignin. Hardwoods, on the other hand, contain almost equal amounts of coniferyl and sinapyl alcohol (syringyl structure) and therefore their lignin is categorized as GS-lignin. [30, 31] Grass and straw lignin contains all of the three monolignols (additionally the coumaryl structure p-hydroxyphenyl) and is thus abbreviated (GSH-lignin) [29–31]. Diverse functional groups can be found in the lignin structure. Predominantly these groups are methoxy, phenolic, and aliphatic hydroxy, benzyl alcohol, non-cyclic benzyl ether, and carbonyl groups [30]. Reported frequencies per C_6C_3 unit in spruce milled wood lignin are 1.09 for aliphatic OH, 0.26 for phenolic OH, and 0.2 for total carbonyl [43].



p-coumaryl alcohol (H) p-coniferyl alcohol (G) p-sinapyl alcohol (S) β–O–4 linkage

Figure 2.3: Aromatic phenylpropane subunits of lignin and most frequent interunit linkage

A multitude of different linkages irregularly connect the various primary monomer unit's allyl ethers to form a network with O–O, ether, and C–C bonds. Depending on the biomass type the proportion of these linkages varies. Softwood and hardwood are connected by ether-moieties in more than two-thirds of the linkages. [14, 30, 43] The most common linkage is β–O–4–aryl ether (cf. Figure 2.3) with e.g. 60 % in birch (hardwood) and 46 % in spruce (softwood). Other important linkages include β–5–phenylcoumaran, α–O–4–, 4–O–5–diaryl ether, β–β–resinol, 5–5–biphenyl and β–1–1,2–diarylpropane motifs [14, 30, 42, 43]. The proportions for birch and spruce wood are given in Table 2.3.

Table 2.2: Lignin composition of phenylpropane units [30]

biomass type	phenylpropane unit, % coumaryl (H)	coniferyl (G)	sinapyl (S)
hardwood	-	50	50
softwood	-	90†-95	5-10
grasses	5	75	25
wheat straw‡	5	49	46

†from [43], ‡from [29]

Table 2.3: Interunit linkages of wood lignin [43]

linkage type	proportion in % softwood (spruce)	hardwood (birch)
β–O–4	46	60
α–O–4	6-8	6–8
4–O–5	3.5-4	6.5
β–5	9-12	6
β–1	7	7
β–β	2	3
5–5	9.5-11	4.5

Molar mass

The molar mass of isolated lignins depends on the pulping conditions and biomass type [44]. Most isolated lignin, e.g. from the Kraft, soda, and sulfite pulping have molar masses in a range between 3000 and 20 000 g/mol. [30, 31] An example is wheat straw lignin from an organolsolv process with $M_{\mathrm{w}} = 3960$ g/mol and $M_{\mathrm{n}} = 2330$ g/mol [45]. The M_{w} values for Kraft lignins are generally below 10 000 g/mol [31].

Glass transition

The lignin glass transition temperature ϑ_{g} depends on moisture content, raw material, production process, molar mass, and measurement procedure. Hardwood lignins have ϑ_{g} values between 65 and 85 °C which is lower than in softwoods (90 to 105 °C). For isolated lignins the following ϑ_{g} values have been found: MWL lignins: 110 to 180 °C [31, 46] and

Kraft lignins: 102 to 174 °C. Moisture has a severe effect: values of 195 °C when dry and 90 °C when containing 27 wt.-% moisture have been reported. The effect of lignin molar mass is even more severe, i.e. a ϑ_g of only 32 °C at low molar mass ($M = 620$ g/mol) and a ϑ_g of 173 °C at the highest molar mass $M = 180\,000$ g/mol. [31, 47] Furthermore, Nowakowski et al. [48] reported softening of amorphous lignin between 120 to 180 °C and Hatakeyama et al. [49] a ϑ_g for dioxane lignin at 122 °C.

2.2 Biomass pyrolysis

Pyrolysis is a thermal decomposition process for organic materials. As opposed to combustion or gasification no oxidation by oxygen (or an oxygen donor) occurs. Pyrolysis, in the absence of air, is utilized to crack the feedstock to gas, char, and oil. The process conditions substantially affect the product composition. At low heating rates < 200 K/s, moderate temperatures < 400 °C, and long solids residence times (up to several days) mostly char is produced [36]. This process, called conventional or slow pyrolysis, is applied since centuries to produce e.g. charcoal. A more recent technology is fast pyrolysis, also called rapid or flash pyrolysis. Fast pyrolysis at higher temperatures between 500 and 1000 °C, short vapor residence times < 2 s, and high heating rates of 1000 to 10 000 K/s [50–53] aims at producing high amounts of liquid product for energetic or chemical valorization [36]. The vapor residence time for high liquid yield pyrolysis has to be kept short (typically less than 2 s) to prevent secondary degradation of liquid to gaseous compounds [54].

A typical layout [55–57] of a biomass pyrolysis process is shown in Figure 2.4. The biomass is fed into the pyrolysis reactor where it is cracked to oil, gas, and char. Downstream, first solids and then permanent gases are separated from the product oil. Separation of the solids is necessary because they promote secondary cracking of pyrolysis oil [25], pyrolysis oil aging, oil instability, and other application barriers. In most cases, cyclones are used as they are easily maintained high-performance separators and downstream separation of solids from the liquid phase proves difficult [53]. Additionally, candle filters, granular filters, and others are investigated for pyrolysis process application [58–62]. To achieve high liquid yields, the oil vapors are cooled rapidly (quenched) to prevent secondary reactions from oil to gas. Optionally, the by-products (permanent gas and char) can be combusted to supply the endothermic pyrolysis energy demand. Furthermore, electrostatic precipitators are widely used to separate aerosols from pyrolysis gas and vapors.

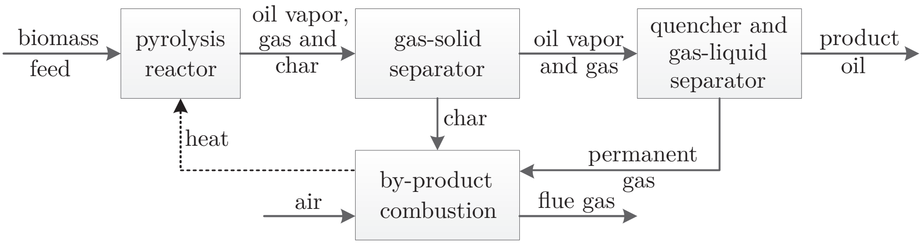


Figure 2.4: General scheme of biomass pyrolysis system

A large variety of reactor types for fast pyrolysis has been investigated mainly at laboratory and pilot scale: ablative reactors in which the feedstock is heated by contact with a hot surface [54, 56, 63] like cyclone reactors [64–68], vortex reactors [54, 69–72], auger or double screw reactors [56, 73, 74], rotating cones, rotary kilns, and hearth furnaces [75–77]. Furthermore, reactors with mainly convective and conductive heat transfer such as fixed bed reactors [78, 79], fluidized beds such as (conical) spouted beds [52, 80–82], bubbling/ stationary fluidized beds [51, 53, 55, 56, 63, 83, 84], fluidized beds with mechanical fluidization [85–87], and circulating fluidized bed reactors [88–93] have been applied to pyrolysis. Additionally, reactors that transport heat by means of radiation and convection: entrained flow reactors [94–96] and microwave pyrolysis reactors [97–99] have been used. Lastly, especially thermogravimetric analysis and tubular reactors coupled with various online product analysis systems are widely applied for analytical investigation of pyrolysis and pyrolysis mechanisms [100–104]. Besides the analytical equipment, of the above reactor types, fluidized beds are used most frequently [54, 105].

2.2.1 Pyrolysis in circulating fluidized bed reactors

Circulating fluidized beds (CFB) have the advantage of short vapor residence time and good heat transfer (about 80 % conduction, 19 % convection, 1 % radiation [54]) leading to high reaction rates. An additional advantage is that CFBs are potentially suitable for larger throughputs, as CFB technology is widely used at very high throughputs in the petroleum and petrochemical industry [56, 106]. Summarized advantages and disadvantages are [54–56, 70]:

+ good mixing
+ good temperature control
+ high heat transfer & reaction rates
+ short vapor residence time
+ large feedstock particle size possible (up to 6 mm)
+ can be coupled with a char combustion reactor for heat supply
+ high throughput possible (∼ 60 t/d and bigger)
+ catalytic bed material can be used

– possible liquid cracking by hot solids
– char attrition and breakage leading to higher solids content in pyrolysis oil
– possible attrition and breakage of catalytic bed material leading to higher process costs
– increased complexity (compared to BFB)

A typical layout [55, 56] of a biomass pyrolysis process with circulating fluidized bed reactor is shown in Figure 2.5. It shows an integrated system with a CFB pyrolysis reactor, which is coupled with a stationary fluidized bed for char combustion. The CFB consists of a pyrolysis riser reactor, a cyclone for gas-solid separation, a connection to the char combustion reactor and a return leg into the riser. Two loop seals are necessary to prevent gas exchange between the reactors. The recirculating bed material is heated by char combustion, supplying the heat demand for pyrolysis. In this example, secondary solid separation (e.g. additional cyclones) is followed by a scrubber for fast quenching of the pyrolysis reaction and an electrostatic precipitator. The non-condensable permanent gas can partly be recycled to supply the fluidization gas for the pyrolysis reactor.

In 1999, ENSYN was the only commercially operating organization giving a performance guarantee for their fast pyrolysis plants [53]. The reactor is a common CFB riser with

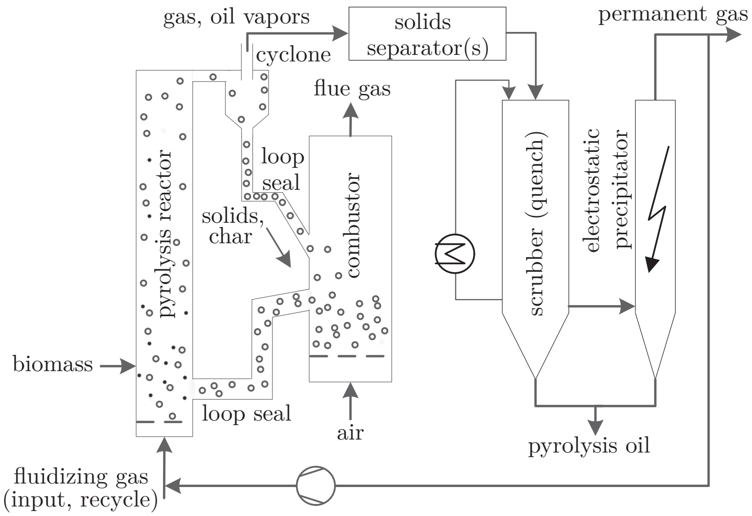


Figure 2.5: Circulating fluidized bed system for biomass pyrolysis with integrated char combustion and product oil separation

syphon and return leg [107–110]. Further examples of plants include a 36 t/d unit at Red Arrow, WI, USA and some plants in research & development organizations (e.g. ENEL, Italy and VTT/Metso/UPM, Finland) [53, 56]. Today, Envergent Technologies (a joint venture of ENSYN and Honeywell) has developed the fast pyrolysis plant with the largest liquid product capacity of about 30 MW [111], although for the produced biofuel no significant market has been established yet [111]. In 2007, another CFB reactor system was investigated. The biomass is fed into the bottom of the riser section. The entrained char is returned to a bubbling fluidized bed at the bottom of the riser, where it is partly oxidized for supply of pyrolysis energy. [88, 89]. A recent 2013 comprehensive review of research and commercial activities in the field is given by Meier et al. [112], but until today no in-depth investigation of lignin pyrolysis in a CFB system has been reported.

2.2.2 Lignin pyrolysis

Lignin can be obtained from various biomass sources by diverse pulping processes. Therefore, a large variety of lignins has been investigated as pyrolysis feedstock. Examples are: wheat straw lignin [113], Kraft lignin [47, 114–116], alcell lignin [117], organosolv lignin (from softwood and wheat straw) [29, 48], soda lignin (from grasses and wheat straw) [48], bamboo lignin [118], alkali lignin [119], lignin from corn cob acid hydrolysis residue [120], and milled wood lignin (MWL) [121]. Next to the lignin variety also different reactors for lignin pyrolysis have been investigated. Analytical methods and reactors range from pyrolysis-GC-MS [47, 48, 120], TG-FTIR [120, 122], TGA [48, 119], pyroprobe [118, 123], heated screen [119] over tubular laboratory scale reactors [102, 116], microwave pyrolysis [97] and centrifuge reactors [124] to fixed bed [115, 117], and fluidized bed reactors [29, 48, 85–87, 125].

Lignin pyrolysis – especially in fluidized beds – has been reported to be difficult by many investigators [29, 48, 87]. Nowakowski et al. [48] carried out round robin pyrolysis of a soda and an organosolv lignin in several laboratories and reactors. They found that the pyrolysis of the soda lignin (94 wt.-% lignin content) led to problems already when feeding pneumatically or by auger feeding into the reactor. It melted in the pneumatic feeding lance and the screw feeder, respectively. Additionally, molten lignin in the fluidized bed resulted in bed agglomeration and subsequent defluidization. The authors conclude that fluidized bed pyrolysis of this lignin is nearly impossible. The same melting behavior leading to bed agglomeration and defluidization was observed for wheat straw lignin (lignin purity > 90 %) pyrolysis at 550 °C. Removing the lignin fines prior to feeding resolved the problem [29]. For the softwood organosolv lignin (about 40 wt.-% carbohydrate content, estimated from elemental analysis) agglomeration was also observed but only in one lab and to less extent [48]. Due to the melting at 150 to 200 °C, which together with slow reaction induces a liquid phase and therefore bed agglomeration and defluidization [87], researchers at ICFAR, University of Western Ontario developed a mechanically agitated fluidized bed reactor with an internal mechanical stirrer [85–87]. For further reading on recent lignin pyrolysis research activities, the work of Lago [85] is suggested.

2.2.3 Influence parameters

2.2.3.1 Main parameters

The yield and composition of pyrolysis products can be adjusted by careful selection of process parameters. The main parameters are temperature, vapor and solids residence time as well as heating rate. Residence time and heating rate are primarily defined by reactor type; nevertheless, they can be adjusted within the limits of a given system.

Temperature

The main control parameter is the pyrolysis temperature. Numerous studies on the influence of this parameter on product yields have been conducted [51, 56, 119, 126–128]. Virtually all feedstock and reactor variations have been studied. Generally, the gas yield increases with rising temperature, because more feedstock is converted into volatile products and secondary reactions convert more pyrolysis oil to gas [51, 56, 84, 126]. Complementarily, the char yield decreases continuously [51, 56, 84, 126], while the oil yield increases until an optimum temperature is reached [51, 56, 84, 119, 126–128]. Beyond this optimum, the secondary cracking reactions from oil to gas become more substantial [51, 56, 84, 119, 126–128]. For illustration, two examples for fluidized bed pyrolysis are given in Fig. 2.6.

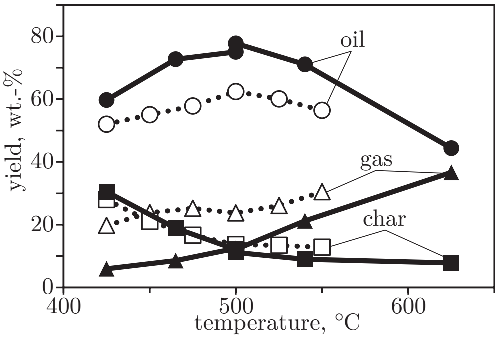


Figure 2.6: Fluidized bed pyrolysis yields of sawdust from wood mixture [128] (empty symbols) and hybrid poplar aspen wood [84] (filled symbols)