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Application of Mechanically Fluidized Reactors to Lignin Pyrolysis

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A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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Application of Mechanically Fluidized Reactors to Lignin Pyrolysis

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by

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Graduate Program in Engineering Science
Department of Chemical & Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

Lignin has great potential for the production of aromatics currently derived from petroleum, since it is the most abundant source of aromatics in nature. At present, Kraft lignin is used as fuel within the pulping process but, alternatively, it could be converted to high-value chemicals using thermochemical processes such as pyrolysis. Kraft lignin, however, is a very cohesive and thermally sensitive powder with foaming and agglomerating tendency under reaction conditions. Therefore, new reactor designs are necessary to efficiently process this raw material.

Consequently, a novel reactor design, designated as Mechanically Fluidized Reactor (MFR) has been developed to successfully process Kraft lignin. To select the optimal stirrer geometry for fast pyrolysis of biomass, its mixing characteristics have been investigated with a technique developed to monitor the aeration resulting from the formation of gases and vapours during pyrolysis. The performance of different stirrers has been compared in terms of time for complete pyrolysis and the best performance, i.e. shortest time, was achieved with a design incorporating a vertical blades stirrer. The mixing provided by this type of stirrer was also simulated by Discrete Element Method model.

In this work, Kraft lignin has been successfully pyrolyzed in the MFR. However, during the reaction, the bed material becomes cohesive and it is not possible to observe the bed aeration generated by the pyrolysis gas and vapours. Different bed materials were tested with the purpose of improving the Kraft lignin behaviour. All the materials capable of improving the processability, resulted in a watery bio-oil, most likely due to the catalytic enhancement of cracking reactions. Kraft lignin was also mixed with birch wood in different proportions. The liquid yield decreased linearly with Kraft lignin content in the initial feed, whereas phenolic compounds in the liquid product were found to increase linearly with increasing Kraft lignin content. The liquid product was analyzed in terms of alkyl phenols, guaiacols, catechols and syringols by GCxGC-TOFMS.

Hydrolysis lignin residues from bioethanol production were much easier to pyrolyze, as the bed material did not become cohesive. The high ash content of these feedstocks, when compared to Kraft lignin, reduced the liquid yield.
Keywords

Mixing, pyrolysis, aeration, mechanically fluidized, rotation speed, lignin, cohesivity, bio-oil, phenolics, DEM.
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Nomenclature

A  contact area
A_c  critical aeration
A_{cell}  cross-sectional area of the shear cell
c_p  average specific heat capacity
d  diameter of particle
df_F  degrees of freedom of full model
df_R  degrees of freedom of reduced model
e  restitution coefficient
E  modulus of elasticity
E^*  effective modulus of elasticity
F_c  elastic contact force
F_{c,i}  contact forces of particle i
F_{c,n}  normal contact force
F_{c,t}  tangential contact force
F_N  normal force
F_S  shear force
F_{S,cr}  critical shear force
g  acceleration of gravity
G  shear modulus
\( G^* \) equivalent shear modulus of the bodies

\( I_i \) moment of inertia of particle \( i \)

\( k_n \) stiffness of the colliding bodies

\( k_t \) tangential spring stiffness

\( L \) length of cylinder

\( m_{\text{cell, total}} \) mass of the shear cell and the solid sample

\( m_{\text{cell, empty}} \) mass of the shear cell

\( m_f \) mass of the loading frame

\( m_i \) mass of particle \( i \)

\( m_{\text{lid}} \) mass of the shear lid

\( m_{\text{ring}} \) mass of the shear ring

\( m_s \) mass of solids and reactor wall

\( m_{\text{total,w}} \) mass of wall sample, shear ring, bulk solid and shear lid

\( m_w \) mass of the weights

\( m_{\text{wall}} \) mass of the wall sample

\( m^* \) reduced mass

\( n_{ab} \) unit vector normal to the contact plane

\( n \) number of observation

\( p \) probability

\( p_F \) number of parameters of full model
\( p_R \)  
number of parameters of reduced model

\( r_a \)  
position vector of particle a

\( r_b \)  
position vector of particle b

\( R_a \)  
radius of particle a

\( R_b \)  
radius of particle b

\( R^* \)  
median radius

\( \text{SSE}_R \)  
sum of squared errors for reduced model

\( \text{SSE}_F \)  
sum of squared errors for full model

\( T_i \)  
torque of particle i

\( T_w \)  
wall temperature

\( T_b \)  
bed temperature

\( U \)  
overall heat transfer coefficient

\( V_{\text{cell}} \)  
volume of the shear cell

\( V_{\text{ring}} \)  
volume of the shear ring

\( v_{ab} \)  
relative velocity at the contact point of particles a and b

\( v_{ab,n} \)  
normal component of relative velocity at the contact point of particles a and b

\( v_{ab,t} \)  
tangential component of relative velocity at the contact point of particles a and b

\( v_i \)  
velocity of particle i

\( v \)  
impact velocity

\( v_R \)  
rebound velocity
\( W_{\text{abs}} \)  energy absorption during impact

\( W_{\text{kin}} \)  initial kinetic impact energy

\( W_{\text{kin,R}} \)  restitution kinetic energy

\( \delta \)  displacement

\( \delta_n \)  normal displacement

\( \delta_t \)  tangential displacement

\( \eta_n \)  damping factor

\( \eta_t \)  tangential damping coefficient

\( \mu \)  internal friction coefficient

\( \mu_w \)  wall friction coefficient

\( \nu \)  Poisson ratio

\( \nu_a \)  Poisson ratio of particle a

\( \nu_b \)  Poisson ratio of particle b

\( \rho_b \)  bulk density

\( \sigma \)  normal stress

\( \sigma_w \)  wall normal stress

\( \tau_w \)  wall shear stress

\( \tau \)  shear stress

\( \tau_c \)  cohesion

\( \bar{\tau}_{cr} \)  critical shear stress
$\omega_a$  angular velocity of particle a

$\omega_b$  angular velocity of particle b

$\omega_i$  angular velocity of particle i
Chapter 1

1. Introduction

The concerns about carbon accumulation in the atmosphere, leading to climate changes, sustainability and energy security have stimulated many countries to diversify energy resources. Biomass is a renewable energy source that could partially replace fossil sources for the production of environmentally friendly and sustainable chemicals and fuels in the future.

Pyrolysis, defined as thermal cracking of organic material in the absence of oxygen, is one of the most attractive processes to convert biomass into valuable products, since it is operated at atmospheric pressure and at relatively low temperatures. A series of consecutive and parallel reactions take place in this process leading to the conversion of biomass into liquid, gaseous and solid products.

Fast pyrolysis, performed at high heating rates and low vapour residence times, minimizes secondary reactions and maximizes the liquid yield (Mohan et al., 2006). In fast pyrolysis, the organic feedstock is rapidly heated up to high temperature in the absence of oxygen, favouring the formation of organic volatiles and char. The vapour residence time is between 0.5 and 2 seconds and the vapours are condensed to produce bio-oil. The liquid product is mainly formed by acids, aldehydes, esters, aromatic, phenolic derivatives and other hydrocarbons as well as water (Goyal et al., 2008). While the non-condensable gases (mainly CO, CO$_2$ and CH$_4$), forming the gas product, might be combusted to provide heat for the process, the solid residue, bio-char, may be used either as a fuel or as the feedstock for higher value applications (bio-char, bio-coal, bio-coke, or bio-carbon-based materials, such as catalysts, adsorbents, carbon nanotubes or fillers in polymeric composites (Dehkhoda et al., 2010; Peterson et al., 2013)).

In the last decade many researchers focused their attention on the pyrolysis of feedstocks which would lead to the production of bio-oils with a high yield of specific chemical fractions. For instance, lignin has great potential for the production of valuable aromatics currently derived from petroleum, being the main aromatic renewable natural resource (Mu et al., 2013). Given this feature, Kraft lignin has attracted considerable attention. Nowadays, paper is losing some of its main markets because of the electronic technology alternatives, and the pulp and paper sector
needs to make the whole process more efficient and, especially, more profitable. Although new high-value applications have been developed for cellulose, such as nanocellulose (Peng et al., 2011; Siró & Plackett, 2010; Sulaiman, 2015), no such applications have been developed for the lignin by-product. Currently, the main application of lignin is as a low-value fuel within the pulping process. However, lignin could be converted to more profitable products than a low-grade fuel.

New hydrolysis technologies have recently been demonstrated on an industrial scale for the conversion of biomass into sugars. These technologies convert most of the biomass cellulose and hemicellulose, leaving a residue, called hydrolysis lignin, containing the original biomass lignin mixed with unconverted cellulose and hemicellulose. The economic feasibility of these new technologies would be enhanced by the development of high value applications for the hydrolysis lignin (Dong et al., 2011).

Technologies for the valorization of lignin are not as developed as the ones for polysaccharides (Azadi et al., 2013). Pyrolysis could exploit its potential for the production of high-value chemicals, but fast pyrolysis technologies have been developed and optimized for whole biomass. The lignin thermal depolymerisation resistance (De Wild et al., 2012) and physical properties during heating and cracking impacts its handling characteristics. In general, lignin has been found to be a very difficult material to feed and to pyrolyze. Lignin is characterized by a very low glass transition temperature, which causes stickiness and agglomeration already in the delivery pipe of the feeder of conventional fluidized bed pyrolyzers. Additionally, reacting lignin agglomerates with fluidized bed particles, result in defluidization (Nowakoski et al., 2010).

New reactor designs are therefore needed for successful pyrolysis of Kraft lignin (Palmisano et al., 2011; Tumbalam et al., 2014). Consequently, a novel reactor design, designated as Mechanically Fluidized Reactor (MFR) has been developed at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) at Western University to process Kraft lignin and similarly sticky feedstocks.

In this study, a new technique is proposed to convert feedstocks that would become cohesive during the pyrolysis process and would, thus, be difficult to process in conventional fluidized beds. The first objective of this study was to investigate the suitability of the MFR for Kraft
lignin pyrolysis. The second objective was the development of a method to determine how cohesive a feedstock becomes when pyrolyzed in order to evaluate alternative solutions to improve Kraft lignin behaviour by mixing it with other non-problematic feedstocks or modifying the bed material. Finally, the performance of Kraft lignin was compared with that of by-products of other lignocellulosic processes in order to evaluate whether its final products are of sufficient interest and value and justify the difficult processing.

1.1 Literature Review

1.1.1 Lignin

Lignin is the second most abundant biomass component, ranging from 18 to 40 wt% in dry wood (Fengel et al., 1984). By virtue of its features, it plays the role of mechanical strengthener agent in the plant world. Its first application in the human world was indeed as fibre-accompanying substance in pulp and paper in order to increase the mechanical strength. Lignin is a complex heterogeneous aromatic molecule, which cannot be described by a number of monomers combined by few types of linkages. However, numerous studies have confirmed that the p-hydroxycinnamyl alcohol, coniferyl alcohol and sinapyl alcohol are the building units of all lignins (Fengel et al., 1984), meaning that it is an important source of oxygenated aromatic compounds (Figure 1.1).

![Figure 1.1 Lignin building units (1- p-hydroxycinnamyl alcohol, 2- coniferyl alcohol, 3- sinapyl alcohol)](image)

Thus, lignin has a large potential for different purposes. Lignin is widely used as additive in the cement and concrete industries. Besides, lignin is attractive also for its adhesive properties replacing 30-50% of the phenol in resins used as plywood adhesive (Czernik and Bridgwater, 2004). Due to the mainly aromatic and aliphatic character, it may be converted into chemicals more commonly derived from petroleum and natural gas. However, lignin structure appears to
have random features (figure 1.2) and varies with the biomass source. Additionally the morphology of extracted lignin is different from native lignin (Evans et al., 1986) and different isolation procedures may lead to significantly different configurations and characteristics and to varying degrees of purity. These procedures can be divided in two major categories: in the first one, lignin is dissolved while cellulose and hemicellulose are removed as insoluble residue, whereas, in the second one, lignin is separated as insoluble residue by solubilizing cellulose and hemicellulose (Pandey and Kim, 2011). The Kraft process belongs to the first category of isolation and the enzymatic hydrolysis that can be classified in the second type.

![Figure 1.2 Schematic structural formula of lignin (Adapted from Adler, 1977)](image)

**Figure 1.2 Schematic structural formula of lignin (Adapted from Adler, 1977)**

**Kraft process**

In pulping and bleaching processes, lignin is degraded and separated from the other wood components. It represents a 50 million tons per year worldwide carbon source (Sixta, 2006).
Worldwide, the Kraft pulping process is used for most of the paper production, making up 90% of the total production capacity (Azadi et al, 2013).

The raw material is treated in a solution of sodium hydroxide and sodium sulphide (cooking liquor) where delignification occurs. After cooking, the pulp and the black liquor leave the digester and the black liquor is separated from the pulp (Sixta, 2006).

During pulping process, lignin is degraded in smaller lignin fragments which results in higher solubility in the water/alkali solution, and then, due to condensation reactions, alkali-stable linkages are formed which reduce the digestion efficiency (Azadi et al, 2013).

The black liquor exiting the digester is called weak black liquor and it goes through multiple-effect evaporators in order to reach a solid content up to 80% (Sixta, 2006). The lignin content of the black liquor ranges from 29 to 45%. Kraft lignin contains 1-2% sulphur and is not representative of native lignin, mostly because of the alterations due to the base-catalyzed reactions occurring in the digester (Evans et al., 1986), which render the depolymerisation process more difficult (Azadi et al., 2013). The majority of the Kraft mills burn the black liquor in the recovery furnace for producing electricity and steam. However, most of the recovery boilers in North America are calorific-load limited (Kouisni et al., 2012), thus, lignin can be separated by a fraction of the black liquor by acidification. In 2013 Domtar started up a Kraft lignin separation plant in Plymouth, NC (Metso, 2015), followed by FPInnovations and West Fraser Timber Co. Ltd., which have lately announced the construction of Canada’s first lignin plant in Hinton, AB (FPInnovations & West Fraser, 2015).

**Lignin from enzymatic hydrolysis**

The first step in lignocellulosic ethanol production is the pretreatment to disrupt the lignin and expose the cellulose and hemicellulose chains. Then hydrolysis of cellulose and hemicellulose, chemical or enzymatic, is needed to produce the sugar solution, which can then be fermented, while removing lignin as insoluble residue. Enzymatic hydrolysis, carried out by cellulase and hemicellulase enzymes, is less destructive than chemical methods (Sixta, 2006), but the process takes longer (Binod et al., 2011). After hydrolysis residual cellulosics and lignins from the hydrolysis vessels are sent to a heat generation unit (Isaacs, 1984).
In 2013 Beta Renewables and Novozymes opened a 75 million litres cellulosic bioethanol production plant in Crescentino, Italy. Lignin is extracted and supplied to a power plant for the generation of power partially used within the bioethanol production process and partially sold to the local grid (Lane, 2013).

In order to improve the competitiveness of bioethanol production from biomass, in line with the biorefinery concept, it is important to utilize all the lignocellulosic components. For this reason, lignin generated as by-product from this process, has attracted considerable attention as a potential feedstock for value-added products (Cotana et al., 2014, Brosse et al., 2011). Lignin isolated by cellulase is more representative of the native lignin, but contains large amounts of residual carbohydrates (Dorrestijn et al., 2000) since cellulase and hemicellulase enzymes retain the bonds between lignin and carbohydrates (Jääskeläinen et al., 2003).

1.1.2 Fast pyrolysis

Fast pyrolysis is an attractive thermochemical conversion route. A series of consecutive and parallel reactions take place in this thermal cracking process and they compete between liquid, gaseous and solid product.

In fast pyrolysis, the organic feedstock is rapidly heated up to high temperature in the absence of oxygen, favouring depolymerisation, dehydration, decarboxylation, esterification, condensation, and cyclization in order to generate vapours and gas, as cracking reactions lead to the formation of organic volatiles, and char, mostly due to lignins cross-linking and condensing to three-dimensional, thermally stable aromatic polymeric structures (Bridgwater et al., 1999a). The vapour residence time is usually from 0.5 to 2 seconds and the bio-oil is formed upon condensation of the vapours produced during the pyrolysis process. While the remaining non-condensable gases (mainly CO, CO₂ and CH₄) might be used within the process, the solid residue, char, may be used either as a fuel or as the feedstock for higher value applications (Dehkhoda et al., 2010; Peterson et al., 2013) such as bio-char, bio-coal, bio-coke, or bio-carbon-based materials (catalysts, adsorbents, carbon nanotubes or fillers in polymeric composites).

Bridgwater (2012) reviewed fast pyrolysis technologies and classified them into:

- Bubbling fluid bed
- Circulating fluid bed
- Rotary cone
- Auger reactors
- Ablative pyrolysis

Bubbling fluidized beds (figure 1.3) are widely utilized because their construction and operation are easier compared to other technologies. The residence time of vapours and char is easily controlled by the fluidizing gas flow rate and it is higher for char. Moreover, the heat transfer in this kind of reactors is very efficient, so that the temperature can be controlled quite accurately. However, even though this reactor is characterized by a ready scale-up, the heat transfer is critical in a large scale plant and it requires more attention. Furthermore it is a well-known technology, already optimized for high liquid yields of 70-75 wt% from wood on a dry-feed basis.

![Fluidized bed reactor](image)

**Figure 1.3 Fluidized bed reactor (Adapted from Bridgwater, 2012)**

Circulating fluid beds (figure 1.4) have some of the characteristic advantages of bubbling fluidized beds, such as a good temperature control. The residence time of char is nearly as low as
the one of gas and vapours. Additionally they potentially suit applications characterized by large throughputs. However, their hydrodynamics are complex and the char is more subject to attrition because of the high velocities. Typically, the char is used as a fuel for the process, burned in a second reactor and recirculated into the primary converter.

Figure 1.4 Circulating fluid bed (Adapted from Bridgwater, 2012)

The rotating cone converter (figure 1.5) works by mean of the centrifugal force which drives hot sand (heat carrier) and biomass up a rotary cone. Then, vapours are collected and the char is usually burned in a bubbling fluidized bed combustor to heat the sand. The amount of gas required in this technology is lower than for the first two technologies discussed above, but gas is needed to burn char and transport sand.
The auger kiln (Figure 1.6) operates without fluidizing gas and the biomass is mechanically conveyed through a hot reactor. It requires a separate vessel to reheat the sand fed with the biomass as heat carrier. It is very difficult to achieve short residence times similar to fluid and circulating fluid beds, feature that leads to somewhat lower liquid yields.
The ablative conversion (Figure 1.7) differs greatly from the other pyrolysis technologies, mainly for the heat transfer process. The biomass is heated up by pressing it, mechanically or by means of centrifugal force, against the reactor wall. In between, an oil film forms acting as a lubricant and then evaporating to give the gas product. Particles need to have a high relative speed on the wall, which should not reach temperature over 600°C. Large feed sizes can fit this system and the inert gas is not required, but the reactor is more elaborate since it is mechanically driven. The limiting factor is the heat transfer to the reactor, not to the pyrolyzing biomass. This technology is not easy to be scaled-up because the process is surface area controlled.

**Figure 1.6 Auger reactor**
1.1.3 Lignin fast pyrolysis

Lignins of different compositions and origins have been tested and they, as expected, presented various behaviours. In general, lignin has been found to be a very difficult material to feed and to process (Table 1.1), because of the thermoplastic behaviour of lignin and its thermal depolymerisation resistance, which impact its handling characteristics and, in particular, its stickiness. Processing lignin, it has been noticed that this feedstock immediately begins to pyrolyze, but keeps reacting for longer than a minute. Many laboratories have not been able to feed lignin into pyrolysis reactors. Lignin was shown to be completely fluid between 200-225 °C and 350 °C as shown in Figure 1.8 (Dufour et al., 2012). Some types of lignin are reported to soften at about 110°C (Ferdous et al., 2002), a temperature often reached in the feeder delivery pipe. As a consequence, lignin typically softens in the feeding system and some decomposes into char resulting in a rapid blockage of the system.
A collaboration of fourteen laboratories carried over an international study on lignin pyrolysis (Nowakowski et al., 2010). The main technology tested in this study was the fluidized bed reactor. The fluidized bed reactor, besides being a technology widely utilized for biomass fast pyrolysis, plays the lead role even in the lignin processing, because of its attractive features. Some fluidized bed reactors had to be operated in batch mode in order to avoid blockage of the feeding system. Although, some laboratories succeed in feeding lignin into the reactor, all of them observed that char formation inside the fluidized bed reactor caused bed agglomeration, preventing continuous char recovery. Besides, the agglomeration limited the amount of lignin they have been able to process because of bed solidification. Appendix A reports the study of Kraft lignin pyrolysis in a bubbling fluidized bed reactor performed in our laboratory, co-authored by this author. Similarly to the literature findings, in our study agglomeration was found to be a major limitation, which was finally overcome by installing a mechanical mixer positioned at the bottom of the reactor.
Table 1.1 Summary of lignin pyrolysis studies

<table>
<thead>
<tr>
<th>Reference</th>
<th>Lignin</th>
<th>Feedrate</th>
<th>Technology</th>
<th>T (°C)</th>
<th>Oil Yield (%)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nowakowski et al., 2010</td>
<td>ETEK (hydrolysis lignin)</td>
<td></td>
<td>Fluidized bed</td>
<td>500</td>
<td>57.7</td>
<td>Agglomeration, but not as extensive as that with ALM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fluidized bed</td>
<td>450-510</td>
<td>72</td>
<td>Lignin dried and ground</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fluidized bed</td>
<td>484-519</td>
<td>40.1 (79.6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 g/h (3h)</td>
<td>Fluidized bed</td>
<td>500</td>
<td>47</td>
<td></td>
<td>No operational problems, but lignin fed at slow feed rate and high sand to feed ratio.</td>
</tr>
<tr>
<td></td>
<td>40 g/h</td>
<td>Entrained flow</td>
<td>700</td>
<td>11.7</td>
<td></td>
<td>Fluidized bed: blockage of the screw feeder or loss of fluidization. Entrained flow reactor: worked with a slow feeding rate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fluidized bed</td>
<td>480</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100g (batch of 3g/2 min)</td>
<td>Fluidized bed</td>
<td>530</td>
<td>31.3</td>
<td></td>
<td>Agglomeration. Pretreatment of lignin to get bigger particles, otherwise they are elutriated and found in the ESP.</td>
</tr>
<tr>
<td></td>
<td>50g (semi-continuous 10g/1-2min)</td>
<td>Fluidized bed</td>
<td>410-560</td>
<td>31</td>
<td></td>
<td>Lignin melted in the auger feeder.</td>
</tr>
<tr>
<td></td>
<td>No result</td>
<td>No result</td>
<td>No result</td>
<td>No result</td>
<td></td>
<td>Pelletizing lignin provided little improvement as the pellets broke down to a similar powder in the feeder and melted in the auger</td>
</tr>
<tr>
<td></td>
<td>100g (240g/h)</td>
<td>Fluidized bed</td>
<td>475-525</td>
<td>49.7</td>
<td></td>
<td>Lignin pelletized and crushed to particle size 1-2mm. Agglomeration not mentioned.</td>
</tr>
<tr>
<td></td>
<td>500g/h (2h)</td>
<td>No result</td>
<td>No result</td>
<td>No result</td>
<td></td>
<td>Unsuccessful: large clumps of lignin and sand, blockage in the feed entrance. Batch: lumps of lignin.</td>
</tr>
<tr>
<td></td>
<td>40g/h</td>
<td>Entrained flow</td>
<td>700</td>
<td>36.6</td>
<td></td>
<td>Fluidized bed: blockage of the screw feeder or loss of fluidization. Entrained flow reactor: slow feeding rate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fluidized bed</td>
<td>480</td>
<td>22</td>
<td></td>
<td>A portion of the feed melted in the injector.</td>
</tr>
<tr>
<td>Reference</td>
<td>Lignin</td>
<td>Feedrate</td>
<td>Technology</td>
<td>T (°C)</td>
<td>Oil Yield (%)</td>
<td>Notes</td>
</tr>
<tr>
<td>--------------------------</td>
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<td>------------------------</td>
<td>--------</td>
<td>---------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Sedat et al., 2010</td>
<td>Indulin AT (kraft)</td>
<td>100g at 0.4 g/min</td>
<td>Fluidized bed</td>
<td>550</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lignoboost (kraft)</td>
<td>100g at 0.4 g/min</td>
<td>Fluidized bed</td>
<td>550</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetocell (Alcell)</td>
<td>100g at 0.4 g/min</td>
<td>Fluidized bed</td>
<td>550</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alcell</td>
<td>batch 40g (rate of 500g/h)</td>
<td>bubbling fluidized bed</td>
<td></td>
<td>38.9</td>
<td></td>
</tr>
<tr>
<td>De Wild et al., 2012</td>
<td>Granit</td>
<td>batch 40g, rate of 500g/h</td>
<td>bubbling fluidized bed</td>
<td>500</td>
<td>47.6</td>
<td>pre-shaped pellets, difficult/impossible to process. Lignin cannot be effectively fast pyrolyzed in reactor systems designed for whole biomass materials</td>
</tr>
<tr>
<td></td>
<td>A (Alcell)</td>
<td>batch 40g (rate of 500g/h)</td>
<td>bubbling fluidized bed</td>
<td>500</td>
<td>54.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B (Alcell)</td>
<td>batch 40g (rate of 500g/h)</td>
<td>bubbling fluidized bed</td>
<td>500</td>
<td>51.9</td>
<td></td>
</tr>
<tr>
<td>Trinh et al., 2013</td>
<td>Lignin from ethanol plant</td>
<td>204-481 g/run (4.1-10.4 g/min)</td>
<td>Pyrolysis centrifuge reactor</td>
<td>550</td>
<td>31</td>
<td>Successful feeding and pyrolysis. Plugging of the nozzles connecting the cyclone and the condenser after 60-70 min of operation</td>
</tr>
</tbody>
</table>


Several studies focused on lignin pyrolysis, but they were carried out in Pyroprobes or micro-pyrolyzers, where only a few milligrams of lignin could be processed, with the objective of investigating kinetics and product composition (Obst, 1983; Evans et al, 1986; Faix et al., 1987; Gaojin et al., 2010; Huang et al., 2012; Lou and Wu, 2011). Therefore, the problem of char agglomeration was not addressed in these studies. Also pyrolysis of lignin model compounds has been extensively studied. Amen-Chen et al. (2001) reviewed the production of monomeric phenols by thermochemical conversion of biomass discussing most of the relevant studies about lignin model compound pyrolysis.

Literature reports lignin to react slower than cellulose and hemicellulose (Brebu and Vasile, 2010). Therefore further cracking may speed up pyrolysis reactions avoiding the cohesivity of the bed material given by softened lignin. Additionally, in order to commercialize fast pyrolysis technology, the products quality has to be improved. Thus, the bio-oil quality might be more important than its quantity (Rover, 2013). For instance, phenolics are very valuable products that are mainly derived from the lignin fraction of biomass (Qu et al., 2011).

Lately, many studies have focused on catalytic pyrolysis of lignin (Jeon et al., 2013; Lee et al., 2013; Mullen and Boateng, 2010). This process was shown to increase the production of valuable compounds such as phenolics and aromatics. However, the recovery of the catalyst is problematic both because of its difficult separation from char and its considerable deactivation resulting from coke deposition, which requires regeneration of the catalyst. An alternative is the ex-situ catalytic upgrading of the pyrolysis vapours, which seems to be more viable, since the deactivation process of the catalyst is slower than in catalytic pyrolysis, and both temperature and residence time can be adjusted independently from the pyrolysis process operating conditions. The upgrading can be performed by hydrodeoxygenation (HDO) or by catalytic cracking. A number of studies focused on HDO of biomass pyrolysis vapours and also some work was performed on lignin pyrolysis vapours. Olcese et al. (2013) investigated HDO of lignin pyrolysis vapours with an iron-silica and iron-activated carbon. They report these catalysts having a good selectivity towards aromatics and phenolics. The disadvantage of HDO is that it is performed with high pressure H₂ (Huber et al., 2006), whereas catalytic cracking needs moderate operating conditions and no additional hydrogen. However, cracking catalysts are deactivated by
coke deposition faster than HDO catalysts (Mortensen, 2011) and, consequently, lower yields are typically observed (Srinivas et al., 2000). A comprehensive review of catalytic cracking is reported in Appendix B. This process still needs to be optimized, more research about the regeneration of catalysts and their performance after a number of regeneration cycles needs to be further investigated, poisoning and effect of carbon deposits needs to be further assessed and the literature most of the time does not include the actual yields of products on bio-oil or biomass basis. For now its economic feasibility seems unlikely, since yields of specific compounds are not reported to be very high and catalysts are expensive. Therefore, an alternative would be to find less expensive catalysts or materials that can be produced within the pyrolysis or upgrading process. An example is activated carbons, which are known to be catalytically active during pyrolysis (Russell et al., 2012). They could be produced starting from the char product, making the process more efficient. Different size and ash content of the activated carbons could affect the lignin behaviour and the liquid product in different ways. Other moderately expensive materials, not produced within the process, are the clays. Literature reports Vermiculite being used to adsorb organics (Gilberto and Jorge, 2003; Socías-Viciana et al., 1998) from water. The literature shows that vermiculite, given its hydrophilic property, cannot adsorb organic compounds from water without a surface treatment to transform it into hydrophobic. Clays have not been extensively studied in pyrolysis of biomass. Wilberink et al. (2011) patented a process for pyrolysis of lignin, where, upon intimately mixing lignin and a phyllosilicate clay, the mixture is fed into the reactor. It is mentioned that the clay improves lignin feeding and pyrolysis behavior without clogging the apparatus because the clay may have a catalytic effect during pyrolysis. Vermiculite, being a phyllosilicate clay, could have adsorption or catalytic properties during pyrolysis reaction that lead to decreasing the formation of a sticky phase. To the best of the author’s knowledge, the literature does not report the effect of absorbent materials on lignin pyrolysis. Molten lignin might be partially and temporarily absorbed by an absorbent material while avoiding the abrupt increase of bed stickiness.

Another option to modify lignin characteristics is to mix it with other non-problematic feedstocks, such as wood. Lappas (2013) investigated pretreatment methods for lignin/biomass mixtures and a method for mixing the two components, involving the impregnation of wood particles with lignin, was developed. Lappas reported successful feeding of the mixture in a continuous pilot scale circulating fluidized bed for the catalytic pyrolysis of biomass.
Lignin is greatly altered in the Kraft process, where the reactive groups are blocked, which results in a structure not representative of native lignin in wood (Evans et al., 1986) and more difficult to depolymerize (Azadi et al., 2013). Lignin separated from cellulose and hemicellulose during bioethanol production, is reported to be more similar to native lignin (Dorrestijn et al., 2000). Therefore it might not be as problematic as Kraft lignin. Although some laboratories (Nowakowski et al., 2010) report agglomeration occurring also with ETEK lignin (residue from bioethanol production), Trinh et al. (2013) successfully pyrolyzed lignin from an ethanol plant. Lignins from different bioethanol processes and from different origins may have different behaviours. In section 1.1.1 lignin from bioethanol production was mentioned to contain quite a high amount of cellulose and hemicellulose residue, which would change the distribution of chemical compounds in bio-oil if compared to Kraft lignin. Specifically, phenolic compounds, derived mostly from the lignin fraction, are expected to exist in lower proportion in the final liquid product.

1.1.4 Bio-oil

The liquid product, bio-oil, is obtained by cooling and condensation of the vapors produced during pyrolysis. It is a multi-component dark brown liquid containing up to 20-25 wt% water (Bridgwater et al., 1999b). The liquid yield from lignocellulosic pyrolysis can reach up to 75 wt% (Azadi et al., 2013). Its high oxygen content, 35-40%, lowers its energy density and makes it immiscible with fossil fuels. Additionally, its high acidity makes it corrosive and unstable (Zhang et al., 2007).

Many factors influence the composition of bio-oil (Diebold, 1999):

- Feedstock composition, particle size and distribution, and moisture content
- Heat transfer rate
- Vapours dilution in the reactor
- Residence time of vapours at high temperature (in the reactor and heated lines connecting the reactor to the quenching zone)
- Presence of a hot-filtration system
- Efficiency of separation of char from pyrolysis vapours
- Efficiency of condensation train
- Water content of bio-oil
- Exposure to contaminants and air during storage, storage time and temperature

Bio-oil is a complex mixture of water, acids, alcohols, aldehydes, esters, ketones, phenols, guaiacols, syringols, sugars, furans, alkenes, aromatics, nitrogen compounds and different oxygenates (Milne et al. 1997, Mohan et al. 2006). The proportion of these compounds depends on the original biomass composition. Phenolic compounds are derived mostly from the lignin component and are high-value products, being important in the production of phenol resins, pharmaceuticals and food additives (Jeon et al., 2013).

Bio-oil from isolated lignins is formed of a large number of aromatic and non-aromatic compounds, ranging from light hydrocarbons to high-molecular weight oligomers (Azadi et al., 2013). Evans et al. (1986) observed a relationship between the lignin isolation process and the composition of the volatile components of the bio-oil. Native or milled-wood lignins were found to lead mostly to monolignols, whereas lignin isolated with more severe processes, such as Kraft and organosolv, was found to lead to guaiacol, syringol and other lighter phenols. Also lignins from different origins produce bio-oils with widely variable chemical compositions; for example, De Wild et al. (2012) reports a higher phenolic yield with wheat straw-derived organosolv lignin (48-55 wt. %) than with Alcell organosolv lignin from hardwood (39 wt. %).

1.1.5 Mechanically Fluidized Reactor

The Mechanically Fluidized Reactor (MFR) is a novel technology developed to perform fast pyrolysis of biomass without fluidizing gas and with a more reasonable particle size in the range 4 to 8 mm. The MFR has been developed in our laboratories at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) at Western University with the objective of making it possible to process cohesive and thermally sensitive biomass materials. Because this technology does not require any fluidization gas, the residence time of the vapors is solely controlled by their production rate, thus the MFR needs to achieve high heat transfer rates to the biomass particles by vigorous mixing and, consequently, rapidly pyrolyze the organic material.
In the past, agitation has been used to improve the fluidization of different materials which are difficult to fluidize. Many studies have been focused on the fluidization of fine powders, since channeling and agglomeration often occur with this kind of material.

Kim and Han (2006) found out that channeling and agglomeration of a fine powder in a fluidized bed are reduced when mechanical agitation is provided. A slow speed stirrer was used to fluidize powders that could not otherwise have been fluidized and they concluded that the mechanical agitation is necessary only to start fluidization, which could then be maintained solely with the fluidization gas. Furthermore, they observed a decrease in the minimum fluidization velocity as the agitation speed was increased and a decrease in the pressure drop due to reduction of cohesive forces between particles. Park et al. (1999) observed that particles classified in the Geldart C group could be fluidized only with mechanical agitation and that the pressure drop in the bed decreased as the agitator speed increased. However, a different behavior was observed at higher agitation speeds, supposedly because of centrifugal forces. Reed and Fenske (1955) used agitation in order to enhance heat transfer between the bed and immersed heat exchange surfaces. They noticed that the agitation increased the pressure drop, mostly at low gas flowrates.

Bait et al. (2011) showed that, when mixing fine powders, a ribbon-type agitator leads to a better mixing than pitch-blade and straight-blade agitator. Reina et al. (2001) studied waste-wood fluidization. They state that fine softwood particles with Geldart group C characteristics are not fluidizable in absence of agitation. The power consumed by the driver is relatively low and is constant after reaching fluidization. Additionally, they found out that the minimum fluidization velocity decreased as the agitator speed increased.

Some other laboratories tried to improve the fluidization of Geldart group D powders. Puspasari et al. (2013) used agitation in order to fluidize crushed oil palm fronds. They found out that mechanical agitation avoids the entanglement between the elongated fibres, so that they can be fluidized. Reyes and Vidal (2000) studied a mechanically mixed spouted bed dryer. The stirrer reduced the airflow required to reach a pseudo-fluidized regime. Han et al. (2012) focused on the observation of polypropylene particles. They claimed that, for constant gas velocity, the pressure drop was independent of the agitator speed, but the fluidization improved with increasing stirrer speed, as bubble size decreased. In a subsequent study, Wang et al. (2013) found that the
pressure drop and the minimum fluidization velocity changed with the agitation speed when using an axial flow impeller, but remained constant with a radial-type impeller. In conventional fluidized beds, the torque required to mix the bed decreases as the superficial velocity of its fluidization gas increases, becoming constant above a critical superficial velocity depending on the stirrer characteristics (Makishima and Shirai, 1968; Makishima and Shirai, 1969).

Few studies focused on Geldart group B powders. Leva (1960) proved that when the bed is aerated, mechanical agitation becomes feasible. Additionally, at minimum fluidization condition, the particles are barely moving in conventional fluidization, while, with a mechanical stirrer, they are mixed at much faster rate. With some mixer geometries, the pressure drop across the bed is lower when stirred and the pressure drop then decreases with increasing agitation speed. The pressure drop curves do not show any discontinuity at minimum fluidization conditions. Unexpectedly, alumina particles characterized by a higher density and a smaller particle size, resulting in much larger surface area, require much less power than sand. However, the alumina particles have a more regular shape and flow more smoothly than sand. Leva concluded that the surface characteristics of the bed material are very important characteristics influencing the power requirements.

1.2 Project Aims & Objectives

The main aim of this research project is the development and optimization of a technology to process successfully Kraft lignin and, by analogy, any other material with difficult handling characteristics due to stickiness and agglomeration tendency upon heating.

In order to address the above aim, the thesis objectives are to:

1. Development of a technique to characterize the performance of the selected technology (Chapter 3)
2. Optimization of the mixing (Chapter 3) and its modelling (Chapter 8)
3. Investigation of the suitability of the Mechanically Fluidized Reactor (MFR) for Kraft lignin pyrolysis (Chapter 4)
4. Investigation of the effect of different bed materials on the reaction process (Chapter 5)
5 Investigation of the influence of different proportions of lignin on the process parameters and on the chemical composition of the liquid product derived from the processing of such materials (Chapter 6 and 7)

In addition, in order to compare with conventional technologies, this research study includes tests carried out in a fluidized bed reactor (Appendix A), and discusses challenges and opportunities associated with catalytic cracking of pyrolysis oil (Appendix B) as an alternative to maximize the production of phenolic and aromatic compounds.

Each of these objectives was the focus of one or more experimental studies, as it is mentioned in the introduction of each chapter.

1.3 Thesis Organization

The thesis is organized into three main sections: methodology, experimental studies and conclusions.

Methodology:

Chapter 2: Experimental & Modelling methodologies

This chapter describes the apparatus, the experimental procedure and the analytical methodology used to analyze the bio-oil. It also provides some background on the modeling tools used in Chapter 8.

Experimental studies:

Chapter 3: Mixing and Operability Characteristics of Mechanically Fluidized Reactors for the Pyrolysis of Biomass

This chapter investigates the validity of a novel technique to evaluate the performance of the Mechanically Fluidized Reactor (MFR). This technique was used to optimize the mixing that this technology provides by comparing three different shaped stirrers.

Chapter 4: Use of the Mechanically Fluidized Reactor (MFR) to investigate the impact of bed hydrodynamics on the pyrolysis of biomass
This chapter investigates the impact of bed hydrodynamics on the liquid product for three different feedstocks: wood pellets, switch grass pellets and Kraft lignin granules.

**Chapter 5: Effect of bed material on pyrolysis of lignin**

This chapter investigates the effect of different bed materials on the cohesivity of Kraft lignin and on the liquid product.

**Chapter 6: Production of pyrolytic bio-oil with high phenolic content**

This chapter investigates how the proportion of Kraft lignin in the starting feedstock affects the cohesivity of the bed during pyrolysis and its effect on the phenolic content of the bio-oil.

**Chapter 7: Pyrolysis of hydrolysis lignin and its impact on the phenolic content of the liquid product**

This chapter investigates the application of the correlations found in Chapter 6 on other types of lignin other than Kraft. The phenolic concentration of the bio-oil is also discussed.

**Chapter 8: Modelling the mixing of a Mechanically Fluidized Reactor**

This chapter describes the mixing provided by the vertical blades stirrer in the MFR by modelling it with Discrete Element Method (DEM) simulation.

**Conclusions:**

**Chapter 9: Conclusions and recommendations**
Chapter 2

2. Methodology

2.1 Introduction

This chapter describes the methodology used to undertake the experimental work reported in chapters 3, 4, 5, 6, 7 and 8. Section 2.2 describes the feedstocks investigated and section 2.3 their characterization. Section 2.4 lists the bed materials tested. Section 2.5 describes the experimental set-up used for the characterization and comparison of different stirrers and the processing of the biomass. This section includes a description of how the preliminary heat transfer, the aeration with inert gases and the pyrolysis studies were carried out. Section 2.6 illustrates the methodology behind the characterization of the bio-oils. Section 2.7 describes the principles behind the Discrete Element Method and how the parameters required by this method were experimentally determined.

2.2 Feedstocks investigated

The biomass feedstocks used in this work are:

- cylindrical pellets of a wood blend consisting of approximately 75% softwood (spruce-pine-fir) and 25% hardwood (oak and maple) with a diameter of about 5 mm and length of 3 mm (Chapter 3 and 4),
- cylindrical switch grass pellets without binder, with a diameter of about 5 mm and length of 1 mm (Chapter 4),
- 2-6 mm Kraft lignin granules containing a small amount of organic binder (Chapter 4, 5, 6),
- 2-6 mm birch wood-Kraft lignin granules containing a small amount of organic binder (Chapter 6),
- 2-6 mm hydrolysis lignin granules from ground aspen wood from eastern Canada (Chapter 7),
- 2-6 mm hydrolysis lignin granules from sugarcane bagasse containing a small amount of organic binder (Chapter 7),
2.2.1 Production of granules

The granules were produced in a granulator specifically modified to handle this type of feedstocks. Granules were produced by using an organic binder and by following a procedure developed in this laboratory.

2.3 Feedstocks characterization

2.3.1 Ultimate analysis and moisture content

Ultimate analysis allows quantifying the major components of the feedstock (C, H, N, O and S) in wt% on dry basis. This analysis was carried out in a Thermo Fisher Scientific Flash EA 1112 series analyzer. The moisture content was analyzed with a Mettler Toledo HB43-S Halogen Moisture Analyzer. Both measurements were conducted in triplicates and the average values are reported herein.

2.3.2 Lignin content

The lignin content was quantified by using a two-step acid hydrolysis according to standard NREL protocol (Sluiter et al., 2008a; Sluiter et al., 2008b). Samples were placed in a 72% sulfuric acid solution in a water bath at 30 °C for 1 hour. The acid concentration was then diluted to 4% and the samples were incubated in an autoclave for 1 hour at 121°C to precipitate lignin. The sample was filtered leaving a solid residue, which was dried and weighted. The dried solid residue was ashed to constant weight and the acid insoluble lignin was quantified. The hydrolysis liquor was analyzed by UV spectroscopy to quantify the acid soluble lignin. The total lignin was quantified as the sum of these two fractions.
2.3.3. Ash content

The ash content was determined by following the procedure described in the standard NREL protocol (Sluiter et al., 2008a; Sluiter et al., 2008c). Samples were weighted and ashed in a muffle furnace at 575 °C to constant weight. The weight was recorded.

2.4 Bed materials investigated

Foamed glass beads with a Sauter mean diameter of 375 μm and an apparent particle density of 560 kg/m$^3$ were used for all the experiments illustrated in chapter 3, 4, 5, 6 and 7. This material was used as a base case for comparison with other bed materials studied in chapter 5:

- granular activated carbon made from bituminous coal with mesh size -12+40, surface area 900 m$^2$/g, bulk density 470-530 kg/m$^3$ and 12% ash content;
- granular activated carbon made from bituminous coal with mesh size -20+50, surface area 950 m$^2$/g, bulk density 430-480 kg/m$^3$ and 12% ash content;
- granular activated carbon made from coconut shell with mesh size -12+40, surface area 1100 m$^2$/g, bulk density 460-530 kg/m$^3$ and 4% ash content;
- acid-washed granular activated carbon made from coconut shell with mesh size -12+40, surface area 1100 m$^2$/g, bulk density 480-530 kg/m$^3$ and 1.5% ash content;
- vermiculite, a mineral clay with lamellar nanostructure which expands on heating;
- sodium potassium aluminum silicate absorbent material typically used to absorb animal, vegetable, mineral, petroleum, and chemical liquids.

2.5 Set-up

The experimental apparatus is shown in Figures 2.1 and 2.2. The reactor is a 0.15 m diameter vessel, 0.25 m tall made of stainless steel grade 316. The reactor is equipped with a hot filter for gases and vapors, consisting of a chamber located above the bed of solids with five holes, 0.032 m in diameter, where 10 μm and 26 μm wire meshes are placed in series. In the experiments discussed in Chapter 3 the pyrolytic vapors exiting the filter are collected using a condensation train, made up of three condensers in series, 0.057 m in diameter and 0.622 m tall, and a cotton filter, 0.089 m in diameter and 0.445 m tall (Figure 2.1). Figure 2.2 shows that experiments discussed in chapter 4, 5, 6 and 7 were performed in the same apparatus except for the
condensation train, which was composed of a condenser, 0.057 m in diameter and 0.622 m tall, an electrostatic precipitator with a cylindrical collector vessel, 0.07 m in diameter and 0.406 m tall, and a cotton filter, 0.089 m in diameter and 0.445 m tall.

Figure 2.1 Schematic of the apparatus 1 (Chapter 3)
The heat is supplied to the reactor with two band heaters (1.8 kW each), controlled by an On-Off controller. The controller regulates the bed temperature, which is measured by a K type thermocouple penetrating 5 mm into the bed, 0.065 m from the bottom. For safety, the maximum temperature limit of the controller uses the external wall temperature, which is measured with a K type thermocouple placed between the bottom band heater and the reactor wall, 0.051 m far from the bottom.

The MFR can be optionally aerated by feeding gas through the bottom, whose flowrate is adjusted with a pressure regulator and a bank of pre-calibrated sonic nozzles. When gas is used, it is introduced through four snubbers placed on the bottom of the reactor, thus preventing the bed material from plugging the sonic nozzles located upstream (Figure 2.1). In the study discussed in chapter 3, nitrogen, argon or helium were injected in the reactor at 550°C to
simulate the range of properties expected for pyrolysis gases and vapors. In chapter 4, 5, 6 and 7, only nitrogen gas was used.

The characterization of each stirrer and all the pyrolysis runs were performed using a ¾ hp air motor, whose torque can be determined from the air pressure supplied to the motor and the rotation speed of the motor shaft (Gast Manufacturing, 2014). Preliminary experiments showed that this motor is much more sensitive to the bed aeration than a standard electric motor. In addition, it is much lighter and compact than DC electric motors, which made it easier to mount and reduced mechanical stress on the shaft seals. The stirrer speed was monitored with a laser, whose beam interruption by a metal clamp placed on the stirrer was monitored with a photodiode connected to a data acquisition system.

Three different stirrer designs, shown in Figure 2.3, have been used and compared in the study presented in chapter 3. The vertical blades stirrer (Figure 2.3a) was designed to provide agitation near the reactor wall and thus promote wall to bed heat transfer; it also promoted the formation of avalanches that folded over the bed surface, covering with hot bed solids the fresh biomass pellets that were dropped on the bed surface. The spiral stirrer (Figure 2.3b) provided agitation near the wall as well as pushing the solids down along the wall. The paddles stirrer (Figure 2.3c) was designed to provide turbulence throughout the bed volume. The vertical blades stirrer was used in the rest of the thesis (Chapters 4, 5, 6 and 7). Its dimensions are reported in figure 8.1. The spiral stirrer is 0.22 m tall, with an external diameter of 0.13 m, an internal diameter of 0.09 m and 0.055 m pitch. 10 tabs, 0.019 m large and 0.0158 m tall, are welded onto the spiral flight. The paddles stirrer is equipped with 6 paddles with external radius of 0.065 m, internal radius of 0.053 m and 0.05 m long, which are supported by 6 arms vertically spaced 0.076 m apart.
The feeder consisted of a simple pipe, 0.025 m in diameter, with two ball valves to provide an airlock. The wood pellets could be fed easily without excessive oxygen contamination. The pyrolysis tests were performed with sequential feeding of 10 pulses of biomass over 30-50 seconds, for a total of 80 g, in order to simulate continuous feeding.

2.5.1 Heat transfer study

The preliminary comparison of the wall-to-bed heat transfer with the three stirrers was performed by heating the reactor up to 400°C while mixing with the three stirrers at 140 and 200 rpm to evaluate whether the heat transfer from wall to bed could limit the pyrolysis reactions. The controller was set to provide full heating power until the bed temperature reached 400°C.

The following equation was used to evaluate the impact of mixing on wall to bed heat transfer:

\[ U A (T_w - T_b) = m_s c_p \frac{dT_b}{dt} \]  \hspace{1cm} (2.1)

where \( U \) is the overall heat transfer coefficient from external wall to bed, \( A \) the contact area (internal wall area), \( T_w \) the external wall temperature, \( T_b \) the bed temperature, \( m_s \) the mass of solids (bed) and reactor wall, \( c_p \) the specific heat capacity, and \( t \) the time (\( c_p \) is a weighted average of the heat capacities of wall and bed materials, averaged over the considered temperature range). This equation was used to calculate the parameter:
\[
\frac{(U A)}{(m_s c_p)} = \frac{1}{(T_w - T_b)} \frac{dT_b}{dt}
\]  

(2.2)

where \( A, m_s, c_p \) are constant in all experiments. Any change in the value of the right-hand side of the above equation is therefore due to a change in the overall heat transfer coefficient \( U \).

### 2.5.2 Aeration with inert gases study

The air motor was set at four different values of air supply pressure: 179, 207, 234 and 262 kPa. Upon setting the air pressure to the motor, nitrogen was fed through the system, as described in section 2.5, and its flowrate was progressively increased, while recording the rotation speed of the stirrer.

The experimental results of the aeration with nitrogen in terms of the rotation speed were converted to power and torque by using data supplied by the air motor supplier (Gast Manufacturing, 2014). The resulting power and torque values were interpolated with TableCurve 2D for each superficial velocity of nitrogen through the bed and the type of equation common to all the data sets with the highest rank was selected. This equation, with different parameters for each superficial velocity, was used to calculate the power and the torque as function of the superficial velocity for constant rpm. An example of this procedure is provided in appendix C. The power and torque results were normalized with respect to their maximum and minimum values because the stirrer rotation speed was affected by the friction in the drive shaft bearings and sealing, which varied between experiments, to give the normalized power:

\[
(Power – Min power) / (Max power – Min power)
\]

(2.3)

These values were further interpolated with TableCurve 2D, in order to obtain the equations to calculate the superficial velocity necessary to reach 98% of power and torque reduction, named in this study as critical aeration (\( A_c \)).

### 2.5.3 Pyrolysis studies

Each pyrolysis experiment proceeded through three stages, while the stirrer rotation speed was recorded:
1) In the first 30 seconds of the experiment, the bed was aerated with nitrogen above the critical aeration rate \((A_c)\), so that the stirrer could reach its maximum rotation speed.

2) Biomass pellets were then fed to the reactor. The time at which feeding ended was recorded.

3) The stirrer kept operating in the absence of either nitrogen aeration or biomass feeding until its rotation speed stabilized.

The time for complete pyrolysis, evaluated in chapter 3, was estimated to be the time between the end of the feeding and the moment when the rotation speed stabilizes to its value in the absence of aeration.

As an example, Figure 2.4 shows pyrolysis of wood pellets performed with the vertical blades stirrer operated with a motive air pressure of 179 kPa. The raw data (Figure 2.5), which were contaminated with some noise, were smoothed with TableCurve 2D.

![Figure 2.4 Example of the rotation speed trend during a pyrolysis experiment with the vertical blades stirrer](image-url)
2.5.4 Data analysis with two linear regressions

Studies presented in chapter 6 and 7 show the impact of Kraft lignin content and lignin content respectively on various parameters. Some of them did not have linear dependence. Therefore they were fitted by two straight lines in order to find the “critical” Kraft and total lignin content.

Given n data points, two models were calculated:

- Full model (F), two linear regressions with $p_F$ parameters;
- Reduced model (R), one linear regression with $p_R$ parameters

with $p_F > p_R$.

The degrees of freedom of both models were calculated as:

\[ df_R = n - p_R \]  \hspace{1cm} (2.4)

\[ df_F = n - p_F \]  \hspace{1cm} (2.5)

where n is the total number of observations.

Figure 2.5 Raw data of the rotation speed during a pyrolysis experiment with the vertical blades stirrer
The two linear regressions of the full model were calculated as:

\[ y_i = m \cdot x_i + q \]  \hspace{1cm} (2.6)  
\[ y_j = p \cdot x_j + r \]  \hspace{1cm} (2.7)

with \( i = 0, \ldots, k \) and \( j = k+1, \ldots, z \), for \( 2 \leq k \leq z-2 \) and \( z \) being the total number of Kraft and total lignin content values. In chapter 6 \( i \) and \( j \) are Kraft lignin content values, whereas they represent the total lignin content in chapter 7.

The sum of squared errors was calculated for the reduced model (SSE\(_R\)) and for each full model (SSE\(_F\)). The F statistic of the two models was determined for each pair of models with the equation:

\[ F^* = \frac{SSE_R - SSE_F}{SSE_F} \cdot \frac{df_F}{df_R - df_F} \]  \hspace{1cm} (2.8)

The probability \( p \) that the full model better fits the experimental data than the reduced model was calculated such that:

\[ F(p, df_R - df_F, df_F) = F^* \]  \hspace{1cm} (2.9)

The full model with the highest probability was chosen.

### 2.6 Bio-oils characterization

#### 2.6.1 Ultimate analysis

The ultimate analysis was conducted as described in section 2.3.1.

#### 2.6.2 Water content analysis

The water content was determined with a METTLER TOLEDO V20 compact volumetric Karl Fischer titrator. The samples were analyzed in triplicates and average values are reported.

#### 2.6.3 GC/MS

This technique was used for a rapid screening of the chemical composition of bio-oils to investigate the need of more accurate analyses.
Instrument and principles

The GC/MS combines two techniques: Gas Chromatography and Mass Spectroscopy. The first technique chromatographically separates compounds present in the sample. As the compounds exit the chromatographic column, they are ionized and the fragments are sorted and fed into a mass analyzer. The fragmentation pattern, spectrum, is characteristic of each molecule and allows the identification of the compounds in the sample.

Sample preparation

Samples were prepared by adding 50 μg of bio-oil to a vial and diluting this amount with 1 mL of GC grade dichloromethane. The vial was vortexed for 1 minute. The sample was filtered through a 0.22 μm filter into a GC vial.

GC/MS analysis

The analyses were performed using a QP2010 GC/MS Shimadzu with an Agilent J&W RTX-1701 capillary column (30 meters x 0.25 mm ID x 0.25 μm film thickness). The carrier gas was Helium at 1.78 ml/min. The oven temperature program was 5 min at 40 °C, then 5 °C/min to 280 °C, the runtime was 63 min, the injector temperature was 250 °C, and the injected volume was 1 μl. The MS was operated in split mode (25:1).

2.6.4 Folin-Ciocalteu colorimetry method

Total Phenolics content was determined in terms of Gallic Acid Equivalents following the Folin-Ciocalteu colorimetry method described by Rover (2013). This method was originally used to analyze total phenolics in wine; Rover (2013) applied it to the quantification of total phenolics in terms of Gallic Acid Equivalents present in bio-oil. The Folin-Ciocalteu method is based on chemical reduction of the reagent, which is a mixture of tungsten and molybdenum oxides, whose products have blue colour. The phenolic concentration is proportional to the intensity of the color. A disadvantage of this method is that it is based on the oxidation of phenolics, but also the other similar oxidized substances would be included in the apparent total phenolic content. Examples of other compounds affecting the result are aromatic amines, sulphur dioxide, ascorbic acid and endiols. Also sugars can interfere with this reaction.
Total phenolic content analysis

Bio-oil was dissolved in ethanol. The gallic acid calibration standards were prepared by dissolving 0.5 g gallic acid in 10 ml ethanol and then diluted to 100 ml with deionized water obtaining a concentration of 5 g/l. This stock solution was used to prepare the standards 50, 100, 250, 500 mg/l by diluting 1, 2, 5 and 10 ml to 100 ml with deionized water.

The sodium carbonate solution was obtained by dissolving 200 g anhydrous sodium carbonate in 800 ml water, which was brought to boil. The solution was stored at room temperature for 24 h and filtered with Whatman #42 filter paper. Water was added to the solution to 1 l.

20 μl of bio-oil sample, deionized water and four standards were placed in different 2 ml polystyrene cuvettes. 1.58 ml of deionized water and 100 μl of FC reagent were added to each cuvette, mixed and held for a few minutes. 300 μl of sodium carbonate solution was, then, added to each cuvette. After 2 h, the samples absorbance was analyzed with a Thermo Scientific Evolution 220 UV-visible Spectrophotometer at 765 nm with 1 cm cells and a 1 nm bandwidth. Each bio-oil was analyzed in triplicates.

2.6.5 GCxGC-TOFMS

Instrument and principles

Complex samples, when analyzed with monodimensional techniques, can lead to coelutions and not all the peaks are resolved. The comprehensive two-dimensional gas chromatography, when coupled to time of flight mass spectrometry, achieves ultimate chromatographic resolution. This is accomplished by using two columns of different polarity separated by a modulator which “splits” each peak in different peaks ensuring that the effluent from the first column is focused before entering the second one.

Sample preparation

Approximately 20 mg of the oil fraction of the bio-oil were transferred to a 15 mL-centrifuge tube and diluted with 10 mL of pure methanol. The tube was first vortexed for one minute and then placed into an ultrasonic bath for 10 min in order to fully dissolve the bio-oil. Finally, 100 μL of the final extract were transferred into a chromatographic vial for further GC analysis.
GC×GC-TOFMS analysis

The analyses were performed by an external laboratory using a Pegasus 4D (Leco Corp., St. Joseph, MI, USA) consisting of an updated GC×GC Agilent 6890 and a TOF-MS with electron ionization (EI) mode. Samples were injected in the hot splitless mode (1 μL, 250°C) into a highly polar × mid-polar column set (SLB-IL111, 30 m×0.25 mm internal diameter -i.d.- × 0.20 μm film thickness -d.f.- and BPX-50, 1.6 m×0.15 mm i.d.×0.15 μm d.f., respectively). Columns were purchased from Sigma Aldrich (Bellefonte, PA, USA) and SGE (Melbourne, Australia) respectively. The main oven was programmed as follows: from 45 °C (1 min) to 250 °C at 3 °C/min. The secondary oven was kept 15 °C above the program of the main oven. Helium was used as carrier gas (constant flow, 1 mL/min). A nitrogen quad-jet dual-stage modulator was used for sample focusing and re-injection in the secondary column. The temperature of the modulator was set 25 °C above that of the main oven. A modulation period of 4 s with hot pulses of 0.6 s was applied during modulation. The transfer line and ion source temperatures were set at 275 °C and 250 °C respectively. MS detection was performed in full scan range (50-500 m/z); the EI energy was 70 eV, the voltage of the multiplier was 1600 eV and the data acquisition rate was set at 100 Hz.

ChromaToF® software (version 4.50) was used during acquisition and sample processing. Peak detection was set at S/N of 500:1 with a minimum library similarity of 750 /00 (mainlib and replib as mass spectra reference libraries).

2.7 Discrete Element Method

The mechanical behaviour of spheres can be described by Discrete Element Method (DEM).

Fundamental model equations

The motion of each individual particle is calculated using Newton’s second law:

\[
m_i \frac{d\mathbf{v}_i}{dt} = m_i g + \mathbf{F}_{c,i}
\]

(2.10)
where $v_i$ is the velocity, $m_i$ the mass of the particle $i$, $g$ the acceleration of gravity and $F_{c,i}$ the contact forces. Because no gas flow is considered in this simulation, there is no drag force of the gas on the particle. The particle rotation is calculated with Euler’s equation:

$$I_i \frac{d\omega_i}{dt} = T_i$$

(2.11)

where $T_i$ is the torque and $I_i$ is the moment of inertia of particle $i$.

In case of collision between two particles or a particle and the wall, a model to calculate the contact forces is required. The soft sphere approach assumes the particle to undergo deformation during their collision. The contact forces can be calculated with different models. In this study a non-linear spring-dashpot model based on Hertz’s theory (1881) for the normal impact is used. The no-slip approximation of Mindlin’s model (1949) is applied for the calculation of the tangential component of the contact force, as suggested by Tsuji et al. (1992). The forces acting on the particles are decomposed in normal $F_{c,n}$ and tangential $F_{c,t}$ component. In case a particle is in contact with other particles, the resultant of the forces is calculated at each time step.

At the time of the impact between two spherical particles a and b (Figure 2.6), with $r_a$ and $r_b$ being their position vectors and $R_a$ and $R_b$ their radii, the relative velocity at the contact point $v_{ab}$ can be defined as:

$$v_{ab} = (v_a - v_b) - (R_a \omega_a + R_b \omega_b) \times n_{ab}$$

(2.12)

where $n_{ab}$ is the unit vector normal to the contact plane. The normal component of the relative velocity is:

$$v_{ab,n} = (v_{ab} \cdot n_{ab}) n_{ab}$$

(2.13)
The relation between the elastic force and the displacement is described as:

\[
F_{c,n} = -k_n \cdot \delta_n^{3/2} \cdot n_{ab} - \eta_n v_{ab,n} \tag{2.14}
\]

The displacement \(\delta_n\) in the contact is

\[
\delta_n = R_a + R_b - |r_b - r_a| \tag{2.15}
\]

The stiffness of the colliding bodies is:

\[
k_n = \frac{4}{3} E^* \sqrt{R^*} \tag{2.16}
\]

where \(E^*\) is the effective modulus of elasticity

\[
\frac{1}{E^*} = \frac{1-v_a^2}{E_a} + \frac{1-v_b^2}{E_b} \tag{2.17}
\]

where \(v\) is the Poisson ratio and \(R^*\) the median radius:

\[
\frac{1}{R^*} = \frac{1}{R_a} + \frac{1}{R_b} \tag{2.18}
\]
The elastic contribution of the impact energy absorbed during compression is released during restitution. The restitution coefficient, described in section 2.7.1, accounts for the absorption of kinetic energy occurring during the impact.

The damping factor $\eta_n$, included in the DEM model, accounts for the energy dissipation due to visco-elastic properties of the material (Tsuji et al., 1992):

$$
\eta_n = -2a\sqrt{m^* \cdot k_n \cdot \delta_n^{3/4}}
$$

$$
\alpha = \begin{cases} 
\frac{\tan e}{\sqrt{\pi^2 + m^* e}} & 0 < e \leq 1 \\
1 & e = 0 
\end{cases}
$$

(2.19)

where $m^*$ is reduced mass given by:

$$
m^* = \left( \frac{1}{m_a} + \frac{1}{m_b} \right)^{-1}
$$

(2.20)

The tangential component of the contact force is calculated with a Coulomb-type friction law:

$$
F_{c,t} = \begin{cases} 
-k_t \delta_t - \eta_t v_{ab,t} & |F_{c,t}| \leq \mu |F_{c,n}| \\
-\mu |F_{c,n}| t_{ab} & |F_{c,t}| > \mu |F_{c,n}|
\end{cases}
$$

(2.21)

where $k_t$, $\delta_t$, $\eta_t$ and $\mu$ are the tangential spring stiffness, tangential displacement, tangential damping coefficient and friction coefficient. The tangential relative velocity is:

$$
v_{ab,t} = v_{ab} - v_{ab,n}
$$

(2.22)

The tangential stiffness $k_t$ is defined as:

$$
k_t = 8G^* \sqrt{R^* \delta_n}
$$

(2.23)

where $G^*$ is the equivalent shear modulus of the bodies

$$
\frac{1}{G^*} = \frac{2 - \nu_a}{G_a} + \frac{2 - \nu_b}{G_b}
$$

(2.24)

The tangential damping coefficient $\eta_t$ is defined as (Tsuji et al., 1992)

$$
\eta_t = 2a\sqrt{m^* \cdot k_t}
$$

(2.25)
2.7.1 Restitution coefficient

The restitution coefficient allows describe particle collisions by taking into account the energy absorption and damping force in numerical discrete modelling of particles (Antonyuk et al., 2010).

This parameter can be defined as the square root of the ratio of elastic energy \( W_{\text{kin},R} \) released during the restitution to the impact energy, i.e., initial kinetic impact energy \( W_{\text{kin}} \)

\[
e = \sqrt{\frac{W_{\text{kin},R}}{W_{\text{kin}}}} = \sqrt{1 - \frac{W_{\text{abs}}}{W_{\text{kin}}}} = \frac{|v_R|}{v} \quad (2.26)
\]

where \( W_{\text{abs}} \) is the energy absorption during the impact, \( v \) and \( v_R \) are the impact and rebound velocities, respectively. The restitution coefficient value ranges from 0 to 1 in case of an elastic-plastic impact (Müller et al., 2008).

The restitution coefficient of wood pellets and 3 mm glass beads on steel and glass plates was measured with the free-fall test (Figure 2.7).

![Free-fall set-up diagram](image)

**Figure 2.7 Free-fall set-up**

The particle is dropped and its trajectory is recorded by means of two timesynchronized high-speed cameras (Imaging Solutions Y-4 and NX-4) with frame rates from 6000 to 8000 fps. The
two cameras are placed in front of the target to record the movement along the xy direction and above the target to capture the movement in the xz direction. The target (steel/glass plate) is placed on an anti-vibration table and can be adjusted in the exact xy-plane relative to the first camera by a positioning table. The measurement area is illuminated from the front by two LED lamps (1000 lm) and from the back by a third LED lamp (2700 lm) which is positioned behind an opal glass to achieve diffuse lighting.

The particles are held at a predetermined height above the target with vacuum tweezers. Upon positioning the particle, the vacuum of the nozzle is released, the recording devices are started and the particle drops onto the target. After the measurement, the coefficient of restitution is calculated according to equation 2.20 as ratio of the mean rebound velocity after the impact to the average velocity right before the impact. The particle velocities were calculated from image series by a MATLAB script. The test was repeated 50 times for each pair of materials in order to increase the accuracy of the restitution coefficient.

2.7.2 Friction coefficients

The internal friction and the wall friction coefficient of 375 µm foamed glass beads were determined with the Jenike shear tester.

Yield loci measurement

The shear cell is formed by a base fixed to a stationary bearing plate and a shear ring placed on the base, which is covered by a shear lid. The bulk solid sample is poured in the base and in the shear ring. Upon covering base and shear ring with the shear lid, the cell is loaded by a normal force, by means of a weight hanger and weights. A stem presses against a bracket attached to the shear lid, while moving horizontally the shear ring and the shear lid. The stem is driven forward by a motor at steady rate and it is also connected to a force transducer that measures the shear force (Schulze, 2008).

The sample needs to be preconsolidated so that at preshear only a small shear displacement is necessary to achieve steady-state flow. The mould ring, the share ring and the base are placed on the bearing plate. The share ring and the mould ring are pressed against locating screws which allow the share ring to have an offset in the shear direction. Upon filling the cell with the bulk
solid, excess material is removed and the surface is levelled with the rim of the mould ring by mean of a spatula. The lid is placed on the sample and a force is applied to the lid by means of a weight hanger and appropriate weights. The sample is then consolidated by mean of a twisting device which will apply a small shear stress to the sample. Upon consolidation the twisting device, the hanger and the lid are removed.

At this point the second step of consolidation (preshear) can be started. The shear lid is placed on the preconsolidated sample. The distance between the pin and the bracket is adjusted by means of a hand wheel in order for it to be about 0.1-0.2 mm. The hanger with weights is placed on the lid. The motor driving the stem is started and the shear force is recorded. After contact between the stem and the bracket, a steep increase of the shear force can be observed, and then it becomes flatter and finally reaches a constant value (steady-state flow). The stem is driven backwards until the shear force is zero. Before shearing to failure, the normal force is reduced by removing weights in order to find a point of yield locus (incipient flow). The stem is driven forward and the sample is sheared again. In this step plastic deformation and volume expansion occurs. For free flowing bulks, as in the case of the 375 μm foamed glass beads, the shear force reaches again a constant value.

The motor driving the stem is reversed again until the shear stress reaches zero. The shear cell is then weighted in order to calculate the overall bulk density. This procedure was repeated 8 times while keeping the normal stress at preshear constant and reducing every two tests the normal stress in the shear stage so as to obtain four points of the yield locus (each point was tested twice).

**Internal friction coefficient evaluation**

The yield locus is the yield limit of a consolidated bulk solid (Schulze, 2008).

The yield locus should be determined for a constant bulk density, thus only a 2% relative deviation was allowed. The bulk density of each sample is:

$$\rho_b = \frac{m_{cell\ total} - m_{cell\ empty}}{V_{cell}}$$  \hspace{1cm} (2.27)
It is known that the consolidation causes fluctuation of the critical shear force $F_{S,cr}$. Therefore, the arithmetic mean of the critical shear forces was taken as:

$$F_{S,cr} = \frac{1}{8} \sum_{i=1}^{8} (F_{S,cr})_i$$  \hspace{1cm} (2.28)

and the shear forces from determination of the yield locus were corrected for each $i$-th sample:

$$(F_{S,corrected})_i = (F_S)_i \cdot \frac{F_{S,cr}}{(F_{S,cr})_i}$$  \hspace{1cm} (2.29)

The shear stress is:

$$\bar{\tau}_{cr} = \frac{F_{S,cr}}{A_{cell}}$$  \hspace{1cm} (2.30)

$$(\tau_{corrected})_i = \frac{(F_{S,corrected})_i}{A_{cell}}$$  \hspace{1cm} (2.31)

The normal stresses for preshear and incipient flow were calculated with the equation 2.26:

$$\sigma = \frac{F_N}{A_{cell}} = \frac{g(m_w + m_f + m_{ld} + \rho_B l v_{ring})}{A_{cell}}$$  \hspace{1cm} (2.32)

The stresses at preshear ($\tau_{cr}, \sigma_{cr}$) and the points of incipient flows must be graphically represented. For the determination of the yield locus, the points were fitted with the equation:

$$\tau = \sigma \cdot \mu + \tau_c$$  \hspace{1cm} (2.33)

where $\mu$ is the internal friction coefficient and $\tau_c$ is cohesion.

**Wall yield loci measurement**

The wall friction angle $\varphi_w$ can easily be tested with Jenike tester. The apparatus is similar to the one used to evaluate the yield loci, but for the base of the cell which is replaced by a plate of steel, since this is the material the MFR is made of.

The shear cell is prepared similarly to a yield locus test. The consolidation is less important in this test since the dependence of wall friction angle on bulk density can usually be neglected.
After placing the shear lid on the bulk solid sample the load is applied by the hanger. As soon as the applied shear force is constant the weight is reduced while the pin is driven forward by the motor. The normal force is reduced until all weights are removed. After the shear test the weight \( m_{\text{total,w}} \) of the wall sample with shear ring, bulk solid and shear lid and the weight of the wall sample \( m_{\text{wall}} \) itself is measured.

To determine the wall yield locus, the shear force \( F_{\text{S,w}} \) which is to be applied to move the bulk solid sample in shear ring on the wall sample is measured. It depends on the normal force \( F_{\text{N,w}} \). Division of \( F_{\text{S,w}} \) and \( F_{\text{N,w}} \) by the cross sectional area of the shear cell leads to the normal stress \( \sigma_w \) and the shear stress \( \tau_w \). The wall yield locus is a straight line through the origin.

**Wall friction coefficient evaluation**

The normal and the shear stress were calculated with the following equations:

\[
\sigma_w = \frac{F_{\text{N,w}}}{A_{\text{shear cell}}} = \frac{g(m_w + m_f + m_{\text{total,w}} - m_{\text{wall}} - m_{\text{ring}})}{A_{\text{cell}}} \tag{2.34}
\]

\[
\tau_w = \frac{F_{\text{S,w}}}{A_{\text{cell}}} \tag{2.35}
\]

The pair of stresses \((\sigma_w, \tau_w)\) were fitted with the equation:

\[
\tau_w = \sigma_w \cdot \mu_w \tag{2.36}
\]

where \( \mu_w \) is the wall friction coefficient.

**2.7.3 Shear modulus evaluation**

The compression tests of wood pellets and 3 mm glass beads were performed using the TEXTURE ANALYSER (Stable Micro Systems Ltd., UK) shown in figure 2.8.
During a compression test, the punch moves towards the particle placed on the lower fixed plate. After creating the contact, the particle is compressed to a predetermined point (strain). The displacement, force and time are measured. The axial stress is applied at a controlled axial deformation rate. During repeated compression tests, the punch moves downwards to the lower fixed plate and presses the granule up to the defined deformation. Then, the punch moves back, and the particle is unloaded. This process was repeated for 20 particles of each type.

During compression of a sphere with two plates the relationship between elastic contact force and displacement is (Hertz, 1881):

\[ F_c = \frac{1}{3} \frac{E}{(1-\nu^2)} \sqrt{d\delta^3} \]  \hspace{1cm} (2.37)

where \( E \) is the modulus of elasticity, \( \nu \) the Poisson ratio, \( d \) the diameter of the particle and \( \delta \) the displacement. Upon obtaining the curve force vs. displacement with the compression test, \( E \) is calculated by solving for \( E \) equation 2.31.

When a cylinder is compressed the relationship between elastic contact force and displacement is described as:
\[ F_c = \frac{\pi E}{8(1-v^2)} L \delta \]  

where \( L \) is the length of the cylinder. Given the Poisson ratio, the shear modulus can be calculated as:

\[ G = \frac{E}{2(1+v)} \]  

(2.39)

### 2.7.4 Material density measurement

The particle density of wood pellets and 375 µm glass beads was determined by mean of a Helium-Pyknometer “Micromeritics 1305”.
Chapter 3

3. Mixing and Operability Characteristics of Mechanically Fluidized Reactors for the Pyrolysis of Biomass

3.1 Introduction

This chapter investigates a technique to track the evolution of pyrolysis gases and vapors and, thus, to determine the reaction time as a function of stirrer geometry and operating conditions in the MFR.

The following was undertaken:

I. Preliminary heat transfer study;
II. Characterization of three different shaped stirrers with inert gases;
III. Pilot-scale pyrolysis processing of wood pellets with different stirrer configurations varying rotation speed and comparison of aeration and time for complete pyrolysis.

3.2 Materials and Methods

The set-up is described in section 2.5. The preliminary heat transfer study was performed as described in section 2.5.1, the study about the characterization of three different stirrers (Figure 2.3) was carried out as explained in section 2.5.2 and the pyrolysis study followed the procedure reported in section 2.5.3.

Foamed glass beads with a Sauter mean diameter of 375 μm and an apparent particle density of 560 kg/m³ were used as inert bed material for the pyrolysis tests. This material was chosen in order to simulate the size and density of typical char particles. Some experiments were performed using silica sand with a Sauter mean diameter of 185 μm and bulk density around 1660 kg/m³.

All experiments reported in this chapter were conducted at 550 °C.
The feedstock for the pyrolysis experiments were cylindrical pellets of a wood blend consisting of approximately 75% softwood (spruce-pine-fir) and 25% hardwood (oak and maple) with a diameter of about 5 mm and length of 3 mm.

3.3 Results and discussion

3.3.1 Heat transfer results

A preliminary comparison of the wall-to-bed heat transfer with the three stirrers was performed following the procedure explained in section 2.5.1.

Figure 3.1 shows that the overall heat transfer coefficient is not greatly affected by either the stirrer design or its rotation speed. Wall-to-bed heat transfer was more than adequate for the experiments of this study. If better heat transfer to the bed was required, heat transfer from the heater to the wall should be improved since it appears to be the limiting step.

![Figure 3.1 Effect of stirrer configuration and rotation speed on wall-to-bed heat transfer](image)

Figure 3.1 Effect of stirrer configuration and rotation speed on wall-to-bed heat transfer
3.3.2 Aeration with inert gases results

The normalized power and the torque required by the three stirrers were obtained by following the procedure described in section 2.5.2. Upon setting any of the values tested for the air pressure to the motor, the rotation speed decreased with increasing the nitrogen superficial velocity until it became constant above a specific value of superficial velocity.

Aeration had a strong impact on the power and torque required for mixing. Figures 3.2-3.7 show the normalized power and the normalized torque required by the three stirrers. Both power and torque at constant rpm first decreased with increasing superficial velocity and then became constant above a critical aeration rate \( (A_c) \). The critical aeration shown in figures 3.2-3.7 is an average value for all rotation speeds. The rotation speed does not affect much the critical aeration for all the stirrers examined (table 3.1). Additionally, it can be observed that there is a good overlap between critical velocities obtained from power and torque calculations.

Figure 3.2 Effect of nitrogen gas aeration on the normalized power required by the vertical blades stirrer
Figure 3.3 Effect of nitrogen gas aeration on the normalized power required by the spiral stirrer

Figure 3.4 Effect of nitrogen gas aeration on the normalized power required by the paddles stirrer
Figure 3.5 Effect of nitrogen gas aeration on the normalized torque required by the vertical blades stirrer

Figure 3.6 Effect of nitrogen gas aeration on the normalized torque required by the spiral stirrer
Figure 3.7 Effect of nitrogen gas aeration on the normalized torque required by the paddles stirrer

Table 3.1 Critical aeration for different stirrers obtained from power and torque calculations

<table>
<thead>
<tr>
<th></th>
<th>Critical aeration</th>
<th>Power</th>
<th>Torque</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical blades stirrer</td>
<td>0.032 - 0.032 m/s</td>
<td>0.026 - 0.036 m/s</td>
<td>0.036 - 0.036 m/s</td>
</tr>
<tr>
<td>Paddles stirrer</td>
<td>0.035 - 0.036 m/s</td>
<td>0.036 - 0.036 m/s</td>
<td></td>
</tr>
<tr>
<td>Spiral stirrer</td>
<td>0.035 - 0.035 m/s</td>
<td>0.035 - 0.036 m/s</td>
<td></td>
</tr>
</tbody>
</table>

Since the minimum fluidization velocity of the bed solids is about 0.015 m/s, the critical aeration superficial velocity for the three stirrers was nearly twice the minimum fluidization flowrate. This agrees with the results obtained by Makishima and Shirai (1969). Since the critical aeration does not vary significantly for different stirrers, it cannot be used as a criterion for stirrer selection.

Above critical aeration, most of the power to turn the stirrer is consumed by the friction in the drive shaft bearings and sealing. Therefore, all the three stirrers are characterized by similar power consumption under this condition.
Tables 3.2 and 3.3 show the comparison of the power and torque normalized by their minimum value, for aeration rates above critical aeration. The relative reduction in power and torque achieved with aeration was smaller for the vertical blades stirrer than for the other stirrers. At low air motor pressures, the spiral stirrer could not even be rotated without aeration.

Table 3.2 Comparison of the different stirrers’ Torque/Minimum torque curves with nitrogen aeration at 200 rpm

<table>
<thead>
<tr>
<th>Superficial velocity (m/s)</th>
<th>Spirals stirrer Torque/Min torque</th>
<th>Paddles stirrer Torque/Min torque</th>
<th>Vertical blades stirrer Torque/Min torque</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.942</td>
<td>0</td>
<td>1.078</td>
</tr>
<tr>
<td>0.010</td>
<td>1.542</td>
<td>0.010</td>
<td>1.067</td>
</tr>
<tr>
<td>0.016</td>
<td>1.340</td>
<td>0.016</td>
<td>1.060</td>
</tr>
<tr>
<td>0.023</td>
<td>1.170</td>
<td>0.023</td>
<td>1.040</td>
</tr>
<tr>
<td>0.030</td>
<td>1.040</td>
<td>0.030</td>
<td>1.007</td>
</tr>
<tr>
<td>0.037</td>
<td>1.004</td>
<td>0.037</td>
<td>1.002</td>
</tr>
<tr>
<td>0.044</td>
<td>1</td>
<td>0.044</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.3 Comparison of the different stirrers’ Power/Minimum power curves with nitrogen aeration at 200 rpm

<table>
<thead>
<tr>
<th>Superficial velocity (m/s)</th>
<th>Spirals stirrer Power/Min power</th>
<th>Paddles stirrer Power/Min power</th>
<th>Vertical blades stirrer Power/Min power</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.981</td>
<td>0</td>
<td>1.083</td>
</tr>
<tr>
<td>0.010</td>
<td>1.477</td>
<td>0.010</td>
<td>1.072</td>
</tr>
<tr>
<td>0.016</td>
<td>1.296</td>
<td>0.016</td>
<td>1.065</td>
</tr>
<tr>
<td>0.023</td>
<td>1.150</td>
<td>0.023</td>
<td>1.040</td>
</tr>
<tr>
<td>0.030</td>
<td>1.040</td>
<td>0.030</td>
<td>1.013</td>
</tr>
<tr>
<td>0.037</td>
<td>0.996</td>
<td>0.037</td>
<td>1.002</td>
</tr>
<tr>
<td>0.044</td>
<td>1</td>
<td>0.044</td>
<td>1</td>
</tr>
</tbody>
</table>

Measurements with helium and argon, by following the same procedure used with nitrogen explained in section 2.5.2, at different rotation speeds with the various stirrers gave results that were similar to the results obtained with nitrogen. Figures 3.8 and 3.9 show the results obtained with the vertical blades stirrer, while table 3.4 shows the critical aeration rate for different gases.
with the vertical blades stirrer operating at 170 rpm. With helium, a much higher superficial velocity is needed in order to reach the maximum rpm than with nitrogen. The critical aeration rate for argon is somewhat higher than for nitrogen. Given the properties of the gases studied at 550 °C and 1 bar as shown in table 3.5, both viscosity and density affect the critical aeration, but there are not enough data to propose a correlation and the effects of the gas properties cannot be estimated from their effects on the minimum fluidization velocity.

![Figure 3.8](image_url)

**Figure 3.8** Effect of different gases aeration on the normalized power required by the vertical blades stirrer at 170 rpm
3.3.3 Pyrolysis results

The results obtained with various gases and various rotation speeds seem to favor the vertical blades stirrer. It requires less power or torque at all aeration rates, while providing adequate wall to bed heat transfer.

Table 3.4 Critical aeration for nitrogen, helium and argon at 170 rpm

<table>
<thead>
<tr>
<th>$A_c$ (m/s)</th>
<th>Torque (Max torque - Min torque)</th>
<th>Power (Max power - Min power)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.035</td>
<td>0.032</td>
</tr>
<tr>
<td>Helium</td>
<td>0.069</td>
<td>0.066</td>
</tr>
<tr>
<td>Argon</td>
<td>0.042</td>
<td>0.044</td>
</tr>
</tbody>
</table>

Table 3.5 Gases characteristics at 1 bar and 550 °C

<table>
<thead>
<tr>
<th></th>
<th>Density (kg/m³)</th>
<th>Viscosity (Pa*s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.416</td>
<td>3.65E-05</td>
</tr>
<tr>
<td>Helium</td>
<td>0.059</td>
<td>4.04E-05</td>
</tr>
<tr>
<td>Argon</td>
<td>0.591</td>
<td>4.83E-05</td>
</tr>
</tbody>
</table>

The results obtained with various gases and various rotation speeds seem to favor the vertical blades stirrer. It requires less power or torque at all aeration rates, while providing adequate wall to bed heat transfer.

The biomass feed rate was varied between 5.7 and 9.6 kg/h. Assuming a yield of 80 wt% (Mohan et al., 2006) for the mixture of product gases and vapors, and 50 g/mole for its molecular weight,
the residence time of the gases and vapors would range between 0.68 and 1.13 seconds, meaning that the MFR can be operated under fast pyrolysis conditions. The superficial velocity during the pyrolysis could be estimated to range from 0.08 to 0.14 m/s, thus, significant aeration of the bed occurred during the reaction.

Figure 3.10 shows that the bed behavior during pyrolysis was greatly affected by the type of stirrer. The vertical blades stirrer rotated faster during pyrolysis (grey line) than when nitrogen was injected at the bottom of the bed (black line). This type of stirrer must, therefore, displace the wood pellets in a way that the pyrolytic vapors and gases aerate the bed more homogenously than when the gas was injected through the four snubbers placed on the bottom. The results show that the vapors are generated at locations where they can more effectively reduce the torque required from the motor.

Figure 3.10 Pyrolysis experiment with different stirrers at 262 kPa

With the paddles stirrer, when biomass is fed (grey line), the rotation speed decreased by less than 10% (Figure 3.10). Although the rotation speed was significantly higher than in the absence of any aeration, the results show that, with the paddle stirrer, the pyrolytic vapors and gases cannot aerate the bed more homogenously than the nitrogen. Similar but worse results were
obtained with the spiral stirrer (Figure 3.10), showing that the pyrolytic vapors and gases (grey line) were much less effective than the artificially aerated bed (black line).

Dedicated experiments were conducted with a transparent vessel to visually observe the mixing behaviour created by the stirrers and to infer where pyrolytic vapors and gases would be generated with each stirrer. While scraping the wall, the vertical blades stirrer lifted a fraction of the bed solids in front of the scraper blade, which would then form an avalanche, burying the biomass pellets fed onto the bed surface. The crest height of the wave formed at the wall increased with increasing the rotation speed. Simultaneously, a vortex was formed, whose depth also increased with increasing rotation speed. Therefore, it is expected that, thanks to the depth of the vortex, the reacting pellets could reach a lower level in the reactor, providing a more effective and homogeneous aeration closer to the reactor bottom. The other two stirrers formed a vortex, but only at very high speed, and it was not as deep as the vortex formed by the vertical blades stirrer.

At the end of each pyrolysis test, the bed containing the foamed glass beads and the char was always collected and observed. No segregation could be observed in any of the experiments performed. This could not, however, help determine whether segregation occurred during pyrolysis, since pyrolytic vapors and gases have been shown to reduce the effective density of the reacting pellets (Bruni et al., 2002). Therefore, some tests were performed with a bed material with a higher density than the regular bed material, to increase the density difference between the unreacted pellets and the bed material. These experiments used silica sand, which has a much higher density (bulk density around 1660 kg/m$^3$) than the foamed glass beads used in the rest of the study (bulk density around 336 kg/m$^3$). Visual inspection showed that, with the vertical blades stirrer, char was homogeneously distributed throughout the bed when the pyrolysis test was performed, and the char-pellets were split in two or three fragments. With the other two stirrers, on the other hand, the char produced during the tests was found to be segregated on top of the bed and the whole char-pellets remained intact.

Figure 3.10 shows that, when biomass feeding stopped, the stirrer rotation speed gradually decreased as the flowrate of pyrolytic vapors and gases gradually decreased. The pyrolysis experiments with the vertical blades stirrer were repeated thrice in order to investigate how to
best evaluate the time for pyrolysis from the decrease in rotation speed. The time at which the rotation speed reached its half-way point between the speed achieved during biomass feeding and the speed in the absence of any aeration was found to be the most reproducible (figure 3.11). Therefore, this parameter was chosen to compare the stirrers in terms of time for complete pyrolysis. Figure 3.11 shows that improving bed mixing through an increase in mixer rotation speed has a strong beneficial impact on the effective pyrolysis kinetics.

![Graph](image)

**Figure 3.11 Reproducibility of pyrolysis half rpm reduction time with the vertical blades stirrer**

Figure 3.12 shows that the vertical blades stirrer is more effective than the other stirrers, since it has much lower times for complete pyrolysis over the whole range of stirrer rotation speeds. With all stirrers, increasing the rotation speed accelerates the pyrolysis. These results show that the quality of the contact of the biomass pellets with the hot bed material has a significant impact on the effective pyrolysis kinetics. This is also confirmed by figure 3.13, which shows that the half rpm reduction time for grass pellets pyrolysis is not much different than the one for wood pellets pyrolysis, at the same rpm: the predominant effect on the effective pyrolysis kinetics is due to the bed hydrodynamics, which depends mostly on the shape of the stirrer and its rotation speed.
Figure 3.12 Effect of pyrolysis rotation speed on the half rpm reduction time for different stirrers

Figure 3.13 Effect of pyrolysis speed on the half rpm reduction time for the vertical blades stirrer during pyrolysis of wood and grass pellets
3.4 Conclusions

The mixing characteristics of a Mechanically Fluidized Reactor were studied. The torque and power required by three stirrers of different geometries were determined at different bed aerations. Both torque and power decreased with increasing aeration rates until becoming constant above a critical aeration rate. The critical aeration rate was found to be nearly independent of the rotation speed and stirrer design. Experiments with three different gases (nitrogen, helium and argon) indicated that both gas density and viscosity affected the critical aeration rates. Experiments with biomass pyrolysis indicated that, with reasonable biomass feed rates, the evolution of product gases and vapors within the bed was sufficient to achieve aeration rates well above the critical aeration rate.

This study showed that the stirrer shape is an important parameter when performing pyrolysis tests using Mechanically Fluidized Reactors. The vertical blades stirrer is the most suitable stirrer for biomass pyrolysis, as it requires the lowest torque and power at any aeration condition and provides adequate heat transfer between the reactor wall and bed. Pyrolysis experiments highlighted the better mixing performance of the vertical blades stirrer, since it minimized the time for complete pyrolysis at any rotation speed, indicating that it promotes better heat transfer between the biomass pellets and the hot bed material.
Chapter 4

4. Use of the Mechanically Fluidized Reactor (MFR) to investigate the impact of bed hydrodynamics on the pyrolysis of biomass

4.1 Introduction

This chapter investigates the pyrolysis of Kraft lignin in the MFR. It focuses on three objectives:

I. Investigation of the suitability of the technique developed in chapter 3 for any feedstock;
II. Development of a method to determine how cohesive a feedstock becomes when pyrolyzed;
III. Comparison of pyrolysis of Kraft lignin, grass and wood to determine the impact of feedstock and stirrer rotation speed on yields and product quality.

4.2 Materials and methods

The experimental apparatus is described in section 2.5. The study described in chapter 3 showed that both power and torque required by the stirrer at constant rpm first decreased with increasing superficial velocity of the aeration gas and then became constant above a critical aeration rate, nearly independent from the rotation speed.

The stirrer used in this study is the vertical blades stirrer shown in Figure 2.3, which was found to be ideal for the MFR (Chapter 3). It was designed to provide agitation near the reactor wall and thus promote wall to bed heat transfer; it also induced avalanches that folded over the bed surface, covering with hot bed solids the fresh biomass feed introduced on the bed surface.

Foamed glass beads with a Sauter mean diameter of 375 μm and an apparent particle density of 560 kg/m³ were used as inert bed material for the pyrolysis tests. This material was chosen in order to simulate the size and density of typical char particles.

Table 4.1 summarizes the ultimate analysis and the moisture content of the biomass feedstocks used in this work. Three different feedstocks were pyrolyzed:
• cylindrical pellets of a wood blend consisting of approximately 75% softwood (spruce-pine-fir) and 25% hardwood (oak and maple) with a diameter of about 5 mm and length of 3 mm;
• cylindrical switch grass pellets without binder, with a diameter of about 5 mm and length of 1 mm;
• 2 - 6 mm lignin granules containing a small amount of organic binder.

**Table 4.1 Ultimate analysis and moisture content of feedstocks**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Wood</th>
<th>Grass</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>2.15</td>
<td>0.27</td>
<td>0.059</td>
</tr>
<tr>
<td>C</td>
<td>47.51</td>
<td>48.10</td>
<td>64.92</td>
</tr>
<tr>
<td>H</td>
<td>6.06</td>
<td>6.40</td>
<td>5.90</td>
</tr>
<tr>
<td>S</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>44.28</td>
<td>45.23</td>
<td>29.13</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Pyrolysis experiments were performed by following the procedure described in paragraph 2.5.3.

### 4.3 Results and discussion

Preliminary experiments have been conducted to characterize the MFR operation and performance during the pyrolysis of traditional biomass feedstocks: wood and grass. Subsequently, systematic experiments have been performed with Kraft lignin.

#### 4.3.1 Wood and grass pyrolysis

The wall-to-bed heat transfer was previously evaluated and found to be appropriate for pyrolysis experiments and not greatly affected by the rotation speed (chapter 3).

Figures 4.1 and 4.2 show the bed temperature measured by the thermocouple placed near the bottom of the reactor vessel, before, during, and after pyrolysis. During pyrolysis, the temperature decreases because of the associated feedstock heating and endothermic thermal cracking reactions. The extent of the temperature drop depends upon wall-to-bed heat transfer and bed mixing. For the sake of simplicity, only the temperatures for the lowest and the highest tested rotation speeds are shown. Figures 4.1 and 4.2 show that bed mixing and wall-to-bed heat
transfer improve significantly with increasing rotation speed during pyrolysis of both wood and grass. However, the wall-to-bed heat transfer was investigated in Chapter 3 and the results with other stirrers suggest that mixing may be more important than wall-to-bed heat transfer. The temperature drop does not imply that the biomass federate could not be sustained in a continuous operation. In continuous operation, the wall temperature would rise and would reach steady state where the heat transferred would include both the heat losses and the heat of pyrolysis, instead of just the heat losses before the biomass injection as in this test.

Figure 4.1 Bed temperature during wood pyrolysis at the lowest and highest rotation speed tested
Figure 4.2 Bed temperature during grass pyrolysis at the lowest and highest rotation speed tested

Figure 4.3 shows that, as the mixer rotation speed during pyrolysis is increased, the maximum temperature drop at first decreases sharply and then remains approximately constant with further increases in mixer speed. At high mixer speeds, the maximum temperature drop during grass and wood pyrolysis is only 15 and 18 °C, respectively. Therefore, very good mixing can be achieved with both feedstocks.
Figure 4.4 shows how the mixer rotation speed varied during pyrolysis of wood and grass. Both tests were performed with the vertical blades stirrer operated with a constant motive air pressure of 179 kPa. The raw data, which were contaminated with some noise, were smoothed with TableCurve 2D. Each experiment was performed as described in 2.5.3.

Figure 4.4 shows that, during the pyrolysis of either grass or wood pellets, pyrolytic vapors and gases can efficiently reduce the torque required to stir the bed with the motor by aerating the bed even more homogeneously than the artificial aeration provided by the nitrogen gas through 4 snubbers. This confirms that the vertical blades stirrer operates well with these feedstocks.
Results are reported in terms of pyrolysis rpm, which is the rotation speed value reached during pyrolysis. It can be seen that grass and wood results are not reported for the exact same rotation speed values. The reason is that the pyrolysis rpm value could not be adjusted since the air pressure to the motor was set at the beginning of the run and then the motor was let free to change its rotation speed in order to evaluate the change in aeration conditions given by the evolution of gases and vapours during pyrolysis reactions.

Figure 4.5 shows that the mixer rotation speed, which was shown to affect mixing and wall-to-bed heat transfer (Figure 4.3), does not have a significant impact on the liquid yield of either feedstock. Therefore, it can be assumed that, even at the lowest rotation speed of 180 rpm, mixing was appropriate for the pyrolysis of wood or grass.
The liquid yield was around 60 wt% for wood pyrolysis and 58 wt% for grass pyrolysis. In the case of pyrolysis of grassy biomass, the liquid yield is within the range of values reported in literature (Bridgwater, 2012). On the other hand, the wood liquid yield was relatively low, if compared to 70-75 wt% reported in literature (Bridgwater, 2012), presumably because the large size of the wood pellets used in this work leads to a significant resistance to heat transfer within the pellets (Shen et al., 2009; Brown et al., 2011).

Although the mixing affected the bed temperature during pyrolysis (Figure 4.3) and the change in bed temperature affected the effective kinetics of the pyrolysis reaction, the rotation speed did not significantly affect the yield and composition of the bio-oil produced from wood or grass. Both wood and grass bio-oils exhibited phase separation between aqueous and oily phases. The rotation speed did not significantly affect the amount of aqueous phase, the elemental composition of the total bio-oil or the water contents of the aqueous and oily phases (Tables 4.2 & 4.3). The GC/MS chromatograms of all the produced wood bio-oils are analogous (Figure 4.6). The composition was not further analyzed at this stage since the purpose of this analysis was only the determination of the potential effect of the rotation speed on the composition. The

Figure 4.5 Liquid yield for pyrolysis of wood and grass performed at different rotation speed (on a dry basis)
same observation applies to the grass bio-oils (Figure 4.7). GPC results are shown in Tables 4.4 and 4.5 in terms of number average molecular weight ($M_n$), weight average molecular weight ($M_w$) and polydispersity index (PDI). These results confirmed that the rotation speed does not have any significant effect on the molecular weight distribution of the wood and grass bio-oils.

**Table 4.2 Characterization of wood bio-oil produced at different rotation speeds**

<table>
<thead>
<tr>
<th>rpm</th>
<th>Collected bio-oil (g)</th>
<th>Aqueous phase (wt% bio-oil)</th>
<th>Elemental composition (%)</th>
<th>Water content %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N</td>
<td>C</td>
</tr>
<tr>
<td>260</td>
<td>35.14</td>
<td>26.5</td>
<td>2.39</td>
<td>61.28</td>
</tr>
<tr>
<td>236</td>
<td>32.52</td>
<td>26.7</td>
<td>2.66</td>
<td>62.02</td>
</tr>
<tr>
<td>215</td>
<td>36.24</td>
<td>24.5</td>
<td>2.27</td>
<td>59.67</td>
</tr>
<tr>
<td>180</td>
<td>34.3</td>
<td>25.3</td>
<td>2.42</td>
<td>62.75</td>
</tr>
</tbody>
</table>

**Table 4.3 Characterization of grass bio-oil produced at different rotation speeds**

<table>
<thead>
<tr>
<th>rpm</th>
<th>Collected bio-oil (g)</th>
<th>Aqueous phase (wt.% bio-oil)</th>
<th>Elemental composition (%)</th>
<th>Water content %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N</td>
<td>C</td>
</tr>
<tr>
<td>255</td>
<td>37.82</td>
<td>25.8</td>
<td>0.54</td>
<td>61.92</td>
</tr>
<tr>
<td>214</td>
<td>35.87</td>
<td>24.8</td>
<td>0.52</td>
<td>63.08</td>
</tr>
<tr>
<td>203</td>
<td>37.3</td>
<td>26.5</td>
<td>0.64</td>
<td>64.62</td>
</tr>
<tr>
<td>186</td>
<td>36.1</td>
<td>25.4</td>
<td>0.66</td>
<td>68.93</td>
</tr>
</tbody>
</table>

**Figure 4.6 GC/MS spectra of the oil phase of wood bio-oils produced at different rotation speeds**
Figure 4.7 GC/MS spectra of the oil phase of grass bio-oils produced at different rotation speeds

Table 4.4 GPC analysis of the wood bio-oils produced at the lowest and highest rotation speed tested

<table>
<thead>
<tr>
<th>rpm</th>
<th>M_n</th>
<th>M_w</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>142</td>
<td>257</td>
<td>1.82</td>
</tr>
<tr>
<td>260</td>
<td>141</td>
<td>255</td>
<td>1.81</td>
</tr>
</tbody>
</table>

Table 4.5 GPC analysis of the grass bio-oils produced at the lowest and highest rotation speed tested

<table>
<thead>
<tr>
<th>rpm</th>
<th>M_n</th>
<th>M_w</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>186</td>
<td>142</td>
<td>276</td>
<td>1.94</td>
</tr>
<tr>
<td>250</td>
<td>137</td>
<td>270</td>
<td>1.97</td>
</tr>
</tbody>
</table>

4.3.2 Lignin pyrolysis

Figure 4.8 shows that the bed temperature during lignin pyrolysis was influenced by the stirrer rotation speed, and hence by the mixing intensity. The temperature did not drop as much as during the pyrolysis of wood or grass. This is likely due to a less homogeneous temperature distribution within the bed, as it took longer for the bed temperature to get back to its set point.
The maximum temperature drop decreased to 15 °C as the rotation speed increased, indicating that good mixing could be achieved during lignin pyrolysis (Figure 4.9).

Figure 4.8 Bed temperature during Kraft lignin pyrolysis at the lowest and highest rotation speed tested
Figure 4.9 Maximum decrease of bed temperature during pyrolysis of lignin at different rotation speed

Figure 4.10 shows the pyrolysis behaviour of Kraft lignin compared to wood and grass at 179 kPa air pressure to the motor. Kraft lignin behaved very differently from the other feedstocks. As Kraft lignin pyrolysis started, the rotation speed dropped significantly, which is the opposite of what was observed with wood and grass. Kraft lignin is known to cause agglomeration problems in conventional fluidized reactors (Palmisano et al., 2011). Lignin has been found to transform into a sticky liquid intermediate before producing the standard pyrolysis products (Baumlin et al., 2006). Therefore, the rotation speed drop can be explained by the formation of viscous “liquefied lignin”, requiring a higher torque to stir the bed. Figure 4.10 shows that the stirrer speed recovered after the lignin had reacted, as the bed particles were dry and no longer cohesive.

Figure 4.10 demonstrates that the MFR can be used to characterize how cohesive feedstocks, such as Kraft lignin, become during pyrolysis: the mixer speed drops instead of increasing. The MFR can, thus, help develop alternative solutions to make it easier to pyrolyze Kraft lignin in
more conventional fluidized beds by pretreating the lignin, modifying the bed material or changing the fluidization gas.

![Graph showing rotation speed trend during pyrolysis of Kraft lignin, wood and grass](image)

**Figure 4.10 Rotation speed trend during pyrolysis of Kraft lignin, wood and grass**

Figure 4.11 shows the effect of mixer rotation speed on lignin pyrolysis. The results shown are for two runs performed with the same air pressure supplied to the air motor (262 kPa), but with the stirrer running at a different initial rotation speed (the different rotation speed can be attributed to different friction in the drive shaft bearings and sealing). A lower drop in rotation speed was observed during lignin pyrolysis when the initial rotation speed, before the lignin was fed, was higher. A higher mixing intensity, therefore, mitigates agglomeration between lignin and glass beads.
As already mentioned for wood and grass results, the pyrolysis rpm could not be adjusted, since it depends on the reactions and as a consequence on the aeration/bed cohesivity. The motor is not able to run smoothly below 80 rpm, especially if it has to provide enough torque to overcome the bed resistance resulting from reacting lignin. Therefore the initial air pressure was chosen accordingly.

The liquid yield resulting from the pyrolysis of lignin was around 45 wt%, which coincides with what was reported by De Wild et al. (2014). Figure 4.12 shows that the liquid yield was not affected when the rotation speed during pyrolysis was increased from 90 to 230 rpm.

Figure 4.11 Rotation speed trend during pyrolysis of lignin at different rotation speed
The rotation speed did not affect the composition of the lignin bio-oil. Lignin bio-oil exhibited phase separation, as did wood and grass bio-oils. The rotation speed did not affect the proportion of the aqueous fraction, or the elemental compositions and water contents of the oily and aqueous phases (Tables 4.6). The GC-MS chromatograms (Figure 4.13) and the GPC results (Table 4.7) confirmed that the rotation speed did not affect the composition of the lignin bio-oil.

**Figure 4.12 Liquid yield for pyrolysis of lignin performed at different rotation speeds**

<table>
<thead>
<tr>
<th>rpm</th>
<th>Collected bio-oil (g)</th>
<th>Aqueous phase (wt% bio-oil)</th>
<th>Elemental composition %</th>
<th>Water content %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N</td>
<td>C</td>
</tr>
<tr>
<td>89</td>
<td>26.86</td>
<td>56.1</td>
<td>0.25</td>
<td>66.7</td>
</tr>
<tr>
<td>130</td>
<td>27.06</td>
<td>57.2</td>
<td>0.27</td>
<td>69.6</td>
</tr>
<tr>
<td>187</td>
<td>27.98</td>
<td>50.7</td>
<td>0.26</td>
<td>69.1</td>
</tr>
<tr>
<td>226</td>
<td>28</td>
<td>52.3</td>
<td>0.25</td>
<td>69.6</td>
</tr>
</tbody>
</table>
Figure 4.13 GC/MS spectra of the oil phase of lignin bio-oil produced at different rotation speeds

Table 4.7 GPC analysis of the oil phase of lignin bio-oils produced at the highest and lowest rotation speed tested

<table>
<thead>
<tr>
<th>rpm</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>81</td>
<td>241</td>
<td>2.95</td>
</tr>
<tr>
<td>226</td>
<td>83</td>
<td>246</td>
<td>2.95</td>
</tr>
</tbody>
</table>

4.4 Conclusions

The Mechanically Fluidized Reactor can maintain nearly isothermal conditions during pyrolysis of wood, grass or Kraft lignin pellets.

The Mechanically Fluidized Reactor successfully pyrolyzed Kraft lignin. However, lignin requires more power for mixing than wood and grass because of the stickiness it exhibits during pyrolysis. While the evolution of pyrolysis gas and vapors reduces the power required for mixing during wood and grass pyrolysis, it is unable to do so during lignin pyrolysis. With lignin, agglomeration of reacting lignin and bed material competes with the aeration due to gas and vapor formation, resulting in a net increase in the required mixing power.
The rotation speed in the studied range does not influence the liquid yield and its composition. This result was observed for wood, grass and Kraft lignin.

Monitoring the mixing power requirements provides a new, accurate tool to characterize how cohesive feedstocks become during pyrolysis. This provides a convenient technique to investigate methods that could reduce the cohesivity during pyrolysis of feedstocks, such as Kraft lignin, that would be difficult to pyrolyze with standard fluidized beds because of cohesivity and agglomeration issues. For this reason, other parameters were varied in order to evaluate their effect on Kraft lignin processability.
Chapter 5

5. Effect of bed material on the pyrolysis of Kraft lignin

5.1 Introduction

This chapter investigates the effect of different bed materials on the processability of Kraft lignin and its liquid product quality.

The following was undertaken:

I. Pilot-scale pyrolysis of Kraft lignin in the MFR varying the bed material;
II. Observation of the effect of the bed material

The objective was to find a material that would improve Kraft lignin processability.

5.2 Materials and Methods

The set-up is described in section 2.5 and the pyrolysis experiments were performed by following the procedure described in section 2.5.3. The stirrer used was the vertical blades stirrer (Figure 2.3).

In this study 2 - 6 mm Kraft lignin granules containing a small amount of organic binder were used as feedstock and in one case granules were made of Kraft lignin and ground activated carbon from coal.

Different bed materials were investigated:

- foamed glass beads with Sauter mean diameter of 375 μm;
- granular activated carbon from coal with mesh size -12+40;
- granular activated carbon from coal with mesh size -20+50;
- granular activated carbon from coconut shell with mesh size -12+40;
- acid-washed granular activated carbon from coconut shell with mesh size -12+40;
- vermiculite;
- a sodium potassium aluminum silicate absorbent material.

More details about these materials are given in section 2.4.
5.3 Results and discussion

Figures 5.1-5.7 show the rotation speed of the stirrer during pyrolysis of Kraft lignin with different bed materials. It can be observed that when activated carbon from coal, both mesh size -20+50 and -12+40 (figure 5.1 and 5.2), either the bed is no longer sticky or the generation of vapors and gas during pyrolysis can balance the cohesivity of Kraft lignin. However, the bio-oil produced in these conditions was a light yellow liquid. Thus, these types of activated carbons could improve lignin behaviour, but their catalytic activity on cracking reactions was too strong.

![Figure 5.1 Rotation speed trend during pyrolysis of Kraft lignin in a bed of activated carbon from coal with mesh size -20+50](image-url)
The activated carbon from coal was characterized by 12% ash content which was probably the cause of its strong cracking activity. Therefore, activated carbon from coconut shells and acid-washed activated carbon from coconut shells with respectively 4 and 1.5% ash content were tested. Figures 5.3 and 5.4 show that these types of activated carbon also decrease the cohesivity of Kraft lignin during pyrolysis. However, the bio-oil produced was a light yellow liquid, showing that the catalytic activity of these types of activated carbon was still too high.
Figure 5.3 Rotation speed trend during pyrolysis of Kraft lignin in a bed of activated carbon from coconut shell with mesh size -12+40

Figure 5.4 Rotation speed trend during pyrolysis of Kraft lignin in a bed of acid-washed activated carbon from coconut shell with mesh size -12+40
Granules of a Kraft lignin and activated carbon mixture 1:1 were produced and fed to a bed of foamed glass beads. As soon as they were fed into the reactor the rotation speed dropped (Figure 5.5) as with granules of pure Kraft lignin (Figure 4.10). The amount of activated carbon used was not enough to improve the processability of Kraft lignin. The bio-oil was not as watery as in the previous experiments with activated carbon as bed material, but the yield was somewhat lower, 38 wt%, than the one obtained with pure Kraft lignin granules, 43-46 wt%. Thus, making pellets containing activated carbon favoured cracking reactions, but did not prevent bed stickiness.

![Graph](image)

**Figure 5.5 Rotation speed trend during pyrolysis of Kraft lignin and activated carbon mixture in a bed of glass beads**

Figure 5.6 shows a Kraft lignin pyrolysis experiment performed with vermiculite as bed material. Unfortunately, vermiculite, when heated up, expands and exfoliates. For this reason it was impossible to observe pyrolysis by mean of recording the rotation speed since this parameter kept fluctuating during the test. Additionally, the bio-oil produced was a light yellow liquid. Hence, this material excessively promotes cracking reactions.
A sodium potassium aluminum silicate absorbent material was also tested. Figure 5.7 shows a pyrolysis experiment using it as bed material. The speed did not increase, meaning that the bed became sticky once again. Additionally, the bio-oil was very watery, thus, this material may be catalytically active in pyrolysis as well, but does not prevent lignin cohesivity.

**Figure 5.6 Rotation speed trend during pyrolysis of Kraft lignin in a bed of vermiculite**

**Figure 5.7 Rotation speed trend during pyrolysis of Kraft lignin in a bed of sodium potassium aluminum silicate absorbent material**
5.4 Conclusions

The bed material, consisting of foamed glass beads in the first study about Kraft lignin pyrolysis, was compared with porous and absorbent materials.

Activated carbons of different origins, size and ash content, one type of clay and one sodium potassium aluminum silicate absorbent material were investigated. The porosity of all the tested activated carbons improved the processability of Kraft lignin, presumably because their pores absorbed the intermediate liquid phase that Kraft lignin goes through when heated. However, the catalytic activity of these materials was so strong that the bio-oil produced was a yellow watery liquid.

The same kind of product resulted also from the processing of Kraft lignin with vermiculite and a commercial absorbent material. An appropriate catalyst would not only improve the processability because of its porous structure but would promote the appropriate reactions.
6. Addition of wood to Kraft lignin to improve its processability in fast pyrolysis reactors

6.1 Introduction

This chapter investigates the pyrolysis behavior of different mixtures of Kraft lignin and birch wood.

The following was undertaken:

I. Thermal conversion of different mixtures of Kraft lignin and birch wood in the pilot-scale MFR;
II. Comparison of the processability of the different mixtures;
III. Analysis of products and yields.

Mixing Kraft lignin with either wood or grass is expected to improve Kraft lignin processability.

6.2 Materials and methods

The experimental apparatus is described in section 2.5 and shown in Figure 2.2. The stirrer used in this study is shown in Figure 2.3. This mixer was found to be ideal for the MFR (Chapter 3).

Foamed glass beads with a Sauter mean diameter of 375 μm and an apparent particle density of 560 kg/m³ were used as inert bed material for the pyrolysis tests. This material was chosen in order to simulate the size and density of typical char particles.

Kraft lignin and birch wood were mixed in different proportions:

- 0 wt% Kraft Lignin 100 wt% birch wood;
- 20 wt% Kraft Lignin 80 wt% birch wood;
- 40 wt% Kraft Lignin 60 wt% birch wood;
- 50 wt% Kraft Lignin 50 wt% birch wood;
- 60 wt% Kraft Lignin 40 wt% birch wood;
• 75 wt% Kraft Lignin 25 wt% birch wood;
• 100 wt% Kraft Lignin 0 wt% birch wood

and granulated with small amount of organic liquid binder to form 2-6 mm granules (Figure 6.1). Granules are required in order to achieve smooth biomass feeding to the MFR.

![Birch wood – Kraft lignin granules](image)

**Figure 6.1 Birch wood – Kraft lignin granules**

These feedstocks were analyzed in terms of lignin and ash content as described in sections 2.3.2 and 2.3.3. Table 6.1 summarizes the results of these analyses.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Kraft lignin</th>
<th>Birch wood</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Insoluble lignin (wt%)</td>
<td>92.6</td>
<td>24.7</td>
</tr>
<tr>
<td>Acid soluble lignin (wt%)</td>
<td>1.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Ash content (wt%)</td>
<td>~0</td>
<td>1</td>
</tr>
</tbody>
</table>

The pyrolysis experiments were carried out by following the procedure described in section 2.5.3. All the tests were performed with a vertical blades stirrer operated with a constant motive air pressure of 179 kPa. The raw data, which were contaminated with some noise, were smoothed with TableCurve 2D.
6.3 Results and discussion

As already mentioned above, granulated feedstocks flow smoothly into the MFR feeder, avoiding plugging and sticking of the biomass inside the feeder. Unfortunately, the granulation of pure birch wood was unsuccessful. Thus, this material was ground with a 2 mm screen and fed in 16 shots of 5 g each. Since the increment of the rotation speed is affected by the instantaneous vapors and gas flowrate evolving during pyrolysis, a lower feeding rate affects the production of gas and vapors, thus, the rotation speed. Hence, the rotation speed trend of the pure birch wood is not comparable to the other experiments and, for this reason, it is not reported. For comparison, the behavior of 100% Kraft lignin and 20% Kraft lignin mixture are here reported.

Figure 6.2 shows how the rotation speed dropped as soon as the feeding of 100 % Kraft lignin started. This phenomenon was already discussed in chapter 4. Kraft lignin becomes cohesive at reaction temperature and tends to agglomerate. Hence, the rotation speed of the stirrer decreases while the lignin is reacting, making the bed particles sticky.

![Figure 6.2 Pyrolysis test of 100 wt% Kraft lignin granules](image-url)
In contrast, figure 6.3 shows that when only 20% Kraft lignin is present in the mixture fed to the reactor, the stirrer speeds up, reaching values higher than the rotation speed relative to the critical aeration, thanks to the aeration provided by pyrolytic gas and vapors. A similar behavior was observed during pyrolysis of wood and grass in a MFR (chapter 4).

![Figure 6.3 Pyrolysis test of 20 wt% Kraft lignin granules](image)

In order to characterize the behavior of different proportions of Kraft lignin in the feedstock, the difference between the rotation speed value reached during pyrolysis and the critical aeration value, indicated as “peak height” in Figures 6.2 and 6.3, was used as indicator of the processability of the mixture. Figure 6.4 shows how this parameter decreases with increasing the Kraft lignin content, meaning that the resistance given by the bed increases when a higher proportion of Kraft lignin is mixed with birch wood in the initial mixture fed into the reactor. The 50% Kraft lignin proportion was identified as the maximum amount of this material whose stickiness would still be balanced by the generation of pyrolytic gases and vapors. The regression was calculated following the procedure described in 2.5.4. Between 40 and 50 wt% Kraft lignin there is a discontinuity. The aeration and the bed cohesivity are almost constant below 40 wt% Kraft lignin and then the bed becomes increasingly cohesive with increasing lignin content above 50 wt% Kraft lignin content.
Figure 6.4 Effect of Kraft lignin content on the processability of the feedstock

The liquid yield, as expected, was affected by the Kraft lignin content of the initial feedstock (Figure 6.5). The bio-oil yield decreased linearly with increasing Kraft lignin content, and, thus, decreasing cellulose and hemicellulose contents. Raveendran et al. (1996) mixed cellulose and lignin in different proportions and found that the liquid yield increases with increasing cellulose to lignin ratio. A feedstock with a high lignin content results in a higher char yield and a lower liquid yield (Singh Chouhan & Sarma, 2013).
Figure 6.5 Effect of Kraft lignin content on the liquid yield

Figure 6.6 shows the concentration of phenolics in bio-oils based on Gallic Acid Equivalents (results were interpolated by following the procedure described in section 2.5.4). Since phenolics are derived for the most part from the lignin fraction, the total phenolics yield increases significantly with increasing Kraft lignin content in the mixture fed to the pyrolysis process. However, the relationship between total phenolics concentration and lignin content displays a discontinuity between 50 and 60 wt% Kraft lignin, as shown by Figure 6.7. These results proved that there is a significant change in bio-oil composition as the Kraft lignin content is varied. Though, this kind of analysis can be affected also by other non-phenolic compounds, as mentioned in section 2.6.4, thus further analyses were performed.
Figure 6.6 Phenolics concentration

Figure 6.7 shows the bubble plots of bio-oils produced with different proportions of Kraft lignin and Birch wood, obtained from GC×GC-TOFMS (see section 2.6.5) where the peak intensity is related to the bubble size. It can be easily observed that the phenolics (red bubbles) are a smaller fraction of the total for the bio-oil produced from only birch wood, whereas they represent the majority of the bubbles, both in terms of number and size, for the 100% Kraft lignin bio-oil.
Figure 6.7 GCxGC-TOFMS Bubble plots of bio-oil from (a) 0% Kraft lignin, (b) 20% Kraft lignin, (c) 40% Kraft lignin, (d) 50% Kraft lignin, (e) 60% Kraft lignin, (f) 75% Kraft lignin and (g) 100% Kraft lignin
Figure 6.8 Phenolics area % GCxGC-TOFMS for different Kraft lignin contents

Figure 6.8 shows a linear relationship between phenolics (alkylphenols, guaiacols, syringols and catechols) and Kraft lignin content. The 100 wt% Kraft lignin feedstock yielded a bio-oil with a phenolics relative area corresponding to about 60% of the GC/MS area. This result agrees with the value found by Stefanidis et al. (2014) for Kraft lignin.
Guaiacols increase almost linearly with increasing Kraft lignin concentration, whereas alkylphenols are almost constant for the mixtures with low amount of lignin and they start increasing significantly above 50 wt. % of Kraft lignin. Phenols with methyl substitutes (alkylphenols) are produced also from cellulose and hemicellulose (Stefanidis et al., 2014), which explains the different initial trend between guaiacols and alkylphenols. Catechol and its derivatives are normally not present in natural lignin. They are products of secondary decomposition reactions of guaiacols, which arefavoured at long residence times (Brebu & Vasile, 2010). For this reason their amount is very small compared to guaiacols and alkylphenols.

Figure 6.10 shows the aqueous phase of tests performed with different mixture of Kraft lignin and birch wood. Visual observation confirms the different composition of this liquid phase. It was not further analyzed since it was not the purpose of this study.
6.4 Conclusions

The Mechanically Fluidized Reactor (MFR) was used to characterize the processability of different mixtures of Kraft lignin and birch wood. Pyrolytic gas and vapors reduce the power required by the bed mixing when pure birch wood is processed, whereas they cannot balance the cohesivity of Kraft lignin during pyrolysis.

The processability of Kraft lignin improves with increasing proportion of birch wood in the initial mixture. Although the liquid yield increases linearly with increasing the amount of birch wood in the initial feedstock, the phenolics yield based on Gallic Acid Equivalents decreases significantly.

Bio-oils were further analyzed by GCxGC-TOFMS which showed the phenolics to increase linearly with the lignin content. The relative area of alkylphenols, guaiacols, catechols and syringols is not linearly dependent on the amount of Kraft lignin, thus, seems to depend on a more complex kinetic scheme.
The MFR can successfully process Kraft lignin, by breaking up the agglomerates which it tends to form, but other technologies might need to mix Kraft lignin with other feedstocks to improve its processability. However, if such technologies were to be used, the decreased phenolics concentration of the bio-oil should be taken into account.
Chapter 7

7. Pyrolysis of hydrolysis lignin: comparison with Kraft lignin

7.1 Introduction

This chapter aims to generalize the correlations developed for Kraft lignin and birch wood mixtures in the study described in chapter 6. Additionally, the lignin residue from bioethanol production could be a valuable alternative to Kraft lignin; mostly if it presented a better processability than Kraft lignin and if the liquid product had a higher phenolics concentration.

The following is undertaken:

i. Investigation of the cohesivity of the reactor bed with hydrolysis lignins from different origins;
ii. Comparison of hydrolysis lignins and Kraft lignin-birch wood mixtures in terms of yields and products.

7.2 Materials and Methods

The apparatus is described in section 2.5 and shown in figure 2.2. The stirrer used in this study is the vertical blades stirrer shown in Figure 2.3. This mixer was found to be ideal for the MFR (Chapter 3).

Foamed glass beads with a Sauter mean diameter of 375 μm and an apparent particle density of 560 kg/m³ were used as inert bed material for the pyrolysis tests. This material was chosen in order to simulate the size and density of typical char particles.

The feedstocks investigated in this chapter are:

- Hydrolysis lignin from aspen wood;
- Hydrolysis lignin from sugarcane bagasse;
- Hydrolysis lignin from Napier grass;
- Hydrolysis lignin from wheat straw.
They will be referred to as H-lignins. Table 7.1 summarizes the lignin and ash content of these feedstocks, obtained as illustrated in sections 2.3.2 and 2.3.3.

Table 7.1 Hydrolysis lignin from different feedstocks characterization

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Acid insoluble lignin (%)</th>
<th>Acid soluble lignin (%)</th>
<th>Ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspen wood</td>
<td>55.4</td>
<td>1.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>55.7</td>
<td>1.6</td>
<td>4.4</td>
</tr>
<tr>
<td>Napier grass</td>
<td>45.2</td>
<td>1.4</td>
<td>4.9</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>39.9</td>
<td>1.8</td>
<td>9.8</td>
</tr>
<tr>
<td>Kraft lignin</td>
<td>92.6</td>
<td>1.2</td>
<td>-0</td>
</tr>
<tr>
<td>Birch wood</td>
<td>24.7</td>
<td>1.8</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Pyrolysis experiments were performed by following the procedure described in section 2.5.3.

7.3 Results and discussion

All four types of H-lignin allowed the stirrer to reach a rotation speed value above the one relative to critical aeration. Their processability is much better than with Kraft lignin, in fact the bed material does not become as cohesive as with Kraft lignin and gas and vapours can aerate the bed better than critical aeration conditions with injected nitrogen. Figure 7.1 shows this behaviour during pyrolysis of H-lignin from sugarcane bagasse. However, the rotation speed momentarily drops below the final rotation speed and it can be speculated that the bed material became more cohesive than when wood and grass pellets were pyrolyzed since in those tests the rotation speed never dropped below the rotation speed value reached at the end of the test (figure 4.4).
Figure 7.1 H-lignin from sugarcane bagasse rotation speed during pyrolysis

Results obtained in the study presented in chapter 6 are here compared with H-lignins results. In this chapter results are referred to total lignin content (soluble and insoluble) instead of Kraft lignin content as in chapter 6.

Figure 7.2 compares the results in terms of rotation speed peak height (see Figure 7.1) during pyrolysis of four types of H-lignins and the correlation presented in chapter 6 calculated for Kraft lignin-birch wood mixtures. All the H-lignins tested fall within, or very close, to the 95% confidence interval. The error can be attributed to the accuracy of the technique used to monitor the rotation speed.
The liquid yield relative to pyrolysis of H-lignins is shown in figure 7.3 and compared with the correlation calculated for Kraft lignin-birch wood mixtures. Only the H-lignin from aspen wood falls into the correlation and this result can be explained by the fact that this material is characterized by very low ash content, comparable to Kraft lignin-birch wood mixtures. As expected, the ash content of the initial feedstock has a high impact on the liquid yield. Therefore a more general correlation should account for the ash content as well. The results from this study are, thus, used to correct the correlation presented in chapter 6 for the effect of ash content.
Figure 7.3 Liquid yield comparison between H-lignins and the correlation found for Kraft lignin-birch wood

Good correlation between experimental results and those corresponding to the calculated liquid yields was obtained (Figure 7.4) even though Kraft and native lignin are significantly different since the Kraft cooking process greatly modifies the structure of lignin (Gellerstedt and Robert, 1987). The correlation developed to calculate the liquid yield ($Y_L$) in function of the ash ($x_A$) and lignin content ($x_L$) is described by equation 7.1:

$$Y_L = 73.28 - 0.30 \cdot x_L - 1.96 \cdot x_A \quad (7.1)$$

The ash content has a higher effect on the final liquid yield than the lignin content as was also observed by Fahmi et al. (2008). Ash, especially high alkali metals, acts as catalyst promoting vapour cracking, thus, decreasing the liquid yield (Nik-Azar et al., 1997). Additionally, the catalytic effect of the ash becomes stronger when above 1.5% (Agblevor et al., 1994).
Figure 7.4 Liquid yield calculated vs liquid yield experimental for Kraft lignin-birch wood mixtures and H-lignins

Figure 7.5 shows the effect of ash content on the liquid yield relative to pyrolysis of different H-lignins. The purpose is to give an idea of the liquid yield that could be achieved if these feedstocks were pretreated through de-ashing. This speculation should be proved experimentally, since the synergistic effects are numerous and the ash composition influences the reactions. For instance, it is reported that potassium and sodium have a stronger catalytic effect than calcium on cracking reactions (Nik-Azar et al., 1997). Additionally, the ratio between the primary lignin monomers varies among different types of biomass (Azadi et al., 2013). Therefore, for lower ash content, the synergistic effects and their potential dependence on species plant morphology (George et al., 2014) are expected to have a more significant role.

The ash can be reduced by washing the biomass before pyrolysis. However, this treatment removes some of the cellulose and hemicellulose through hydrolysis, which results in lower biooil yields and quality (Bridgwater, 2012).
Figure 7.5 Effect of ash content on the calculated liquid yield for different H-lignins

Figure 7.6 shows the bubble plots obtained from GC×GC-TOFMS (see section 2.6.5) for the bio-oils produced from different H-lignins. Bubble plots provide a quick way to identify differences between bio-oils. In chapter 6, major differences between 0% and 100% Kraft lignin could be easily detected, but for these samples it is quite difficult to speculate about differences.
Figure 7.6 GCxGC-TOFMS Bubble plot representations of the composition of bio-oils from
a) Aspen wood, b) Sugarcane bagasse, c) Wheat straw and d) Napier grass

Figure 7.7 shows the phenolics relative area (alkylphenols, guaiacols, catechols and syringols) in terms of GCxGC-TOFMS relative abundance of the bio-oils produced from H-lignins compared to the correlation found for bio-oils produced from Kraft lignin and birch wood mixtures. Bio-oils from aspen wood and sugarcane bagasse H-lignins have the same relative area of phenolics. These feedstocks are characterized by same amount of lignin, thus, the different origin of the H-lignin does not seem to have a significant effect on the relative abundance of these compounds. Also the ash content, which showed to have a major effect on the liquid yield, did not affect the conversion to this kind of products. All the bio-oils produced from H-lignin of different origins are more or less described by the correlation found for Kraft lignin and birch wood mixtures. It seems that the phenolics concentration, in terms of relative abundance, is not significantly affected by the origin of the lignin or its extraction process.
Figure 7.7 GCxGC-TOFMS phenolics relative area

Figure 7.8 shows slight differences between the bio-oils obtained from H-lignins in the alkylphenols, guaiacols, catechols and syringols relative area in terms of GCxGC-TOFMS relative abundance. These differences are most likely due to the characteristics of the native lignin. The difference is more significant between H-lignins and Kraft lignin. In fact, all the H-lignins studied produced bio-oils with higher relative area of alkylphenols than guaiacols, whereas the opposite result was obtained with Kraft lignin.

Guaiacols and syringols are produced in the first pyrolysis stage, whereas alkylphenols and catechols are guaiacol-type compounds derivatives produced by secondary cracking reactions (Shen, 2011). Alkylphenols have higher relative area than guaiacols in the bio-oils produced from H-lignins, which could be explained by the presence of residual carbohydrates in the H-lignins tested and by the reaction of the primary products with ashes. As expected, guaiacols were predominant over syringol-type compounds (Shen, 2011).

Aspen is classified as hardwood, whose lignin is known to have mostly guaiacyl and syringyl-based monomers (Obst, 1982), while all the monomers (guaiacyl, syringyl and p-hydroxyphenyl) exist in grass lignin (Li et al.; 2014), sugarcane bagasse (Lopes et al., 2011) and wheat straw.
The higher relative abundance of syringols compared to the other H-lignins might be due to the composition of native lignin in aspen wood. Monolignols were found only in small amounts since the lignin tested was exclusively separated lignin (Evans et al. 1986).

![Graph showing the relative abundance of alkylphenols, guaiacols, catechols, and syringols in bio-oil from H-lignins produced from aspen wood, sugarcane bagasse, wheat straw, Napier grass, and Kraft lignin.]

**Figure 7.8 Relative abundance of alkylphenols, guaiacols, catechols and syringols in bio-oil from H-lignins produced from aspen wood, sugarcane bagasse, wheat straw, Napier grass and Kraft lignin**

### 7.4 Conclusions

Hydrolysis lignins from different origins were compared to Kraft lignin. Their processability during pyrolysis was much better than for Kraft lignin. They were characterized by higher ash content than Kraft lignin and birch wood mixtures, which showed to have higher impact on the liquid yield than the lignin content does.

Moreover, they contain quite a high amount of cellulose and hemicellulose residue, resulting in a lower phenolics relative abundance in the final liquid product than in pure Kraft lignin bio-oil.

The proportion of alkylphenols, guaiacols, catechols and syringols presents some difference among hydrolysis lignins and even more when compared to Kraft lignin. When single classes of
compounds are considered, lignin origin and isolation process seem to play a more important role than lignin content.
Chapter 8

8. Modelling the mixing of a Mechanically Fluidized Reactor

8.1 Introduction

This chapter models the mixing in the MFR when the vertical blades stirrer is adopted. A detailed experimental study of mixing in a MFR is difficult due to the presence of the stirrer which does not allow for access to the reactor through the wall. It is difficult to monitor the progress of the mixing. Non-intrusive techniques are expensive and they are complex to be developed given the presence of the stirrer. Therefore, the Discrete Element Method was used to simulate the bed material and the biomass particles behavior when mixed by a vertical blades stirrer. Biomass, when pyrolysis occurs, tends to flow upward. The feeding into the reactor is done through the top of the reactor, thus, the stirrer needs to push the biomass downward in order to provide enough heat transfer from the hot bed particles to the biomass particles.

The following is undertaken:

I. Experimental determination of the parameters needed for the simulation
II. Simulation of the mixing provided by the selected stirrer

The determined parameters were the restitution coefficient, friction coefficient, Young modulus and particle density.

This study is meant to be the first step towards understanding the mixing behaviour of the MFR during pyrolysis.

8.2 Materials and methods

The commercial software EDEM 2.5.1 (DEM Solutions Ltd., Edinburgh) was used to simulate the mixing in the MFR. In order to model this process with a Discrete Element Method, the generation of vapours and gas during pyrolysis was not considered in this study. The description of the Discrete Element Method implemented in this software can be found in section 2.7.
This method requires the evaluation of some parameters. The majority of them were analyzed as illustrated in sections 2.7.1-2.7.4. Glass beads with a diameter 3000 μm instead of 375 μm were simulated in order to have a number of particles that could be reasonably simulated with this software. These were used also to measure the restitution coefficients and the Young modulus, since the measurement of these properties for 375 μm glass beads was not possible. Biomass particles were assumed to be spherical since this software does not allow the generation of cylindrical particles.

The time step used in the simulation was 2e-06 s. The computer runtime for one case was approximately 6 days. The values of the parameters used in the simulation are reported in table 8.1, 8.2 and 8.3. The geometry of stirrer, vessel and lid is reported in figure 8.1.

Table 8.1 Geometry and particles parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel diameter (m)</td>
<td>0.15</td>
</tr>
<tr>
<td>Vessel height (m)</td>
<td>0.25</td>
</tr>
<tr>
<td>Number of glass beads</td>
<td>96000</td>
</tr>
<tr>
<td>Number of biomass particles</td>
<td>40</td>
</tr>
<tr>
<td>Stirrer speed (rad/s)</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>153</td>
</tr>
</tbody>
</table>

Table 8.2 Materials characteristics

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (kg/m³)</th>
<th>Shear modulus (GPa)</th>
<th>Poisson ratio</th>
<th>Diameter (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass beads</td>
<td>996</td>
<td>0.22</td>
<td>0.2</td>
<td>0.003</td>
</tr>
<tr>
<td>Biomass</td>
<td>1452</td>
<td>0.03</td>
<td>0.5</td>
<td>0.005</td>
</tr>
<tr>
<td>Steel</td>
<td>8000</td>
<td>76.9</td>
<td>0.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 8.3 Parameters relative to pairs of materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Friction coefficient</th>
<th>Restitution coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Static</td>
<td>Rolling</td>
</tr>
<tr>
<td>Glass beads-Glass beads</td>
<td>0.66</td>
<td>0.05</td>
</tr>
<tr>
<td>Glass beads-Steel</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td>Biomass-Biomass</td>
<td>0.39</td>
<td>0.002</td>
</tr>
<tr>
<td>Biomass-Steel</td>
<td>0.22</td>
<td>0.001</td>
</tr>
<tr>
<td>Biomass-Glass beads</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Glass beads were generated inside the reactor and mixed for 1.36 s before introducing biomass. The following discussion considers the time when the biomass generation was completed (1.36103 s) as the initial time (t = 0). Biomass particles were generated in the top part of the reactor in a cylindrical volume with diameter 0.025 m, as the feeder used in the experimental tests, and height 0.03 m.
8.3 Results and discussion

Figures 8.2 and 8.3 show the velocity profile in different sections of the bed. Higher velocities are reached close to the wall and the velocity of particles decreases going towards the core of the reactor. In the part of the bed close to the central shaft, a dead zone can be observed. The section orthogonal to the x direction shows the profile of a vortex, which was noticed also by visual observation. The velocities at the periphery of the reactor show to be higher in the section perpendicular to the x axis because at that time the stirrer was placed orthogonal to this direction, thus, the blades are transferring energy to the particles in their path, while in the section perpendicular to Y axis, the energy is already somewhat dissipated.

![Figure 8.2 X and Y section view of the bed velocity at 0.26 s](image)

Some snapshots of sections perpendicular to the Z axis are shown in figure 8.3. The highest velocity is reached at the periphery and is more homogeneous along the circumference at the top of the reactor. The velocity close to the wall decreases going towards the bottom while the portion characterized by medium velocity starts prevailing in this direction. Also the poorly agitated zone near the central shaft becomes wider from the top view to the section at 0.02 m from the bottom.
Figure 8.3 Sections of the bed at different heights (a) 0.25 m, (b) 0.15 m, (c) 0.10 m, (d) 0.08 m and (e) 0.02 m at 0.26 s

Figure 8.4 shows snapshots of the biomass particles position at 0.26, 1.14 and 2.34 s. In the first snapshot, biomass particles have just been injected into the bed, in the second one they are progressively going towards the bottom of the reactor and the last one is more representative of the steady state regime. The particles look well distributed throughout the bed. Although, they do not reach the very bottom of the reactor, this type of stirrer pushes them towards the bottom. This is very important in the pyrolysis process, because, in the absence of suitable mechanical mixing, biomass particles tend to rise while reacting, because of gas and vapours evolution. Therefore, in order to maximize the heat transfer between biomass and glass beads, the stirrer needs to provide downward axial mixing. Additionally, the coloring shows a higher velocity at the beginning of the process and while the biomass starts going downward, its velocity somewhat decreases, but it never reaches stagnant zones. Therefore, there is no segregation.
Figure 8.4 Frontal view of the axial distribution of biomass particles over time

Figure 8.5 shows the average particle position in the z direction as a function of time after injection of the biomass particles. The glass beads are more concentrated in the bottom part of the vessel. Their average position on the z direction is about 0.08 m from the bottom. Biomass particles take about 2 seconds, around 5 rotations of the stirrer, to reach the final average position at around 0.10 m from the bottom.

Figure 8.5 Average axial position of biomass particles over time (z = 0 m: bottom of the bed, z=0.23 m: average height where the biomass particles were generated)
Figure 8.6 shows how the number density distribution of the biomass particles changes throughout the height over time. It can be observed that the particles are represented by one major peak right after their injection, afterwards they start falling toward the bottom while they spread over the height and finally they are represented by a lower and wider distribution with the left tail almost reaching the bottom.

Figure 8.6 Biomass particle number density distribution over time

The top view of the reactor over time is shown in figure 8.7. Biomass particles are not yet well distributed over the circumference after 0.26 s, they are spreading at 1.14 s and at 2.34 s they are better distributed. However, they are not homogeneously distributed in radial direction, as shown in more detail in figures 8.8 and 8.9. The segregation of large particles to the wall was reported also by Conway et al. (2005). Experimental tests with smaller bed particles did not result in this kind of behaviour. The formation of avalanches that folded over biomass particles, thus helping the axial mixing, was observed. Additionally, this simulation does not account for the generation
of vapors from biomass particles, which results in lighter particles that would not be moved as far towards the periphery of the vessel.

Figure 8.7 Top view of the distribution of biomass particles over time

Figure 8.8 Average biomass particles radial position over time
Figure 8.9 Biomass particle radial number density distribution over time

Figure 8.10 shows the vertical velocity of biomass particles. Their velocity first increases when they are dropped inside the reactor and when they settle on the glass beads bed, it starts slowing down. It becomes almost constant for a few milliseconds because the biomass particles are on the crest heap. After less than one rotation of the stirrer they move away from the blade, down the surface of the heap, which can be observed in figure 8.10 when the velocity increases again. Biomass particles settle on the glass beads which in the simulation do not fold over them as an avalanche, while the actual glass beads used in the experimental apparatus were observed to form avalanches in front and behind the scraper blade sliding inward. This behaviour was observed also by Conway et al. (2005) with a four-bladed mixer with 45° radial pitched blades; though in the present study the blades are axial. The smaller glass beads used in the experimental tests exceed their angle of stability and the avalanche occurs (McCarthy et al., 1996) while the glass beads simulated, which are one order of magnitude bigger, do not.
The collision rate between biomass and glass beads is shown in figure 8.11. Interactions between biomass and glass beads increase significantly over 2.5 s. Mostly the increase occurs during the second rotation of the stirrer (0.6 – 1 s), when the particles start making their way towards the bottom and their average axial position is between 0.14 and 0.12 m from the bottom. It can be observed that also the velocity decreases in this time interval because of the increased number of collisions (Figure 8.10). Nearly steady-state conditions with collision rate of about 160 000 s\(^{-1}\) are achieved after 2 s (5 rotations of the stirrer), as it was shown also in terms of vertical position of the particles in the bed (Figure 8.5).
Figure 8.11 Collision number between biomass-glass beads and biomass-vessel over time

8.4 Conclusions

The mixing provided by the vertical blades stirrer was simulated by means of a Discrete Element Method model. The results showed that this type of stirrer gives adequate axial mixing, which is a very important point during pyrolysis reaction, given that, in the absence of suitable mechanical mixing, biomass particles tend to rise while reacting, because of gas and vapours generation. Additionally, the vertical blades stirrer moved the biomass particles toward the bottom quite quickly and no biomass segregation was observed.

In this simulation some differences from the visual observations in the experiments were found, suggesting that parameters still need to be adjusted in order to simulate more realistically the MFR mixing during pyrolysis. Additionally, this simulation did not account for the generation of pyrolytic vapors and gas, which are expected to affect significantly the mixing pattern.
9. Conclusions and Recommendations

This chapter summarizes the overall conclusions and recommends future work based on the findings of the present thesis.

9.1 Conclusions

Lignin is more recalcitrant to thermal depolymerization than other lignocellulosic feedstocks. Kraft lignin is a by-product of the Kraft process and it is currently burned within the process to produce electricity and steam. Kraft lignin is a potentially valuable feedstock given its aromatic character. Pyrolysis technologies have been developed and optimized for other types of biomass, such as wood, and are not suitable to process Kraft lignin. Therefore this work developed new technologies optimized for this feedstock.

A Mechanically Fluidized Reactor (MFR) was developed to process Kraft lignin. A technique to determine the performance of the process was first investigated with the objective of optimizing this process both in terms of technology and operating conditions. Three stirrers were compared by means of this technique and the vertical blades stirrer was found to be the most suitable for pyrolysis of biomass. The vertical blades stirrer distributes the biomass pellets to the bottom region of the bed, where the pyrolytic gases and vapors are generated, greatly reducing the required power for mixing. The vertical blades stirrer also minimizes the time for complete pyrolysis by promoting better heat transfer between the biomass pellets and the hot bed material.

A preliminary study simulated the mixing provided by the vertical blades stirrer by the Discrete Element Method. The simulation confirmed that the vertical blades stirrer quickly moves the biomass particles toward the bottom of the bed. This is a very important characteristic, since biomass particles would otherwise tend to rise during pyrolysis reactions because of the generation of gas and vapours.

The Mechanically Fluidized Reactor is suitable for Kraft lignin pyrolysis. However, the formation of a sticky intermediate phase which tends to agglomerate the bed material was observed, confirming the effect of temperature on Kraft lignin that was observed in other studies.
Different bed materials were tested with the purpose of improving Kraft lignin processability by decreasing its stickiness. Activated carbons of different size and origin improved Kraft lignin processability. However, their catalytic effect was too strong leading to a very watery bio-oil.

Feedstocks with different proportions of lignin were investigated in order to observe its effect on processability, and on liquid yield and chemical composition. For lignin contents below 60 wt%, there are no processability issues during the pyrolysis process. The liquid yield decreases with increasing lignin and ash content. The relative abundance of phenolic compounds in the bio-oil increases linearly with the lignin content. However, the relative abundance of specific classes of phenolics (alkylphenols, guaiacols, catechols and syringols) is greatly affected by lignin morphology, which depends on its origin and isolation procedure.

### 9.2 Recommendations

The development of a continuous feeder and char removal system for the MFR is recommended. As a result of having a continuous system, testing would be faster. Additionally, the system could be brought to steady-state regime and then operating conditions could be adjusted to observe how the process responds. Moreover, a continuous system could be more easily commercialized both for research and business purposes.

Testing of other porous materials is also recommended. Not only can lignin processability be improved with the appropriate bed material, but also the power consumption would decrease.

Quantification of phenolics in terms of actual yield on biomass basis should be performed if the objective is to increase the productivity of specific classes of compounds. About 90 different phenolics were detected in the bio-oils analyzed, but the purpose of this study was only to determine how lignin content affects their total concentration.

DEM modelling is a very powerful tool to study solid particulate. This thesis presents only a preliminary study using this type of simulation, but further experimental testing is necessary in order to adjust the parameters used in this simulation and develop a more realistic model of the MFR. Additionally, in the present work, the pyrolysis reactions were not taken into account, although the evolution of gas and vapours is expected to have a great impact on the mixing. It is, thus, recommended to couple DEM and CFD in order to simulate also the gas phase. Moreover,
a simulation of the mixing with the spiral and paddles stirrer would be very interesting to
determine whether modeling can predict the advantages and drawbacks of differently shaped
stirrers.
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Appendix A

A. Kraft Lignin Pyrolysis in a Fluidized Bed Reactor

This appendix section is a published presentation from the International Conference on Thermochemical Conversion Science (tcbiomass 2011) in Chicago, Illinois, USA. The authors were Pietro Palmisano, Federico M. Berruti, Valentina Lago, Franco Berruti, and Cedric Briens. The presentation illustrates the agglomeration occurring during pyrolysis of Kraft lignin in a fluidized bed reactor, which was controlled by breaking the char agglomerates with a mechanical stirrer placed on the bottom of the reactor.

Appendix B

B. Catalytic cracking of bio-oil and vapors to maximize the production of aromatics and phenolics

B.1 Abstract

This review provides an overview of the research on catalytic upgrading of bio-oil for the production of aromatics and phenolics.

Numerous parameters influence the concentration of these high value compounds in the final liquid product. Therefore, collaborative research and unified analytical methods are required in order to compare different studies.

The main reaction mechanisms involved in this process and currently identified are described. The concentration of aromatics and phenolics obtained with zeolite catalysts and metal oxides are reported and compared in order to highlight the research gaps that need to be addressed to better understand the process. However, based on the current literature, a correlation between characteristics of the catalyst, reaction conditions, technology scale, type of feedstock and selectivity towards aromatic hydrocarbons and phenols is not clear yet.

Further research and more sophisticated catalysts are needed to improve this process and develop a marketable technology.

B.2 Introduction

The production of renewable fuels and chemicals from biomass has lately been boosted because of the increasing concerns about environmental protection, climate change and sustainability of natural resources. Bio-oil deriving from the thermochemical conversion of biomass has been shown to have some undesired characteristics (instability, corrosiveness, acidity, etc.) which limit its application for transportation fuels (Berni et al., 2013). Therefore, many studies focused on methods to increase the concentration of valuable chemicals present in the bio-oil to make their production and extraction economically feasible. Aromatic hydrocarbons and phenolics compounds are among the most abundant and valuable products contained in pyrolysis bio-oils.
Aromatic hydrocarbons, such as BTX, are very important products and building blocks in the petrochemical sector. Phenols are used in the production of phenol-formaldehyde resins, pharmaceuticals, dyes, food and fragrances (Roy et al., 2000; Pakdel et al., 1997).

There are two main pathways to catalytically upgrade pyrolysis bio-oils: catalytic cracking and hydrodeoxygenation (HDO). HDO, which leads to a naphta-like product, requires high pressure and high amounts of hydrogen (100-200% stoichiometric excess) (Bridgwater, 1996). The research about this treatment has the objective of minimizing the amount of hydrogen needed (Ruddy et al., 2014). Currently, this process needs further investigation because bio-oil cost, capital cost and hydrogen cost are to be minimized relatively to the product value (Elliot and Neuenschwander, 1996). Dynamotive (DYMF) and IFP Energies Nouvelles developed a two stage hydroprocessing process called BINGO (Radlein and Quignard, 2013). The first stage is a hydroreforming process with low consumption of hydrogen. The bio-oil partially upgraded in this step is more stable, miscible with hydrocarbons, less viscous, less corrosive and its oxygen content is reduced from about 50 wt% to less than 15 wt%. The hydroreforming step can be combined with conventional refinery processes such as hydrotreatment and/or hydrocracking in order to convert the partially upgraded bio-oil into motor fuel grade products (Radlein, 2013). Although the H₂ consumption is minimized and this process uses as mild conditions as possible, it has been demonstrated only at lab scale. Therefore large scale economic conclusions about this process cannot be drawn yet.

Catalytic cracking seems to be promising over hydrodeoxygenation because it needs moderate operating conditions and no hydrogen is required (Bridgwater, 1996). However, cracking catalysts are deactivated by coke deposition faster than HDO catalysts (Mortensen, 2011) and, consequently, lower yields are typically observed (Srinivas et al., 2000). Catalytic cracking processes cannot produce fuels of high quality, but they can produce a liquid product with high concentration of high-value compounds, which then need to be separated.

Furthermore, pyrolysis vapors can be upgraded by in situ catalytic fast pyrolysis or by ex situ catalytic cracking of pyrolysis vapors or bio-oil. Yildiz et al. (2013) report that in situ catalysis typically performs much better than the ex situ mode. However, the ex situ mode requires less catalyst. According to Ruddy et al. (2014), the ex situ mode can be used for a better
understanding of the reactions involved and the findings can be used to improve the in situ approach. The economic analysis of both options can then be compared. The coupling of pyrolysis and catalysis reactions requires more sophisticated catalysts, able to withstand higher temperatures and mechanical stress (Bridgwater, 2012). Furthermore the upgrading kinetics are slower than the pyrolysis ones, therefore decoupling them appears to be a better option. Biomass, when compared to petroleum feedstocks, is considered to be a low effective hydrogen-to-carbon ratio feed, but bio-oils are characterized by a higher value of this parameter than carbohydrates, since pyrolysis reactions remove part of the oxygen from biomass (Corma et al., 2007). The advantage of the ex situ upgrading over the in situ is also that it increases the catalyst life by reducing the coking of the catalyst (Huber and Corma, 2007; Lappas et al., 2012). Moreover, in the in situ catalytic pyrolysis, the char cannot be separated from the catalyst, since the char incorporates it. Char is a potentially high value product for the production of activated carbon, but, in the case of catalytic pyrolysis, it can only be burned to produce heat during the regeneration of the catalyst.

This review aims at providing a comprehensive overview of the studies on bio-oil and pyrolysis vapours cracking, focusing on the performance of various catalysts to yield aromatic hydrocarbons and phenolics. Special attention has been given to zeolite catalysts, both micro and mesoporous, and to metal oxides. The literature provides reviews about the reaction mechanisms involved in catalytic cracking and states that the characteristics of the catalyst, the reaction conditions, the technology scale and the type of feedstock influence the diverse reactions. The current knowledge about this technology does not allow developing a correlation between these parameters and the bio-oil composition because of the variability of the parameters involved in this process. This paper has the purpose of gathering the available data regarding these parameters with the relative yield of the valuable compounds mentioned above, in order to simplify the identification of the most promising conditions.

B.3 Bio-oil feedstock characteristics

Bio-oil is a dark-brown free-flowing liquid composed of polar organics and water (Bridgwater et al., 1999). More than 300 compounds have been found in bio-oil. Its composition is very variable and it is strictly dependent on the biomass and on the operating conditions (Zhang et al., 2007).
Bio-oil is characterized by 10-40% oxygen, high water content, high corrosivity and thermal instability which make it unsuitable in applications as fuel.

Chemically, bio-oil is a complex mixture of water, acids, alcohols, aldehydes, esters, ketones, phenols, guaiacols, syringols, sugars, furans, alkenes, aromatics, nitrogen compounds and miscellaneous oxygenates.

Water in bio-oil results from the original moisture in the feedstock, which breaks the biomass structure and then evaporates, and it is also a product of the dehydration reactions occurring during pyrolysis (Mohan et al., 2006). Therefore, the water content varies over a wide range (15-30%) depending on the feedstock and process conditions (Czernik and Bridgwater, 2004).

Typical bio-oil yields from fast pyrolysis of biomass are 60-75 wt%, depending on the composition of the feedstock. High lignin contents usually mean lower liquid yield, but higher energy density. An average high heating value of the bio-oil is 17 MJ/kg (Mohan et al., 2006).

Many compounds present in the bio-oil offer promising potential. Aromatics and phenolics are likely the most valuable components. Benzene, toluene and xylene are important chemicals and key building blocks used in the petrochemical sector. Phenolic compounds are also important in the chemical industry, specifically for the production of phenol-formaldehyde resins, pharmaceuticals and food additives (Jeon et al., 2013). Many studies have been focusing on optimizing the selectivity of the reactions leading to the production of these compounds.

**B.4 Reaction mechanisms for the production of aromatics and phenols from bio-oil**

Catalytic cracking is a process widely used in petroleum refineries to convert complex hydrocarbons into various chemicals in the gasoline pool (Zakzeski et al., 2010). Furthermore, it is an effective deoxygenation process where oxygen is removed as CO₂ (Augustínová et al., 2013) through numerous pathways, which not always lead to the desired products.

Catalytic cracking of pyrolytic bio-oil has been considered by a number of investigators since it requires mild operating conditions, relatively inexpensive catalysts and does not require
additional reagents. A number of studies investigated the mechanisms involved in this process, with the objective of improving the synthesis of aromatics and phenolics.

Corma et al. (2007) proposed a reaction scheme based on a study on catalytic cracking of some model compounds over zeolites. They reported that the production of aromatics results from a combination of dehydration, hydrogen producing and hydrogen-transfer reactions. Figure B.1 shows the hydrogen producing and consuming reactions starting from glycerol proposed in their work. The first mechanism leads to the formation of CO, CO$_2$, graphitic coke and H$_2$ and then hydrogen can be consumed through the second one. According to this reaction scheme, aromatics are produced by aldol condensation and Diels-Alder condensation of olefins (Corma et al., 2007; Gayubo et al., 2004b). The hydrogenation reactions are known to usually occur on metal surfaces and also with acid catalysts via reaction between a carbenium ion and molecular hydrogen. Hydrogen-transfer reactions occur as long as a hydrogen source is present. The aromatics yield strongly depends on what pathway the oxygen is removed through. Analysis on the theoretical maximum yield can be found elsewhere (Corma et al., 2007) and it explains why the coke formation has to be minimized in order to maximize the production of aromatics. Potentially coke can derive from the volatile oxygenated compounds, the dehydrated species or the aromatic molecules (Carlson et al., 2009).
Carlson et al. (2011) reports that the anhydrosugars can produce furans, smaller aldehydes and water through dehydration and re-arrangement reactions in either the gas phase or in the presence of a catalyst. These reaction intermediates then diffuse into the zeolite catalyst pores and undergo decarbonylation, decarboxylation, dehydration, and oligomerization to form both monocyclic aromatics and olefins. The formation of aromatics is accompanied by the formation of coke which occurs through the polymerization of furans ad it represents the major competing reaction. The aromatic formation reaction proceeds through a common intermediate within the zeolite catalyst. The polycyclic aromatics are formed in subsequent reactions between aromatics and other oxygenates (figure B.2).
Gayubo et al. (2004a,b) carried out a comprehensive study where they investigated the reaction pathways of aldehydes, ketones, acids, alcohols and phenols with bio-oil model compounds over HZSM-5. These authors report that, in the transformation of 1-propanol and 2-propanol (figure B.3), aromatics, mainly toluene and xylenes, occur in low proportion above 310 °C. Above 400 °C the amount of aromatics remains constant because of their cracking to lighter compounds. However, above 400 °C the aromatics concentration increases with increasing the space time.

It is reported that phenols are not significantly reactive on HZSM-5 and their main product is coke. Gayubo et al. (2004a) suggested to separate the phenolic fraction before treating bio-oil with zeolites. Bertero and Sedran (2013) report the main products of catalytic conversion of phenol and syringol being mostly olefinic.
According to Gayubo et al. (2004b), aldehydes are not very reactive over this catalyst and they form high amount of thermal coke. For this reason, they suggested to separate most of them leaving a residual maximum concentration of about 3.6 wt% per unit mass of components.

Ketones model compounds considered in their study were acetone and butanone. The acetone reaction mechanism illustrated in figure B.4 starts producing aromatics among other compounds above 350°C. The concentration of aromatics is very much influenced by blockage of acid sites by coke which affects aromatization, oligomerization of light olefins and cracking to C5+ olefins. Butanone (figure B.5) is completely converted at 450°C with a high concentration of aromatics. C5+ olefins increase with increasing the space time and their formation is followed by cracking and Diels-Alder condensation producing aromatics. The results show that at 400°C the production of aromatics is affected by coke deactivation.

As far as acids are concerned, the behavior of acetic acid was investigated (Gayubo et al., 2004b). Above 400°C it forms acetone thanks to an autocatalytic effect and it is completely converted for lower space time than the one required by ketones. In turn, acetone would produce...
aromatics as discussed earlier, and their concentration would decrease with decreasing the time on stream.

Amen-Chen et al. (2011) conducted a thorough review on the thermochemical reactions for the production of monomeric phenols. They report that the reaction mechanism leading to the formation of phenols arises from the dehydration of the alkyl chain of the phenylpropane unit, which composes lignin. The reaction proceeds with the cleavage of interaromatic bonds (figure B.6).

![Lignin pyrolysis mechanism](image)

**Figure B.6 Lignin pyrolysis mechanism (Adapted from Evans et al. 1986)**

Chantal et al. (1985) report on the catalytic conversion results of phenolic compounds over HZSM-5 in presence of water and methanol. They report the conversion of phenol to be higher in presence of methanol than in presence of water, mostly due to the higher production of
alkylated phenols. However these compounds are abundant also among the products of the reaction of phenol in presence of water. Benzene and syringol were found in higher concentration among the products of the reaction in presence of methanol, but they were produced in lower amount also when phenol was fed with water. The reaction in presence of water resulted in lower production of coke. The conversion of syringol is reported to be lower than that of phenol, which is explained with the lower diffusion rate into the HZSM-5 structure of the former. Phenol and alkyl phenols were found to be the predominant products of syringol reaction both in methanol and water. Also aromatics were present. Methylated phenols showed a lower conversion than phenol and similar formation of coke. The most important products in the reaction of eugenol and isoeugenol are alkyl phenols, which are very important products also in the reaction of guaiacol in presence of methanol.

B.5 Catalysts for the production of light phenols and light aromatics

It has been reported that the aromatics yield can be increased by using catalysts with a high concentration of Brønsted acid sites. This type of catalyst can catalyze the oligomerization of short chain olefins to form longer chain olefins, which produce dienes by dehydrogenation reactions. The reaction proceeds through cyclization and dehydration resulting in aromatics (Park et al., 2010b; Lee et al., 2011). Some of the aromatic hydrocarbons can polymerize to form coke (Vitolo et al., 1999).

Acidity, pore size and surface area are very important factors for the production of light phenols and aromatics (Mortensen et al., 2011). As already mentioned above, also the feedstock, the scale of the technology, the amount of catalyst and the operating conditions influence the final liquid product composition and the yield. The absence of a unique correlation between these parameters and the concentration of aromatics and phenolics, does not imply that is impossible to determine one, but only that many gaps are present and need to be filled up in order to have a more organized and complete overview of the mechanisms involved. Tables B.1 and B.2 gather most of the literature about this topic and have the objective of providing the reader with a better idea about the knowledge gaps. Often the results are reported in different terms and, therefore, they cannot be directly compared. For this reason table B.1 shows the results of aromatics and phenolics concentration in terms of wt%, whereas table B.2 shows these values in terms of
GC/MS peak area %. For comparison, table B.3 reports the results of the blank runs when performed. Moreover, table B.4 summarizes the characteristics of the different catalysts and table B.5 the type and scale of the technology.
Table B.1 Quantitative analysis of aromatics and phenolics – effect of temperature, feedstock and catalyst

<table>
<thead>
<tr>
<th>Authors</th>
<th>T (°C)</th>
<th>Feedstock</th>
<th>Catalyst</th>
<th>Aromatics (wt% of organic fraction)</th>
<th>Phenols (wt% of organic fraction)</th>
<th>Liquid yield (wt% on feedstock basis) (water content (wt% on bio-oil basis))</th>
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<tr>
<td></td>
<td>T&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
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<td>Adam et al. 2006</td>
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<td>Phenols (wt% of organic fraction)</td>
<td>Liquid yield (wt% on feedstock basis) (water content (wt% on bio-oil basis))</td>
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<td>T&lt;sup&gt;c&lt;/sup&gt;</td>
<td>a</td>
<td>b</td>
<td>c</td>
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<td>48.1-40.8</td>
<td>6.6 15.2 9.1 45.4 (50) 46.2 (25.2)-44.4 (26) 49.2 (25)</td>
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<td>30.1</td>
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<td>2.1</td>
<td>9.1</td>
<td>50.1 (67.3)</td>
</tr>
</tbody>
</table>

a – Conditions for maximum aromatics concentration  
b – Conditions for maximum phenolics concentration  
c – Conditions for maximum liquid yield  
d – Hydrocarbons, not only aromatics  
e – On dry lignin basis  
f – On dry lignin basis, benzenes included in phenolics, but they are a very small percentage  
g – Temperature of reactor 1  
h – Temperature of reactor 2
### Table B.2 GC/MS area % of aromatics and phenolics - effect of temperature, feedstock and catalyst

<table>
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<th>Phenols (area %)</th>
<th>Liquid yield (wt%) (water content wt% on bio-oil basis)</th>
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<td></td>
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<td>Vitolo et al. 1999</td>
<td>490</td>
<td>Canadian Oak bio-oil</td>
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a – Conditions for maximum aromatics concentration  
b – Conditions for maximum phenolics concentration  
c – Conditions for maximum liquid yield  
d – GC/MS peak area provided only for most abundant compounds  
e – Hydrocarbons, not only hydrocarbons  
f – The authors provided only the total GC/MS peak area
Table B.3 Blank runs - concentration of aromatics, phenolics and liquid yield

<table>
<thead>
<tr>
<th>Authors</th>
<th>T (°C)</th>
<th>Biomass</th>
<th>Aromatics</th>
<th>Phenolics</th>
<th>Liquid yield (wt%) (water content, wt% on bio-oil basis)</th>
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</thead>
<tbody>
<tr>
<td>Adam et al. 2006</td>
<td>500</td>
<td>Barkless spruce wood milled, moisture 6%</td>
<td>0.7 wt%</td>
<td>18.9 wt%</td>
<td>35 (49.7)</td>
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<tr>
<td>Adjaye et al. 1996</td>
<td>525</td>
<td>Maple wood</td>
<td>5.6 wt%</td>
<td>10.9 wt%</td>
<td>74 (21)</td>
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<tr>
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<td>Pinus sylvestris sawdust</td>
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<td>15.12e+7b</td>
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<td>Choi et al. 2012</td>
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<td>Alcell lignin</td>
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<td>22.6 wt%</td>
<td>49.6</td>
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<td>-</td>
<td>25.1 wt%</td>
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<td>Organosolv lignin</td>
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<td>560</td>
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<td>-</td>
<td>24.8 wt%</td>
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<td>470</td>
<td>Kraft lignin</td>
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<td>Beech wood</td>
<td>~7 wt%</td>
<td>17.5 wt%</td>
<td>46.2 (54.6)</td>
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<td>Iliopoulou et al. 2012</td>
<td>500</td>
<td>Beech wood</td>
<td>0.06 area%</td>
<td>29.25 area%</td>
<td>58.67 (36.2)</td>
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<tr>
<td>Jeon et al. 2012</td>
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<td>Rice husk</td>
<td>&lt;1 area%</td>
<td>~27 area%</td>
<td>7.8e+9c</td>
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<td>500</td>
<td>cellulose</td>
<td>0</td>
<td>traces</td>
<td>-</td>
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<tr>
<td></td>
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<td>xylan</td>
<td>traces</td>
<td>~4 area%</td>
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<td></td>
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<td>lignin</td>
<td>traces</td>
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<td>Kaewpengkrow et al. 2014</td>
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<td>Jatropha wastes</td>
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<td>lignin</td>
<td>~2 area%</td>
<td>55.3 area%</td>
<td>~25</td>
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<td>Li et al. 2008</td>
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<td>Lu et al. 2009</td>
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<td>Cottonstraw</td>
<td>0.45 area%d</td>
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<td>Lu et al. 2010a</td>
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<td>Poplar wood</td>
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<td>Lu et al. 2010c</td>
<td>500</td>
<td>Poplar wood</td>
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<tr>
<td>Authors</td>
<td>T (°C)</td>
<td>Biomass</td>
<td>Aromatics</td>
<td>Phenolics</td>
<td>Liquid yield (wt%) (water content, wt% on bio-oil basis)</td>
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<td>500</td>
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<td>~41 area%</td>
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<td>Srinivas et al. 2000</td>
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<td>the initial biomass, moisture 21%</td>
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<td>Triantafyllidis et al. 2007</td>
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<td>17.49 wt%</td>
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<sup>a</sup> – on dry lignin basis  
<sup>b</sup> – GC/MS peak area  
<sup>c</sup> - total GC/MS peak area  
<sup>d</sup> – hydrocarbons, not only aromatics
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<th>Authors</th>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
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<th>Si/Al</th>
<th>Pore volume (cm³/g)</th>
<th>Total acid sites (mmol NH₃/g)</th>
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<td>Ce/ZrO₂</td>
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<tr>
<td></td>
<td>Ni/Ce/ZrO₂</td>
<td>11.61</td>
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<td>-</td>
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</tr>
<tr>
<td>Authors</td>
<td>Catalyst</td>
<td>Surface area (m²/g)</td>
<td>Pore size (nm)</td>
<td>Si/Al</td>
<td>Pore volume (cm³/g)</td>
<td>Total acid sites (mmol NH₃/g)</td>
</tr>
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<tr>
<td>Kaewpengkrow et al. 2014</td>
<td>Rutile</td>
<td>4.15</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>Ce/Rutile</td>
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<td>Pd/CE/Rutile</td>
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<td></td>
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<td>3.48</td>
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<td></td>
<td>Ni/CE/Rutile</td>
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<td>Anatase</td>
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<td>Pd/CE/Anatase</td>
<td>40.72</td>
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<td>Lee et al. 2014</td>
<td>MFI</td>
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<td>6.3</td>
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<td>Al-SBA-15</td>
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<td>Li et al. 2008</td>
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<td>381.9</td>
<td>0.56</td>
<td>50</td>
<td>0.1729</td>
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<tr>
<td>Lu et al. 2009</td>
<td>HZSM-5</td>
<td>360</td>
<td>0.55</td>
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<td>HY</td>
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<td>0.85</td>
<td>84</td>
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<td></td>
<td>ZrO₂(60 wt%)&amp;TiO₂(40 wt%)</td>
<td>80</td>
<td>11</td>
<td>-</td>
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<td>SBA-15</td>
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<td>9.1</td>
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<tr>
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<td>Al-SBA-15</td>
<td>511</td>
<td>7.2</td>
<td>10</td>
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<td>Lu et al. 2010a</td>
<td>SBA-15</td>
<td>642.3</td>
<td>6.9</td>
<td>-</td>
<td>1.04</td>
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<td>0.79wt%Pd/SBA-15 (1)</td>
<td>427.8</td>
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<td>3.01wt%Pd/SBA-15 (3)</td>
<td>397.2</td>
<td>9.2</td>
<td>-</td>
<td>0.98</td>
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<tr>
<td>Lu et al. 2010b</td>
<td>Rutile</td>
<td>3</td>
<td>&gt;160</td>
<td>-</td>
<td>&gt;0.15</td>
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<td>Anatase</td>
<td>40</td>
<td>28</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
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<tr>
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<td>ZrO₂(60 wt%)&amp;TiO₂(40 wt%)</td>
<td>80</td>
<td>11/16/121</td>
<td>-</td>
<td>0.46</td>
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<tr>
<td>Park et al. 2007</td>
<td>HZSM-5</td>
<td>-</td>
<td>-</td>
<td>26</td>
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<td>4</td>
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<tr>
<td></td>
<td>1 wt% Ga/HZSM-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Park et al. 2010a</td>
<td>fresh HZSM-5</td>
<td>330</td>
<td>-</td>
<td>15</td>
<td>0.46</td>
<td>-</td>
</tr>
<tr>
<td>Authors</td>
<td>Catalyst</td>
<td>Surface area (m²/g)</td>
<td>Pore size (nm)</td>
<td>Si/Al</td>
<td>Pore volume (cm³/g)</td>
<td>Total acid sites (mmol NH₃/g)</td>
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<tr>
<td></td>
<td>spent HZSM-5</td>
<td>310</td>
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<tr>
<td>Park et al. 2010b</td>
<td>HZSM-5</td>
<td>450</td>
<td>-</td>
<td>20.1</td>
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<td>0.35</td>
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<tr>
<td></td>
<td>Meso-MFI</td>
<td>647</td>
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<td>17.5</td>
<td>0.67</td>
<td>0.53</td>
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<td>1wt% Ga/Meso-MFI</td>
<td>570</td>
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<td>17.5</td>
<td>0.6</td>
<td>0.28</td>
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<td>5wt% Ga/Meso-MFI</td>
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<td>17.5</td>
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<td>0.22</td>
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<td>MMZ ZSM-5</td>
<td>850</td>
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<td>18.2</td>
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<td>Park et al. 2012</td>
<td>Al-MCM-41</td>
<td>950</td>
<td>2.6</td>
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<td>0.93</td>
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<td>Al-MCM-48</td>
<td>1350</td>
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<td>20</td>
<td>1.21</td>
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<td>HZSM-5</td>
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<td>0.7</td>
<td>0.22</td>
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<tr>
<td>Park et al. 2012</td>
<td>0.5 wt% Pt/HZSM-5</td>
<td>386</td>
<td>0.51x0.55</td>
<td>15</td>
<td>0.2</td>
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<tr>
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<td>Meso-MFI</td>
<td>567</td>
<td>4.1</td>
<td>15</td>
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<td>0.5 wt% Meso-MFI</td>
<td>472</td>
<td>4.1</td>
<td>15</td>
<td>0.6</td>
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<td>Sharma and Bakhshi 1993</td>
<td>HZSM-5</td>
<td>365</td>
<td>-</td>
<td>59</td>
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<td>Srinivas et al. 2000</td>
<td>HZSM-5</td>
<td>324</td>
<td>0.52</td>
<td>56</td>
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<td>-</td>
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<td></td>
<td>Silica-alumina</td>
<td>321</td>
<td>3.15</td>
<td>0.79</td>
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<td>-</td>
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<td>80 wt% Silica-alumina/20 wt% HZSM-5</td>
<td>322</td>
<td>2.6</td>
<td>11.8</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Triantafyllidis et al. 2007</td>
<td>MSU-S/HBEA (hexagonal)</td>
<td>1017</td>
<td>3</td>
<td>50</td>
<td>0.97</td>
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<tr>
<td></td>
<td>MSU-S/WBEA (wormhole)</td>
<td>923</td>
<td>3.5</td>
<td>50</td>
<td>1.53</td>
<td>0.24</td>
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<td>Al-MCM-41</td>
<td>990</td>
<td>3</td>
<td>50</td>
<td>0.95</td>
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<td>Vitolo et al. 1999</td>
<td>HZSM-5(50)</td>
<td>705</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>HZSM-5(80)</td>
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<td>-</td>
<td>80</td>
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**Table B.5 Type of technology, amounts of catalyst and substrate used**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Set-up</th>
<th>Catalyst</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adam et al. 2006</td>
<td>Bench scale fixed bed reactor (ID 1.25 cm). The biomass was initially pyrolyzed on a hot glass-wool layer placed on the top of the catalyst bed.</td>
<td>0.7 g</td>
<td>1.5 g</td>
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<tr>
<td>Adjaye et al. 1995</td>
<td>Fixed bed micro-reactor.</td>
<td>2 or 4 g</td>
<td>3.6 g</td>
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<tr>
<td>Adjaye et al. 1996</td>
<td>Fixed-bed microreactor 400 mm long, 11.5 mm i.d.</td>
<td>1.2 or 4g</td>
<td></td>
</tr>
<tr>
<td>Aho et al. 2010</td>
<td>Fluidized bed reactor (i. d. of 34 mm with a wall thickness of 4 mm): pre-heating of the fluidization gas in the lower part of the reactor (267 mm long), pyrolysis of the organic material was performed in the middle fluidizing part (102 mm long), catalytic upgrading accomplished in the upper part (79 mm long).</td>
<td>2.51 - 2.52 g</td>
<td>20-22 g</td>
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<tr>
<td>Choi et al. 2012</td>
<td>vTI-Mini Fast Pyrolyzer: the biomass was placed in the middle of a quartz pyrolysis tube, the catalyst bed is located after the biomass sample and placed between the quartz wool.</td>
<td>40 mg</td>
<td>40 mg</td>
</tr>
<tr>
<td>Choi et al. 2013</td>
<td>vTI-Mini Fast Pyrolyzer: the biomass was placed in the middle of a quartz pyrolysis tube, the catalyst bed is located after the biomass sample and placed between the quartz wool.</td>
<td>40 mg</td>
<td>40 mg</td>
</tr>
<tr>
<td>Iliopoulou et al. 2012</td>
<td>Benchscale fixed bed tubular reactor (ID 1.4 cm, height 36 cm)</td>
<td>0.7 g</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Iliopoulou et al. 2007</td>
<td>Fixed bed reactor (i.d. 1.25 cm)</td>
<td>0.7 g</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Jeon et al. 2012</td>
<td>Py-GC/MS: biomass placed in a metal cup, intermediate wool layer and catalyst on top</td>
<td>1 mg</td>
<td>1 mg</td>
</tr>
<tr>
<td>Jeon et al. 2013</td>
<td>Py-GC/MS: biomass placed in a metal cup, intermediate wool layer and catalyst on top</td>
<td>2 mg</td>
<td>2 mg</td>
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<tr>
<td>Kaewpengkrow et al. 2014</td>
<td>Py-GC/MS: biomass sample placed in a cup and the catalyst was placed above.</td>
<td>4 mg</td>
<td>0.4 mg</td>
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<tr>
<td>Lee et al. 2014</td>
<td>Py-GC/MS: biomass placed in a metal cup, intermediate wool layer and catalyst on top.</td>
<td>2 mg</td>
<td>1 mg</td>
</tr>
<tr>
<td>Li et al. 2008</td>
<td>Pyrolysis in a fluidized bed reactor and online upgrading of the vapor phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Authors</td>
<td>Set-up</td>
<td>Catalyst</td>
<td>Substrate</td>
</tr>
<tr>
<td>-------------------------</td>
<td>------------------------------------------------------------------------</td>
<td>----------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Lu et al. 2009</td>
<td>The pyrolysis tube was successively filled with a short quartz filler rod, some quartz wool, catalyst, some quartz wool, biomass, some quartz wool, catalyst and some quartz wool.</td>
<td>0.5 mg + 0.5 mg</td>
<td>0.5 mg</td>
</tr>
<tr>
<td>Lu et al. 2010a</td>
<td>CDS Pyroprobe 5250 pyrolyser. The pyrolysis tube was successively filled with a quartz rod, some quartz wool, catalyst, some quartz wool, biomass, some quartz wool, catalyst and some quartz wool.</td>
<td>0.3 mg + 0.3 mg</td>
<td>0.2 mg</td>
</tr>
<tr>
<td>Lu et al. 2010b</td>
<td>The catalyst was placed at both sides of the poplar wood and functioned as a fixed bed, so that all the pyrolysis vapors would pass through the catalyst layer. The biomass and the catalyst layer were separated by the quartz wool.</td>
<td>1 mg</td>
<td>0.5 mg</td>
</tr>
<tr>
<td>Lu et al. 2010c</td>
<td>CDS Pyroprobe 5250 pyrolyser. The pyrolysis tube was successively filled with a quartz rod, some quartz wool, catalyst, some quartz wool, biomass, some quartz wool, catalyst and some quartz wool.</td>
<td>0.5 mg + 0.5 mg</td>
<td>0.5 mg</td>
</tr>
<tr>
<td>Park et al. 2007</td>
<td>Catalyst bed reactor (height of 420 mm and 76 mm i.d.) installed at the upper part of a primary pyrolysis reactor (height of 200 mm and 20 mm i.d.).</td>
<td>15, 30 g</td>
<td>150 g</td>
</tr>
<tr>
<td>Park et al. 2010a</td>
<td>Catalyst bed reactor (height of 420 mm and 76 mm i.d.) installed at the upper part of a primary pyrolysis reactor (height of 200 mm and 20 mm i.d.).</td>
<td>6 g</td>
<td>-</td>
</tr>
<tr>
<td>Park et al. 2010b</td>
<td>The main pyrolysis reactor was U-type quartz with an inner volume of 50 mL, a height of 160 mm and an internal diameter of 15 mm. The fixed catalyst bed reactor was a tubular quartz type, with a height of 70 mm, an internal diameter of 15 mm.</td>
<td>0.5 g</td>
<td>5 g</td>
</tr>
<tr>
<td>Park et al. 2010c</td>
<td>The main pyrolysis reactor was U-type quartz with an inner volume of 50 mL, a height of 160 mm and an internal diameter of 15 mm. The fixed catalyst bed reactor was a tubular quartz type, with a height of 70 mm, an internal diameter of 15 mm.</td>
<td>0.5 g</td>
<td>5 g</td>
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<tr>
<td>Park et al. 2012</td>
<td>The main pyrolysis reactor was a quartz reactor. The fixed catalyst bed reactor was a tubular quartz type reactor.</td>
<td>0.5 g</td>
<td>5 g</td>
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<td>Sharma and Bakhshi 1993</td>
<td>Fixed bed microreactor, 380 mm long and 12.5 mm in diameter.</td>
<td>2 g</td>
<td></td>
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<tr>
<td>Authors</td>
<td>Set-up</td>
<td>Catalyst</td>
<td>Substrate</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Srinivas et al. 2000</td>
<td>Dual reaction system: 2 reactors 400 mm long and i.d. 11.5 mm. Only the reactor 2 contained the catalyst</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yildiz et al. 2013</td>
<td>Auger reactor: the last section of this screw is the &quot;pyrolysis reactor&quot;, the vapours are carried to the vapour phase upgrading reactor. The catalyst–sand mixture flows from the storage hopper through a long heated screw to upgrading reactor (moving bed reactor).</td>
<td>3 kg/h (catalyst-to-sand ratio was 3:1/w:w) Catalog/biomass ratio=5</td>
<td>200 g/h</td>
</tr>
</tbody>
</table>
However, the observations from different studies can be compared in order to point out the current most promising catalysts.

The majority of the work about catalytic cracking of bio-oil or vapors found in literature was performed with the zeolite HZSM-5 (Adjaye et al., 1995; Sharma and Bakhshi, 1993; Vitolo et al., 1999; Gayubo et al., 2004a; Torri et al., 2010; Samolada et al., 1998; Park et al., 2007; Park et al., 2010a; Li et al., 2008; Park et al., 2010b; Choi et al., 2012; Yildiz et al., 2013; Pattiya et al., 2010; Corma et al., 2007; Carlson et al., 2009; Choi and Meier, 2013).

HZSM-5 has high concentration of strong acid sites and a three-dimensional framework of elliptical straight channels (0.51 x 0.55 nm) and near-circular zig-zag channels (0.54 x 0.5 nm) (Bhatia, 1990). It showed to be very effective in the conversion of bio-oil towards aromatics. The effectiveness of this catalyst is due to its strong acid-shape selectivity (Williams and Horne, 1995). It was compared in the catalytic upgrading of bio-oil, vapors and model compounds with HY-zeolite, H-mordenite, silicalite, silica-alumina, beta zeolite, FCC and Meso-Al₂O₃ and it had the best performance in terms of aromatics production (Adjaye et al., 1995; Carlson et al., 2009; Corma et al., 2007; Park et al., 2007). The acidity plays an important role. Generally the availability of acid sites depends on the Si/Al ratio, where a low Si/Al ratio results in many acid sites. For instance, Vitolo et al. (1999) compared two HZSM-5 catalysts with different Si/Al ratio, the one characterized by the lower value of this ratio enhanced the formation of these compounds further than the other one, with lower acidity, did. Pattiya et al. (2010) claim that this catalyst increases the deoxygenation of lignin compounds and increases the production of aromatics and phenols. Corma et al. (2007) used glycerol and sorbitol feeds, proving that HZSM-5 increased aromatic compounds. Furthermore, Torri et al. (2010) agrees with the high concentration of aromatics in the product of catalytic treatment of bio-oil over HZSM-5, but the liquid product was only a small fraction of the overall products, consisting mostly of char and gas.

Some researchers modified HZSM-5 by doping it with different metals in order to increase the catalytic activity toward the formation of aromatics (Dao et al., 1988; Park et
Glucose and fructose were used as feedstock for the catalytic pyrolysis process over ZnZSM-5 and MnZSM-5 (Dao et al., 1988). Both Zn and Mn doped catalysts showed to have higher catalytic activity towards aromatics formation than the undoped ZSM-5. Not only model compounds showed this result, but also raw bio-oil catalytically upgraded over GaZSM-5 resulted in a higher concentration of aromatics than over HZSM-5 (Park et al., 2007). Additionally, other zeolites, such as Beta and Y, showed a higher deoxygenation activity when doped with metals. For instance, when doped with iron led to methyl substituted phenols and decreased the formation of methoxy substituted phenols (Aho et al., 2010).

Some metal oxides have been tested in the upgrading of bio-oil. Moens et al. (2009) reported that ZnO, ZrO₂, CeO₂ did not increase aromatics and phenolics content because of the low surface area. Additionally they tested slates, which were not effective either in enhancing the content of these products, but, in this case, the surface area was quite high, thus they claimed that this material did not have enough acid sites. However, CuO, Fe₂O₃, a mixed metal catalyst and ZnO reduced the fraction of heavy compounds (Torri et al., 2010; Nokkosmäki et al., 2000). Fe/Cr catalysts were compared with HZSM-5 and, as mentioned earlier, HZSM-5 increased the production of aromatics, whereas the metal catalysts led to a higher concentration of phenols and light phenolics (Samolada et al., 1998). Furthermore, the structure of the metal oxides affects the compounds distribution. Rutile, Anatase and a ZrO₂&TiO₂ catalyst were studied as catalysts for bio-oil upgrading (Lu et al., 2010b). Rutile enhanced the formation of phenols, whereas Anatase did not affect much their concentration and the ZrO₂&TiO₂ catalyst decreased it. In this study, these catalysts were impregnated with other elements and Pd/Ce/Rutile had the best performance. Pd increased the cracking of pyrolytic lignin, whereas Ru, impregnated with Ce/Rutile did not. On the other hand, ZrO₂&TiO₂ was effective for the production of aromatics, although increasing also some PAHs. Pd doping on Alumina, Zirconia, Rutile and Anatase increased the production of aromatics (Kaewpengkrow et al., 2014), although the pure Anatase resulted in the highest aromatic production, followed by a Ni/Ce/alumina and then by the same catalyst but modified with Pd. In another study, Lu et al. (2010c) investigated the catalytic activity of nano metal oxides, such as MgO, CaO, TiO₂, NiO, ZnO and Fe₂O₃. Only CaO and Fe₂O₃ formed various hydrocarbons, but only
in relatively low amounts. All these nano metal oxides increased the concentration of light phenols, except NiO, and slightly increased the total phenolic concentration, whereas some zeolites showed to increase the concentration of light phenols, while reducing the total phenolic fraction.

Lately, mesoporous catalysts attracted great interest for this process because they are expected to selectively crack and deoxygenate the large molecules present in pyrolysis vapors. Al-MSU-F and Al-MCM-41 were compared with ZSM-5. Al-MSU-F is a zeolite-like catalyst consisting of a cellular foam framework of 150 Å pores, whereas Al-MCM-41 has a uniform structure with about 30 Å pores. Al-MCM-41 presents both Lewis and Brønsted acid sites and a relatively moderate acidity (Iliopoulou et al., 2007). Both catalysts decreased the concentration of lignin-derived compounds and Al-MSU-F had a performance similar to ZSM-5, increasing aromatic hydrocarbons and phenols (Pattiya et al., 2010). On the contrary, Triantafyllidis et al. (2007) observed a decrease of the aromatics with Al-MCM-41 and an even higher decrease with MSU-S, but Al-MCM-41 increased significantly the concentration of phenols. The discordance of these results can be explained by the effect of the higher concentration of acid sites of Al-MCM-41, which affects the hydrocarbons (aliphatic, aromatic and alkylated derivatives) content of the liquid product (Iliopoulou et al., 2007). Al-MCM-41 increased phenols concentration and its acidity is a fundamental factor affecting this catalytic effect. However, phenols concentration does not have a direct dependence on the acidity, since also higher surface area leads to a higher content of these compounds in the liquid product (Iliopoulou et al., 2007). Other studies focused on the mesoporous SBA-15 catalyst (Adam et al., 2006; Lu et al., 2009; Lu et al., 2010a; Jeon et al., 2013). Lu et al. (2009) reported that SBA-15 was not effective for the production of light phenols, whereas decreasing the Si/Al ratio of Al-SBA-15 increased their concentration. Although this catalyst yielded a higher concentration of aromatics, they were not the main product of this process (Lu et al., 2009). Pd, as well as Pt, proportionally enhanced the activity of SBA-15 toward the production of phenols (Lu et al., 2010a; Jeon et al., 2013). On the other hand, when Pt was added to Al-SBA-15, the phenolic fraction decreased, because of their further decomposition towards aromatics and other compounds (Jeon et al., 2013). Regarding the aromatics production, Pt does not have a significant effect on their concentration when
added to SBA-15, whereas the effect is more pronounced for Al-SBA-15, meaning that a combination of acid sites and Pt is needed to increase the conversion towards aromatics (Jeon et al., 2013). Lee et al. (2014) compared Al-SBA-15 with unilamellar mesoporous MFI nanosheets in the upgrading of pyrolysis vapors of biomass components. Because of the strong Brønsted acid sites, the MFI catalyst resulted in a higher yield of mono-aromatics with all the biomass components tested. The cracking of lignin pyrolysis vapors showed the weaker catalytic activity of Al-SBA-15, which could convert heavy phenolics to light ones, but not to aromatics, whereas MFI promoted the production of mono-aromatics by aromatization of the light phenolics. Additionally, doubling the amount of catalyst further increased the mono-aromatics fraction and decreased the phenolic one. Table B.2 shows the results for the lower amount of catalyst, because the liquid yields were provided solely for these experiments, even though the higher amount led to higher concentration of aromatics. Similarly, Meso-MFI showed to be more selective towards the production of aromatics than Al-MCM-48 (Lee et al., 2011). This result was explained as due to the presence of strong acid sites on Meso-MFI, while Al-MCM-48 contains weak acid sites. Lee et al. (2011) claimed that strong acid catalyst increases the oligomerization of ethylene and propylene to form C4-C10 olefins, which then form diolefins through dehydrogenation. Thanks to cyclization and dehydrogenation, aromatics are produced. In fact, they report that paraffinic hydrocarbons are the main products of treatment over Al-SBA-15 and Al-MCM-41, whereas HZSM-5 yields to higher concentration of aromatics (Lee et al., 2011). Additionally, Lee et al. (2011) studied the formation of phenolics, which resulted to be promoted by Meso-MFI-zeolite, but, unfortunately, PAHs increased as well. Meso-MFI showed to be very promising in terms of aromatics production, even more than HZSM-5, due to its structure, the larger pore size and strong acid property (Lee et al., 2011; Jeon et al., 2012). The pore size needs to be tuned accurately though, since if too large pores are present, PAHs formation is favoured (Park et al., 2010b; Park et al., 2010c). Metals were observed to increase the dehydrogenating activity of mesoporous catalysts (Park et al., 2010b; Jeon et al., 2012) as well as the one of zeolites, as mentioned above, although the concentration of monoaromatics is not directly dependent on the concentration of the metals. For instance, Park et al. (2010b) doped Meso-MFI catalysts with 1 wt% Ga and 5
wt% Ga and the catalyst with the lower Ga content led to the higher concentration of monoaromatics. This is due to the decrease of the concentration of strong acid sites, of the surface area and of the pore volume as Ga content increases. Therefore, the catalyst composition has to be a trade-off between acidity and metals content. Pt-Meso-MFI and Meso-MFI showed to decrease the total concentration of phenols, while increasing the content of light phenols, with Pt-Meso-MFI even more significantly than Meso-MFI (Jeon et al., 2012).

B.6 Effect of catalysts on products yield

It is well known that cracking catalysts can favour the decrease of the liquid yield. The change is due to two different pathways: products are further cracked into gasses or they can polymerize forming coke or char and additionally catalysts can decompose non-volatile oligomers into volatile monomers (Lu et al., 2010a).

Most of the studies are conducted with a Py-GC/MS, which does not allow collecting the bio-oil and, consequently, measuring the liquid yield. Therefore, these studies report only the comparison of the total peak area of the detected compounds between the non-catalytic run with the catalytic ones, as an index for the liquid yield.

HZSM-5 is reported to decrease the liquid yield by about 10-20 wt% on the biomass basis and the relative water content is always higher in the upgraded bio-oil (Adjaye et al., 1995; Torri et al., 2010; Sharma and Bakhshi, 1993; Vitolo et al., 1999; Park et al., 2007; Park et al., 2010a; Li et al., 2008; Park et al., 2010b; Yildiz et al., 2013). In fact the main deoxygenation pathway this catalyst promotes is the dehydration, which results in a higher water content (Park et al., 2007). Torri et al. (2010) state that this catalyst, when used with a high catalyst to biomass ratio, leads predominantly to gas and char, only 14 wt% of bio-oil is produced and it is mainly composed by aromatic hydrocarbons. It is worth noting that Ga mitigates the effect of this catalyst on the decrease of the liquid yield and also on the formation of water, meaning that its deoxygenation activity is reduced, since the presence of Ga decreased the number of strong acid sites (Park et al., 2007). However, Choi et al. (2012) claimed that the bio-oil yield increases by some percentage points when both Alcell and Organosolv lignin pyrolysis vapors are converted
over HZSM-5. In a subsequent study, Choi and Meier (2013) reported the same result when cracking of Kraft lignin vapors over HZSM-5, FCC and Olivine.

Another zeolite that has been tested in numerous studies is HY. The liquid yield deriving from the upgrading over this catalyst does not differ much from the one relative to HZSM-5, but the water content appears to be always at least 10 wt% lower than the one resulting from tests using HZSM-5 (Adjaye et al., 1995; Vitolo et al., 1999; Park et al., 2007; Aho et al., 2010). Park et al. (2007) claimed that HZSM-5 catalytic activity is higher since strong acid sites are properly distributed. Aho et al. (2010) modified HY with iron and compared it with ferrierite, beta zeolite and their iron modified form. The lowest bio-oil yield was obtained with the iron modified HY, which was the catalyst characterized by the highest surface area, and the highest water content with the iron modified beta zeolite, which had a very high surface area and higher concentration of both Brønsted and Lewis acid sites than the iron modified HY.

Silica based materials decrease the liquid yield while producing large amount of water (Adjaye et al., 1995; Torri et al., 2010).

Torri et al. (2010) show that some metal oxides (CuO, MoO3, TiO2, WO3) increase the bio-oil yield, while Fe3O3 decreases this yield and ZnO does not affect it. These results agree with the conclusions reported by Lu et al. (2010c) in terms of total GC peak area. Lu et al. (2010b) tested different mineral forms of TiO2: Rutile, Anatase, ZrO2&TiO2 and their modified form doped with Ce, Ru or Pd. Their study reports the results only in terms of total GC area as an index for the liquid yield. The total area referred to the Rutile run is basically identical to the non-catalytic one. Anatase and modified forms decrease the total area and the ZrO2&TiO2 results in even lower total GC area.

Al-MCM-41 has lower acidity than microporous aluminosilicate zeolites and larger pore size, promoting the catalytic cracking of large hydrocarbon molecules (Park et al., 2010b) and even large lignocellulosic macromolecules (Liu et al., 2014). MCM-41 increased the liquid yield compared to the non-catalytic pyrolysis while increasing the water content (Iliopoulou et al., 2007; Adam et al., 2006). The liquid yield decreased proportionally with the decrease of the Si/Al ratio, whereas the water content did not have a proportional
relationship with this parameter. For instance, Iliopoulou et al. (2007) reported a higher organics concentration for Al-MCM-41 with a Si/Al ratio of 50 than with MCM-41 and Al-MCM-41, with Si/Al ratio equal to 30. They suggested that an optimal Al content is necessary in order to obtain reasonable amounts of organic phase. The organic fraction increased with increasing the pore size of this catalyst, although remaining always lower than the non-catalytic run and the highest organics yield was obtained when Cu was incorporated within this catalyst (Adam et al., 2006).

The framework structure seems to play an important role in this process. Triantafyllidis et al. (2007) showed the different results obtain with Al-MCM-41 and with MSU-S. The MSU-S catalysts tested were characterized by a wormlike and hexagonal framework. The three catalysts had high surface area and comparable acidity, but the MSU-S catalysts led to a lower liquid yield than Al-MCM-41 did as well as the organic yield, meaning that the MSU-S catalyst has a stronger catalytic activity than Al-MCM-41. Besides, this effect is even greater with the wormlike framework, since this structure favors the catalytic conversion of bulky molecules by giving fewer limitations to the diffusion than the channel-like structure of the Al-MCM-41.

The current preparation of MCM-41 does not result in a hydrothermal stable product. This characteristic depends on the preparation method, the thickness of the wall and the aluminum content (Mokaya, 2001). Instead, the hexagonal SBA-15 is more thermally stable because of the large monodispersed mesopores and the thicker walls (Zhao et al., 1998). Adam et al. (2006) reported it to increase the total liquid yield compared to the non-catalytic run, while increasing the water content and decreasing the organic fraction. On the other hand, when Al was incorporated into this catalyst, the organic yield resulted to be higher than the non-catalytic and the MCM-41 run and the water content lower. Lu et al. (2010a) showed that, when Pd is incorporated into this catalyst, the total GC peak area decreases, which can be interpreted as a decrease in the liquid yield.

The mesoporous MFI zeolite has also been studied and compared with HZSM-5 and a mesoporous material derived from HZSM-5 (MMZ) (Park et al., 2010b). All these catalysts decreased both the bio-oil yield and its organic fraction compared to non-
catalytic run. The largest decrease, meaning the highest catalytic activity, was given by Meso-MFI, producing a bio-oil with higher water content than the one produced over HZSM-5 and MMZ. The incorporation of Ga into the Meso-MFI zeolite reduced this effect, resulting in higher organic yield and lower water content with increasing the percentage of Ga from 1 to 5 wt. %, presenting similarities to the MMZ’s performance. Jeon et al. (2012) reports that, when Pt is incorporated into Meso-MFI, the decrease of the total GC peak area detected is even lower than with the Meso-MFI’s one.

B.7 Catalyst deactivation

Deactivation is mainly caused by coke deposition on the most acid sites of the catalyst structure. Coking is increased by the acidity of the catalyst, which unfortunately promotes also the production of monoaromatics and light phenolics. Therefore, the coke deposition limits the transformation of oxygenates towards hydrocarbons. The coking reaction and the cracking of heavy compounds compete during the catalytic upgrading of bio-oil. Iliopoulou et al. (2007) suggested that low Si/Al ratios favour the conversion of the hydrocarbons contained in the organic phase towards coke and char. As previously said, zeolites partially crack heavy organics to lighter ones, whereas some of these heavy compounds act as coke precursors depositing on the catalyst (Vitolo et al., 1999). According to Gayubo et al. (2004a,b), molecules with different functional groups in the bio-oil present very different reactivity and coke formation. For instance 2-methoxyphenol, acetaldehyde, acetic acid and acetone lead to coking, while alcohols do not seem to affect much the deactivation process. This behavior may be explained by the need of moderate acid sites for the dehydration of alcohols, whereas cracking of heavy compounds requires strong acid sites (Gayubo et al., 2004a). Sharma and Bakhshi (1993) claimed that coke derives from the phenolic fraction and reported that removing it decreases the coke formation. Guo et al. (2009) analyzed the coke precursors on the catalyst. They identified two kinds of precursors: aliphatic hydrocarbons on the outer surface of the catalyst and aromatic compounds in the pores.

Moreover, coke formation is a shape selective reaction. Vitolo et al. (1999) showed a higher production of coke with HY zeolite than with HZSM-5. HY structure is characterized by larger pores than HZSM-5, thus they suggested that the large molecules,
such as coke precursors, cannot make their way into the HZSM-5 framework. Also Park et al. (2010b) observed that the coking is limited by the pore size. They reported that increasing the pore size increases the amount of coke. In that study, HZSM-5 had the lowest production of coke, followed by a mesoporous catalyst produced from HZSM-5 (MMZ) and then by Meso-MFI. Mesoporous catalyst potentially can crack larger molecules, but it seems they worsen the coking problem. However the incorporation of gallium in Meso-MFI seemed to decrease the deactivation, because of the lower concentration of strong acid sites. Triantafyllidis et al. (2007) reported that Al-MCM-41 forms less coke than MSU-S, because of its milder catalytic activity.

Lu et al. (2010c) studied the nano metal oxides upgrading performance, as an alternative to zeolites, in order to overcome the coking problem. They claimed that these catalysts might avoid the polymerization of phenols, therefore, the formation of coke. Also Torri et al. (2010) stated that metal oxides are less predisposed to yield coke.

In addition to the characteristics of the catalyst, also the water content, the temperature, the space time, the time on stream, the heating rate and the catalyst to feed ratio affect the coking process (Gayubo et al., 2004b; Carlson et al., 2009). According to Gayubo et al. (2004b), the higher the water content the lower the coke formed. Water and hydrocarbons intermediates compete for the same adsorption sites. On the other hand, if water is adsorbed, the activity of the catalyst decreases. Deactivation by coking is significant above 400°C, since the polymerization/ condensation reactions that lead to the formation of polyaromatic structures, which are in part further cracked and in part retained on the catalyst acting as coke precursors, are favored above this temperature. Adjaye et al. (1995) and Vitolo et al. (1999) reported that a higher space velocity leads to lower coke yield, but also that the deoxygenation process is affected, since the catalyst does not have enough time to further crack the heavy compounds. Carlson et al. (2009) showed that high heating rates and high catalyst/feed ratio decrease the formation of coke and that the latter also increases the aromatics yield.

Another unfortunate characteristic of zeolites and mesoporous catalysts is the low hydrothermal stability. Gayubo et al. (2004a) reported that HZSM-5 conserves its
catalytic activity for 10 reaction-regeneration cycles, when reaction is performed at 400°C and the coke is burned with air at 550 °C. If the reaction takes place at 450 °C and the water content is above 75 wt%, HZSM-5 goes through dealumination even though the coke is completely removed. Dealumination is irreversible and leads to a decrease in the number of acidic sites (Liu et al., 2014). Brønsted sites predominate in zeolites and, if heated above 500°C, OH- and H+ are eliminated producing water, leading to an increase of Lewis acid sites. Aho et al. (2010) showed the change of surface area from fresh zeolites to spent and then regenerated ones. This parameter decreases drastically from fresh to spent zeolite, but it is almost fully recovered after regeneration. However, the number of Brønsted acid sites decreases significantly from fresh to regenerated zeolites, whereas the number of Lewis acid sites is nearly not affected by the treatment.

Mesoporous catalysts, such as Al-MCM-41, showed to be hydrothermally unstable as well as zeolites. Upon severe steaming, their structure collapses and the acidity drops. Additionally, during regeneration, water is produced deactivating these catalysts (Iliopoulou et al., 2007).

In conclusion, only few studies focused on the deactivation, the residual activity and the regeneration of these catalytic materials. It is important to characterize the long-time longevity of the catalyst and the number of regeneration cycles that can be performed. Studies should be carried out using steady state catalyst (after a certain number of regenerations) and not with fresh catalyst. Further work is needed to find the trade-off between a moderate catalytic activity and coke resistance.

### B.8 Conclusions

Catalytic cracking is a promising technology because of the mild operating conditions and the relatively inexpensive catalysts. Most of the research is still limited to the laboratory scale, hence this process needs to be investigated at a larger scale and both carbon and energy balances have to be determined in order to evaluate its feasibility.

Further improvement of catalysts is required in order to increase the selectivity towards high value products and the catalysts hydrothermal stability. The necessity of more
research in this field is unquestionable, but also a unified method for bio-oil analysis is needed in order to compare different studies. Additionally, the composition of the products is usually discussed whereas the actual pyrolysis yields are not always reported.

Catalysts poisoning has not been assessed yet, since coking is still the major deactivation process.

This process does not seem to be very attractive for the production of aromatics. Although the selectivity towards these products has improved, the effective amount of this fraction is quite low, mostly because of the concurrent decrease of the liquid yield. However, catalytic cracking showed to be promising for the conversion of heavier phenolics into lighter ones.

Other routes for the production of these compounds should be considered and compared with catalytic cracking. For example, fractional condensation allows separating the heavy fraction of the bio-oil, which could be recycled and further thermally cracked without the need of catalyst. Moreover catalytic oxidative depolymerization of biomass components can be another option to obtain monomeric compounds or new materials (Collinson and Thielemans, 2010; Crestini et al., 2010).

Currently the objective of selectively catalyze the production of specific compounds by catalytic cracking does not seem to be economically feasible, but, after optimization, its combination and integration with some other process may be an option for the near future.

B.9 References


Radlein, D., Quignard, A. (2013). A short historical review of fast pyrolysis of biomass. Oil and Gas Science and Technology, Institut Français du Pétrole, 68 (4), 765. <hal-00909065>


Appendix C

C. Example: Vertical Blades Stirrer Power

The following is the procedure followed to calculate normalized power and torque as function of the superficial velocity for constant rpm.

The motor was set at four different values of air supply pressure: 179, 207, 234 and 262 kPa. Upon setting the air pressure to the motor, nitrogen superficial velocity was increased while the rotation speed of the stirrer was being recorded.

Table C.1 shows the experimental results of the aeration with nitrogen in terms of rotation speed. These values were then converted to power by using the equations in table C.2 and plotted in figure C.1, obtained from data supplied by the air motor supplier (Gast, 2014). The resulting values of power are shown in table C.3.

**Table C.1 Rpm values varying the nitrogen superficial velocity and the air supply pressure (Vertical blades stirrer)**

<table>
<thead>
<tr>
<th>Superficial velocity</th>
<th>179 kPa</th>
<th>207 kPa</th>
<th>234 kPa</th>
<th>262 kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 m/s</td>
<td>130</td>
<td>173</td>
<td>210</td>
<td>243</td>
</tr>
<tr>
<td>0.0063 m/s</td>
<td>131</td>
<td>175</td>
<td>213</td>
<td>245</td>
</tr>
<tr>
<td>0.0103 m/s</td>
<td>133</td>
<td>176</td>
<td>215</td>
<td>246</td>
</tr>
<tr>
<td>0.0162 m/s</td>
<td>141</td>
<td>180</td>
<td>219</td>
<td>252</td>
</tr>
<tr>
<td>0.0234 m/s</td>
<td>149</td>
<td>189</td>
<td>222</td>
<td>254</td>
</tr>
<tr>
<td>0.0304 m/s</td>
<td>157</td>
<td>190</td>
<td>222</td>
<td>256</td>
</tr>
<tr>
<td>0.0436 m/s</td>
<td>158</td>
<td>191</td>
<td>222</td>
<td>256</td>
</tr>
</tbody>
</table>

**Table C.2 Power as a function of rpm at different supply pressure (Vertical blades stirrer)**

<table>
<thead>
<tr>
<th>Supply pressure</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>179 kPa</td>
<td>Power = -0.0014<em>rpm^2 + 0.7125</em>rpm - 0.1087</td>
</tr>
<tr>
<td>207 kPa</td>
<td>Power = -0.0015<em>rpm^2 + 0.8365</em>rpm + 0.0192</td>
</tr>
<tr>
<td>234 kPa</td>
<td>Power = -0.0016<em>rpm^2 + 0.965</em>rpm - 0.0739</td>
</tr>
<tr>
<td>262 kPa</td>
<td>Power = -0.0017<em>rpm^2 + 1.097</em>rpm - 0.0928</td>
</tr>
</tbody>
</table>
Figure C.1 Power characteristic of the air motor

Table C.3 Power values varying the nitrogen superficial velocity and the air supply pressure (Vertical blades stirrer)

<table>
<thead>
<tr>
<th>Superficial velocity</th>
<th>179 kPa (W)</th>
<th>207 kPa (W)</th>
<th>234 kPa (W)</th>
<th>262 kPa (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 m/s</td>
<td>69</td>
<td>100</td>
<td>132</td>
<td>166</td>
</tr>
<tr>
<td>0.0063 m/s</td>
<td>69</td>
<td>100</td>
<td>133</td>
<td>167</td>
</tr>
<tr>
<td>0.0103 m/s</td>
<td>70</td>
<td>101</td>
<td>133</td>
<td>167</td>
</tr>
<tr>
<td>0.0162 m/s</td>
<td>73</td>
<td>102</td>
<td>135</td>
<td>168</td>
</tr>
<tr>
<td>0.0234 m/s</td>
<td>75</td>
<td>105</td>
<td>135</td>
<td>169</td>
</tr>
<tr>
<td>0.0304 m/s</td>
<td>77</td>
<td>105</td>
<td>135</td>
<td>169</td>
</tr>
<tr>
<td>0.0436 m/s</td>
<td>78</td>
<td>105</td>
<td>135</td>
<td>169</td>
</tr>
</tbody>
</table>

The values of power for each superficial velocity were interpolated with TableCurve 2D and the type of equation common to all the data sets with the highest rank was selected. Table C.4 shows the equations and the different parameters for each superficial velocity. These equations were used to calculate the power as function of the superficial velocity for constant rpm (table C.5).
Table C.4 Regression equations for the power at different superficial velocities
(VERTICAL BLADES STIRRER)

\[
\frac{1}{y} = a + \frac{b}{\ln x}
\]

<table>
<thead>
<tr>
<th>1/y = a + b/lnx</th>
<th>0.0063 m/s</th>
<th>0.0103 m/s</th>
<th>0.0162 m/s</th>
<th>0.0234 m/s</th>
<th>0.0304 m/s</th>
<th>0.0436 m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-0.056</td>
<td>-0.056</td>
<td>-0.056</td>
<td>-0.056</td>
<td>-0.060</td>
<td>-0.061</td>
</tr>
<tr>
<td>b</td>
<td>0.342</td>
<td>0.343</td>
<td>0.346</td>
<td>0.346</td>
<td>0.367</td>
<td>0.372</td>
</tr>
</tbody>
</table>

Table C.5 Power as function of superficial velocity for constant rpm (Vertical blades stirrer)

<table>
<thead>
<tr>
<th>Superficial velocity</th>
<th>130 rpm (W)</th>
<th>170 rpm (W)</th>
<th>200 rpm (W)</th>
<th>230 rpm (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 m/s</td>
<td>71</td>
<td>97</td>
<td>121</td>
<td>151</td>
</tr>
<tr>
<td>0.0063 m/s</td>
<td>71</td>
<td>96</td>
<td>119</td>
<td>149</td>
</tr>
<tr>
<td>0.0103 m/s</td>
<td>70</td>
<td>95</td>
<td>119</td>
<td>148</td>
</tr>
<tr>
<td>0.0162 m/s</td>
<td>69</td>
<td>94</td>
<td>116</td>
<td>144</td>
</tr>
<tr>
<td>0.0234 m/s</td>
<td>67</td>
<td>91</td>
<td>113</td>
<td>141</td>
</tr>
<tr>
<td>0.0304 m/s</td>
<td>66</td>
<td>90</td>
<td>112</td>
<td>140</td>
</tr>
<tr>
<td>0.0436 m/s</td>
<td>66</td>
<td>89</td>
<td>111</td>
<td>140</td>
</tr>
</tbody>
</table>

The power results are normalized with respect to their maximum and minimum values:

\[
\frac{\text{Power} - \text{Min power}}{\text{Max power} - \text{Min power}} \quad \text{(C.1)}
\]

resulting in the values shown in table C.6 and in graph 3.2 as points. These points were further interpolated with TableCurve 2D, in order to obtain the equations (table C.7) to calculate the superficial velocity necessary to reach 98% of power and torque reduction, named in this study as critical aeration \( A_c \).
Table C.6 Normalized power as function of superficial velocity for constant rpm (Vertical blades stirrer)

<table>
<thead>
<tr>
<th>Superficial velocity</th>
<th>130 rpm</th>
<th>170 rpm</th>
<th>200 rpm</th>
<th>230 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 m/s</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.0063 m/s</td>
<td>0.90</td>
<td>0.88</td>
<td>0.87</td>
<td>0.84</td>
</tr>
<tr>
<td>0.0103 m/s</td>
<td>0.81</td>
<td>0.80</td>
<td>0.78</td>
<td>0.77</td>
</tr>
<tr>
<td>0.0162 m/s</td>
<td>0.64</td>
<td>0.56</td>
<td>0.48</td>
<td>0.38</td>
</tr>
<tr>
<td>0.0234 m/s</td>
<td>0.17</td>
<td>0.16</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>0.0304 m/s</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>0.0436 m/s</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table C.7 Regression curves of normalized power as function of superficial velocity (Vertical blades stirrer)

<table>
<thead>
<tr>
<th>f = a + b / [1+exp(-(x-c)/d)]</th>
<th>130 rpm</th>
<th>170 rpm</th>
<th>200 rpm</th>
<th>230 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-0.010</td>
<td>-0.013</td>
<td>-0.011</td>
<td>-0.001</td>
</tr>
<tr>
<td>b</td>
<td>0.981</td>
<td>1.011</td>
<td>1.030</td>
<td>1.034</td>
</tr>
<tr>
<td>c</td>
<td>0.018</td>
<td>0.017</td>
<td>0.016</td>
<td>0.014</td>
</tr>
<tr>
<td>d</td>
<td>-0.004</td>
<td>-0.004</td>
<td>-0.005</td>
<td>-0.005</td>
</tr>
</tbody>
</table>
Curriculum Vitae

Name: Valentina Lago

Post-secondary Education and Degrees:
Politecnico di Torino
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Publications:


Lago, V., Berruti, F., Briens, C. Use of the Mechanically Fluidized Reactor (MFR) to investigate the impact of bed hydrodynamics on the pyrolysis of biomass. In preparation

Lago, V., Berruti, F., Briens, C. Effect of bed material on the pyrolysis of lignin. In preparation

Lago, V., Berruti, F., Briens, C. Addition of wood to Kraft lignin to improve its processability in fast pyrolysis reactors. In preparation
Lago, V., Berruti, F., Briens, C., “Review: Catalytic cracking of bio-oil and vapors to maximize the production of aromatics and phenolics”, In preparation

Lago, V., Berruti, F., Briens, C., “Pyrolysis of hydrolysis lignin: comparison with Kraft lignin”, In preparation