

Regulation for Optimal Liquid Products during Biomass Pyrolysis: A Review

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Abstract. The liquid product obtained from biomass pyrolysis is very valuable that it could be used for extraction of chemicals as well as for liquid fuel. The desire goal is to obtain the most bio-oil with desired higher heating value (HHV), high physicochemical stability. The yields and chemical composition of products from biomass pyrolysis are closely related to the feedstock, pyrolysis parameters and catalysts. Current researches mainly concentrated on the co-pyrolysis of different biomass and introduce of novel catalysts as well as the combined effect of catalysts and pyrolysis parameters. This review starts with the chemical composition of biomass and the fundamental parameters and focuses on the influence of catalysts on bio-oil. What is more, the pyrolysis facilities at commercial scales were also involved. The classic researches and the current literature about the yield and composition of products (mainly liquid products) are summarized.

1. Introduction

At present, the fossil fuels including coal, petroleum and natural gas, dominate the energy which we are depending on. However, the fossil fuels are estimated that they might be used up until 2050[1]. Confronting the increasing energy crisis and the severe environmental pollution resulted from abuse of fossil fuels, we have to explore the renewable substitutes for present fossil fuels. As the only one renewable organic resource, bio-energy has attracted more and more attention because of its abundance and non-pollution to environment [2][3][4].

Biomass pyrolysis is the most attractive one among thermochemical process[5]. In the absence of air or oxygen, at the temperature range of 350°C-700°C biomass can be converted into three kinds of substances: bio-oil, char and the non-condensate gas. Especially, the bio-oil is a kind of valuable oxygenic liquid that it consists of anhydrosugars, C2-C6 light oxygenates along with phenolics and

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aromatics hydrocarbons, so that it can be used for combustion as well as for extracting valuable chemicals[6]. The phenols and sugars in bio-oil could be extracted from bio-oil for chemicals. Hydrocarbons as the best substitution for fossil fuel can be obtained from biomass catalytic pyrolysis. Biomass pyrolysis deeply depends on the parameters, by which the yield and composition of products can be controlled. Catalysts used in biomass pyrolysis could increase the content of hydrocarbons and increase the stability of bio-oil. Javaid reviewed operating parameters for optimum liquid oil yield during biomass pyrolysis[7]. Furthermore, in this review the control of feed, pyrolysis parameters as well as catalysts for optimal bio-oil is overviewed.

2. Properties of Bio-oil

Physical and chemical properties of bio-oil are necessary to determine the potential of bio-oil used for liquid fuel and extraction of chemistry. Gas chromatography and mass spectrometry detector (GC-MS), gas chromatogram(GC) and high performance liquid chromatography (HPLC) are always used for analysis of chemical components in bio-oil[8][9][10]. FTIR and NMR are also applied for the analysis of characterization of bio-oils[9]. Among physical properties of bio-oil, including higher heating value (HHV), lower heating value (LHV), water content, pH value, viscosity and stability, HHV and LHV are considered the most important factors. The HHV means the total energy released from fuel when it burns in oxygen, while the LHV presents the energy which doesn't include the vaporization energy contained in the water vapour[11]. The HHV of bio-oil is always measured with oxygen bomb calorimeter[12][13]. However, the HHV and LHV of bio-oil could also be estimated empirically from the ultimate and proximate analysis by the following formulas[14][15]:

$$HHV = 0.3491 \times C + 1.1783 \times H + 0.1005 \times S - 0.1034 \times O - 0.0151 \times N - 0.0211 \times A$$

In the formula the unit of HHV is MJ/kg. C, H, S, O, N mean the mass percent of carbon, hydrogen, sulphur and nitrogen respectively and A is the weight percent of ash.

$$LHV = HHV - 218.3 \times H$$

In this formula the unit of LHV and HHV is KJ/kg. H means the mass percent of hydrogen.

In the Table 1, the HHV of bio-oil from various biomass pyrolysis is listed according to the previous researches.

Table 1. HHV of bio-oil under different conditions.

| Feedstock | Condition | HHV(MJ/kg) | Analysis method of HHV | Ref |
|-----------------------------|---|-------------|-------------------------|------|
| Bio-oil from pine sawdust | Feeding rate of 1.47 kg·h ⁻¹ ; Pyrolysis temperature: 700°C; Solid residence time: 6 min | 18.76 | Oxygen bomb calorimeter | [12] |
| Bio-oil of pine sawdust | Feeding rate of 1.47 kg·h ⁻¹ ; Pyrolysis temperature: 800°C; Solid residence time: 6 min | 17.13 | Oxygen bomb calorimeter | [12] |
| Bio-oil of pine sawdust | Feeding rate of 1.47 kg·h ⁻¹ ; Pyrolysis temperature: 700°C; Solid residence time: 3 min | 13.76 | Oxygen bomb calorimeter | [12] |
| Bio-oil of coconut core | Pyrolysis temperature: 550°C; Grain size: 1.18-1.8 mm; Heating rate: 60 °C·min ⁻¹ | 14.75-10.88 | Calorimeter pump | [16] |
| Bio-oil of hazelnut cupulae | Pyrolysis temperature: 600°C; Sweep gas atmosphere; | 35.70 | Calculation | [11] |

| | | | | |
|---|--|-------|-------------|------|
| Bio-oil of hazelnut cupulae | Fixed-bed reactor Pyrolysis temperature: 600°C; Sweep gas atmosphere; Fixed-bed reactor; ZnO catalyst | 40.03 | Calculation | [11] |
| Bio-oil of willow | Pyrolysis temperature: 450°C; Nitrogen gas; | 16.10 | Calorimeter | [17] |
| Bio-oil of 1:1 of willow/PHB | Pyrolysis temperature: 400°C; Nitrogen gas; | 20.22 | Calorimeter | [17] |
| Linseed residue | Pyrolysis temperature: 450°C; Particle size: 1.75-2.36 mm | 33.35 | Calorimete | [18] |
| Nutshel | Pyrolysis temperature: 450°C; Particle size: 300-600 µm | 19.34 | Calorimete | [18] |
| Switchgrass with moisture contents of 5% | Pyrolysis temperature: 500°C; Fluidized-bed pyrolysis reactor | 17.4 | Calorimeter | [19] |
| Switchgrass with moisture contents of 15% | Pyrolysis temperature: 500°C; Fluidized-bed pyrolysis reactor | 18.0 | Calorimeter | [19] |

3. The Effect of Feedstock

3.1. Composition of biomass

Lignocellulosic biomass is mainly composed of cellulose, hemicelluloses and lignin. In addition, a little of mineral is also present in biomass. Every type of biomass has its specific chemical composition depending on proportions of cellulose, hemicellulose, lignin as well as minerals.

Cellulose, hemicellulose, lignin perform in different ways during pyrolysis process due to their entirely different chemical compositions and structures. Every component of biomass including cellulose, hemicellulose, lignin has its optimal thermal cracking temperature range. Hemicellulose decomposes easily at about 220°C-320°C because of amorphous structure with many branched units so that it has low activation energy. Cellulose cracks in higher temperature range about 300°C-400°C while lignin in broad temperature range about 150°C-600°C[20]. What is more, the yield and compositions of the products from each component are distinctly different. Cellulose yields more bio-oil, hemicellulose prefers vast gaseous product while lignin products the most char. Stefanidis *et al* studied the effect of cellulose, hemicellulose and lignin on bio-oil and found that through pyrolysis, cellulose mainly yielded dehydrated sugar and phenols, while hemicellulose produced ketones and phenolic compounds, and simultaneously the main products from lignin were exclusively complex phenols which were different from those derived from cellulose and hemicelluloses[21].

The products from various biomass are different due to difference of contents of cellulose, hemicellulose, lignin and mineral. Herbaceous biomass is mainly composed of cellulose and hemicellulose, while woody biomass consists of lignin. Moreover, woody biomass has low ash content compared with herbaceous biomass[22]. Burhenne *et al* compared the difference between woody biomass and herbaceous biomass during pyrolysis process and the result indicated that herbaceous biomass produced a larger fraction of gaseous products, while the woody biomass led to higher yield

of char[23]. In the study of Părpăriț *et al*, the more amounts of carboxylic acids, ketones and furans and a lower phenols were obtained from forestry biomass compared with agricultural biomass[24]. Considering various composition of biomass, co-pyrolysis were conducted. Zhang *et al* conducted the catalytic pyrolysis using the mixture of corn stalk and food waste and the result indicated that apparent synergistic effect between corn stalk and food waste promoted the production of aromatics dramatically[25]. In another research, sewage sludge and rice straw were used for co-pyrolysis, the result showed calorific value of the pyrolyzed biomass increased with the addition of rice straw[26].

The minerals in the biomass mainly contain K, Na, Mg, Ca, Si (Table 2). Minerals act as catalysts for biomass decomposition and charring reactions.

Table 2. Composition of switchgrass ash.[27]

| Compound | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | SO ₃ | CaO | MgO | Na ₂ O | K ₂ O | P ₂ O ₅ | TiO ₂ | SrO | BaO |
|---------------|------------------|--------------------------------|--------------------------------|-----------------|------|------|-------------------|------------------|-------------------------------|------------------|------|------|
| Content (wt%) | 72.2 | 3.74 | 1.28 | 0.39 | 6.19 | 2.33 | 0.77 | 6.17 | 2.63 | 0.18 | 0.02 | 0.01 |

Pretreatment of biomass could really eliminate the minerals from biomass. Compared with raw biomass, the biomass after pretreatment leads to higher liquid product, less char and gaseous product[28]. The properties of bio-oil obtained from pretreated biomass are showed in Table 3. Furthermore, Richards & Zheng[29] studied the influence of metal ions and salts on pyrolysis of wood and found that Fe or Cu which were incorporated into the biomass resulted in the high content of levoglucosan and levoglucosenone.

Table 3. The properties of bio-oil obtained from pretreated biomass.

| T/°C | Feedstock | Pretreatment | Ash content/% | Organic yield /wt% | Char yield /wt% | Gas yield/wt% | Water yield /wt% | Composition of Bio-oil | Ref |
|------|--------------------------|---------------------------------------|---------------|--------------------|-----------------|---------------|------------------|---|------|
| 530 | Pine wood | 90°C, 120min, Synthetic condenser | 0.04 | 58.0 | 8.6 | 24.9 | 8.6 | Levoglucosan concentration increased to 35.9 wt% | [29] |
| 530 | Pine wood | 90°C, 120min, Real condenser 2 liquid | 0.02 | 56.2 | 8.7 | 29.8 | 6.5 | Levoglucosan concentration increased to 37.0wt% | [29] |
| 500 | Northern red oak | 0.40 wt%, sulphuric acid | | decrease | increase | decrease | | Sugar yield increased by 8.1wt%; Light oxygenates yield decreased. | [30] |
| 500 | Switchgrs | 2.0 wt%, sulphuric acid | | slightly increase | increase | decrease | | Sugar yield increased by 11.7wt%; Light oxygenates yield decreased. | [30] |
| 500 | Hardwood trembling aspen | Hot Water Treatment, 90°C | | | | | | Anhydrosugars, Fatty Acids increased; | [31] |

| | | | | |
|-----|-----------------------------|---------------------------------|---|------|
| 500 | Softwood white spruce | Hot Water Treatment, 90°C | Phenols decreased | [31] |
| | | | Phenols, Anhydrosugars, Furans increased | |

3.2. Particle size of feedstock

The finer particle has a larger surface areas compared with the larger so that it has a high heating rate, less mass and heat limitation and cracks at lower temperature. The apparent activation energy values reduced with the particle size decreased so that the small sample cracked easier[32]. Moreover, Bridgeman *et al* analyzed two size fractions of switch grass and reed canary grass, the result indicated that smaller particles have a higher concentration of inorganic matter and moisture content as well as higher cellulose concentration than larger particles[33].

In general, the decrease of size of feedstock resulted in higher liquid product, less char and gaseous product. However, when the particle is very small, the biomass particle would splice each other and lead to inadequate cracking of biomass, so that the content of char increases with the decrease of bio-oil and gaseous products. Therefore, the particle size of biomass has an optimal value for the content of products. From the research of Pütün *et al*[34], in the pyrolysis of soybean-cake with particle size range of 0.425 mm to $D_p > 1.800\text{mm}$, $0.850\text{ mm} < D_p < 1.250\text{ mm}$ particle size led to the highest yield of bio-oil. The size of particle also makes a difference in the compositions of bio-oil. Zhou *et al* studied the effects of the particle size on bio-oil during fast pyrolysis of beech wood and found that when the wood particle size increased from 0.3 mm to 3 mm, the yields of pyrolytic lignin decreased drastically[35]. However, when the particle size was more than 3 mm, the yield of pyrolytic lignin was constant. Shen *et al* proved that with the increase of particle size, the light bio-oil fraction increased and heavy bio-oil fraction decreased. Meanwhile, the content of water improved and the viscosity of bio-oil reduced[36]. However, in the research of Septien *et al*, during fast pyrolysis of woody biomass at high temperature (1000-1400°C), the size of particle had less effect on the final pyrolysis products due to the thorough decomposition at high temperature[37]. It can be deduced that the influence of size of particle on compositions of bio-oil is closely related to the decomposition degree of biomass.

4. Pyrolysis Parameters

4.1. The final pyrolysis temperature

Among all parameters, the final pyrolysis temperature and catalysts are the most effective factors affecting the products during pyrolysis of biomass[38]. The degree of heating influences the decomposition of biomass directly. When the final pyrolysis temperature is below 250°C, the biomass has no obvious change almost in either structure or composition. However, when the temperature exceeds 250°C, the chemical structure of biomass changes drastically. In general, the pyrolysis of biomass starts at 350°C. Under high temperature, the abundant energy from outside ruptures the active chemical bonds in biomass, such as O-H, C-H, olefinic C=C, C-O and C=O.

Plentiful researches have studied the role of the final pyrolysis temperature on the yields of products[39][40][41]. With the increase of temperature, the yield of char decreases while the yield of gas increases markedly. In the temperature range of 500°C-600°C, the most liquid oil is obtained. Depending on difference of the others parameters, the temperatures which result in the highest yield of liquid are various. As the final temperature increases, the cracking degree of the feedstock improves so that leads to the increasing amount of bio-oil and gas. At high pyrolysis temperature, the second cracking reaction takes place in the char and bio-oil to generate more gaseous product. This process leads to further decrease of char and slight degree of bio-oil, conversely, the increase of gas.

The high final temperature ruptures structure of biomass thoroughly, thus obtains the products which are different from that at low temperature. The liquid product from pyrolysis of biomass is a

very complex mixture of oxygenated compounds with water content about 20 wt%-30 wt%. The water in bio-oil which is harmful to the property of bio-oil in aspects of lower calorific value and physical stability, derives from not only the initial water in biomass but also dehydration reaction. Amutio *et al* operated flash pyrolysis of Pinewood sawdust with conical spouted bed reactor and found that with improvement of the final temperature, the water content increased slightly[42]. This change was related to the intense dehydration reaction in high temperature. What is more, the amount of phenols was next to water and it peaked at 500°C. However, when the temperature exceeded 600°C, the yield of phenols decreased notably. What is more, the yields of ketones and saccharide decreased with the increase of temperature because of their instability in high temperature. In the research of Horne & Williams, the relation between temperature and concentrations of the polycyclic aromatic hydrocarbons (PAH) as well as high-value oxygenated aromatic compounds in bio-oil were studied[39].

4.2. Heating rate

The heating rate also performs a critical role on the yield and composition of products during biomass pyrolysis. High heating rate promotes vast outflow of primary volatile from solid feed, thus leads to high yield of liquid and gaseous production leaving low char amount. The results from study of Sensöz & Angin indicated that only the high heating rate above 50°C/min could make a great difference in yield of bio-oil. As the heating rate changed from 10 to 50°C/min, the temperature for maximum yield of bio-oil had no change[43]. Nevertheless, from result of the research of Demirbas, when the heating rate varied from 50 to 250°C/min, the temperature for maximum yield of bio-oil changed significantly[44]. The heating rate could also upgrade the bio-oil by change its composition. Debdoubi *et al* studied the effect of heating rate on oil products from esparto pyrolysis and found that with the increase of heating rate, H/C ratio increase and O/C decrease that contributed to improved energy content of pyrolysis oil[45]. In another study, when the heating rate increased, the improved higher heating value of bio-oil was detected[46].

4.3. Sweep gases

4.3.1. The types of sweep gases.

During biomass pyrolysis, the sweep gases are necessary to remove the vapors instantly and restrain the reactions of feedstock with oxidizing medium as well as provide hydrogen. The inert gases including nitrogen, helium, argon gas and active gases containing steam, methanol can be used as the sweep gases. In general, the use of nitrogen gas and steam are common. The inert gases used in biomass pyrolysis not only restrict the reactions between the biomass and oxidizing medium, but also remove the vapors out reactors timely. However, the steam not only as vehicle sweeps the volatile, but also reacts with the products by providing hydrogen. At the same time, the water vapor permeates through solid and results in desorption, distillation and removal of volatile. The steam as sweep gas drastically increased the yield of liquid and decreased the yield of gaseous and solid products[46]. The steam also influences the composition of bio-oil significantly. Pütün *et al* compared the effects of steam with inert gases and static atmosphere on the composition of bio-oil, and found that polar fractions dominated during the steam pyrolysis while inert gases and static atmospheres favored aliphatic and aromatic compounds[34]. In the research of Minkova *et al*, the solid from steam pyrolysis had a higher absorption compared with inert gases and static atmospheres[47].

4.3.2. The rate of sweep gases.

The rate of sweep gas influences the biomass pyrolysis because it determines the residence time of vapor. The vapors from biomass in pyrolysis would experience the secondary reactions, for instance, decomposition and repolymerization if they are not instantly removed out with long residence time. Through the decomposition reaction, preliminary vapors are converted into permanent gases, while the repolymerization leads to high yield of char. The short residence time yields more liquid product, but the quality of bio-oil decreases simultaneously because of its heavy molecular weight[48]. Rapid

sweep gas sweeps the volatile instantly so that avoids the secondary reactions. If the volatiles are quenched timely, the high amount of liquid products is obtained with the expense of char and gaseous products. The researches in regard to this respect were conducted[46][49]. Jae *et al* studied the influence of velocity of sweep gas on catalytic fast pyrolysis of wood using ZSM-5 catalyst and found that increase of the velocity led to decreased aromatic and increased olefin due to the reduced vapor residence time[50]. What is more, with the increase of velocity of sweep gas, the selectivity of benzene, toluene and C4 olefins was improved.

5. Catalysts

The composition of rude bio-oil derived from biomass pyrolysis is complex highly. There are vast oxygenated group in bio-oil, such as carboxyl, ketone group, methoxyl groups, hydroxyl so that the rude bio-oil has some negative factors (difficult ignition, corrosiveness, coking) to use directly[51]. The catalysts applied in biomass pyrolysis can efficiently upgrade the products. Abundant catalysts with high catalytic performance of cracking, aromatization, deoxygenation as well as esterification have been tested. Depending on the various reaction conditions, the specific catalysts could be chosen.

5.1. The catalysts for hydrocarbons

The aromatics from biomass pyrolysis have high motor octane number so that they can be used directly as fuels and a high octane fuel additive. To yield more aromatic hydrocarbon as well as less oxygenated compounds is beneficial to improve the bio-oil quality by the catalysts which possess excellent catalytic activity. The aromatics obtained by catalysts in two routes: either from depolymerization and dehydration of phenols or condensation-dehydrocyclization-aromatization reaction of light olefins on ZSM-5 with strong acid sites[52]. A mass of catalysts have been tested for production of aromatics in biomass pyrolysis, the related research results are summarized in Table 4.

Table 4. The influence of catalysts on bio-oil.

| Feed | Catalysts | Temp °C | Process types | Bio-oil yield /wt% | Hydrocarbon yield /wt% of biomass | Change of bio-oil composition | Ref |
|---------------|--------------------------------------|------------|------------------|--------------------------|---|---|------|
| White pine | Na _{0.2} H _{0.8} Y | 500 | ex-situ | 50 | 9.5 | Hydrocarbon, phenols increased drastically; Sugar and furans decreased | [51] |
| White pine | HY | 500 | ex-situ | 45 | 3.4 | Hydrocarbon, phenols increased drastically; Sugar and furans decreased | [51] |
| Beech wood | Al-MCM- 41 | 500 | in-situ | 45.34 | 1.53 | Phenols decreased; | [52] |
| Beech wood | H-ZSM-5 | 500 | in-situ | 43.95 | 7.49 | Mainly hydrocarbon; Phenols decreased; | [52] |
| Beech wood | Silicalite | 500 | in-situ | 47.58 | 7.47 | Ether increased; | [52] |
| Food waste | BEA zeolite | 500 | in-situ | | 43(of bio- oil) | Aromatics including polyaromatic hydrocarbons increases | [53] |
| Food waste | Al-SBA-15 | 500 | in-situ | | 30(of bio- oil) | Reduction of polymeric fatty acid species; Increase of hydrocarbons | [53] |
| Rice | ZSM-5 | 550 | in-situ | | 12.8 | | [54] |

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| talk | | | | | | | |
| Rice stalk | LOSA-1 | 550 | in-situ | | 10.0 | | [54] |
| Rice stalk | spent FCC catalysts | 550 | in-situ | | 6 | | [54] |
| Rice stalk | γ -Al ₂ O ₃ | 550 | in-situ | | 5 | Mainly unidentified compounds, lower molecule-weight oxygenating compounds Oxygenates decreased considerably; | [54] |
| Lignin | Beta | 650 | in-situ | 2.0×10 ⁹ (peak area) | 90 (of bio-oil) | Aromatics increased; substantially 3-ring and 4-ring polyaromatics increased | [55] |
| Lignin | Mordenite, | 650 | in-situ | 1.0×10 ⁹ (peak area) | 30 (of bio-oil) | Oxygenates decreased considerably, aromatics increased | [55] |
| Lignin | Y zeolites | 650 | in-situ | 0.5×10 ⁹ (peak area) | 90 (of bio-oil) | Oxygenates decreased considerably; Aromatics increased | [55] |
| Lignin | ZSM-5 | 500 | in-situ | 4×10 ⁹ (peak area) | 69 (of bio-oil) | Mainly aromatics; Oxygenates decreased considerably, aromatics increased; | [55] |
| Radiata pine | Meso-MFI | 500 | ex-situ | 42.9 | 4.1 | Oxygenates reduced significantly; Aromatic hydrocarbons increased | [56] |
| Radiata pine | 1 wt%Ga/Meso-MFI | 500 | ex-situ | 45.9 | 6.2 | Oxygenates reduced significantly; Aromatic hydrocarbons increased, mainly mono aromatic. | [56] |
| Radiata pine | HZSM-5 | 500 | ex-situ | 46.6 | 3.7 | Oxygenates reduced significantly; Aromatic hydrocarbons increased | [56] |
| Radiata pine | Mesoporous ZSM-5 | 500 | ex-situ | 50.6 | 0.3 | Oxygenates reduced significantly; Mainly phenolics; | [56] |
| Beech wood | ZSM-5 | 650 | in-situ | | 23.7 | Aromatic hydrocarbons increased; Oxygenates decreased significantly | [61] |
| Beech wood | Mesoporous ZSM-5 | 650 | in-situ | | 30.1 | Aromatic hydrocarbons increased; Oxygenates decreased significantly | [61] |

Various catalysts were tested in biomass pyrolysis for upgrading bio-oil. In the research of Nguyen & Williams, H-faujasite (Na-FAU, Na_{0.2}H_{0.8}-FAU and H-FAU) were carried out in pyrolysis of pinewood and Na_{0.2}H_{0.8}-FAU led to the high-quality bio-oil by decreasing the acid content, aldehydes and ketones as well as increasing content of the phenols and hydrocarbon (mainly aromatics)[39]. Park *et al* studied the effect of β zeolite and Al-SBA-15 catalyst on the composition of bio-oil and the result indicated that β zeolite converted polymeric acid compounds into aromatics and

PAHs due to its strong acidic sites, while Al-SBA-15 tended to hydrocarbons and oxygenates[52][53]. By now ZSM-5 is considered as the optimal catalysts for optimizing aromatic hydrocarbons because of its remarkable effect of shape-selectivity. Zhang *et al* compared the ZSM-5 with various catalysts for catalytic pyrolysis of biomass and ZSM-5 resulted in maximum yields of aromatics (12.8%) and olefins (10.5%)[54]. ZSM-5 and LOSA-1 exhibited higher deoxygenation and cyclization than γ -Al₂O₃ and FCC catalysts. In another researches, ZSM-5 showed similar property[55].

In catalysts, Brønsted acid sites are critical to convert oxygenates to aromatic hydrocarbon, while the pore structure possess effect of shape-selective[56]. Carlson *et al* tested the relationship between catalytic parameters and catalytic activity using ZSM-5, silicalite and SiO₂-Al₂O₃. Silicalite which has the same pore structure with ZSM-5 produced primarily coke, whereas, SiO₂-Al₂O₃ containing Brønsted acid sites also yielded mainly coke[57]. The high selectivity for aromatic of ZSM-5 attributes to its proper density of Brønsted acid sites and unique pore structure.

ZSM-5 catalysts can be optimized by changing its acid sites, pore structure as well as other characters. The density of Brønsted acid sites determines catalytic activity of ZSM-5 for the deoxygenation and aromatic formation. Changing the acid sites on ZSM-5 catalysts through adjusting SiO₂/Al₂O₃ can apparently increase the content of aromatics at the cost of oxygenates[55][58]. However, if the numbers of acid sites further increase, two acid sites are close exceedingly so that the repolymerization dominates to lead to more char[59]. From the previous researches, the lignin-derived oxygenates in the CFP (catalytic fast pyrolysis) of biomass can not enter into the micropores of conventional ZSM-5 because the size of reactants is larger than ZSM-5[47]. However, enhancing the external areas of ZSM-5 and introducing the mesopores into the bulk can improve evidently the conversion of heavy lignin-derived oxygenates. Zheng *et al* studied the effect of crystal size (2 μ m, 200 nm and 50 nm) of ZSM-5 on the aromatic yield and selectivity and the result indicated that ZSM-5 with crystal size 200 nm produced the maximum aromatic yield, minimum BTX selectivity and char yield. This attributed to the highest micropore surface area, amount of weak acid sites and maximum B/L ratio[60]. Creating mesopores permits the larger oxygenated molecules into the ZSM-5 and converts them to aromatics afterwards through reaction of cracking, deoxygenation and aromatization. What is more, the intraparticle mesopores in the bulk of ZSM-5 shorten micropore diffusion path length inhibiting secondary reaction of monoaromatics for char. Compared with regulating the particle size of catalysts introducing mesopore in ZSM-5 is more useful to convert the large volatile intermediate into light products. Li *et al* carried out pyrolysis of biomass with mesoporous ZSM-5 zeolites prepared by desilication with NaOH and found that mesoporous ZSM-5 has less influence on the products distribution in the process of cellulose pyrolysis, but increases the yield of aromatic yield and decreases the coke yield pronouncedly in pyrolysis of lignin[61]. The similar result also came about in another research[59]. What is more, in the research of Rownaghi *et al*, the mesoporous ZSM-5 obviously reduced the coke formation and enhanced production of alkyl aromatics from methanol[62]. In addition, the effect of other important parameters such as pyrolysis temperature, ratio of catalyst/lignin as well as biomass weight hourly space velocity on products from catalytic pyrolysis of biomass was also studied[58][63].

5.2. The catalysts for ester

The raw bio-oil from biomass during pyrolysis is acid and corrosive because of presence of a mass of organic acids such as formic, acetic and propionic acids. It is necessary to upgrade the bio-oil to convert organic acids and aldehydes to stable and valuable esters. With the help of catalysts, organic acids are firstly converted into aldehydes and water through deoxygenation and then the aldehydes are transformed into alcohols which can esterify with the residual acids. Xu *et al* studied the effect of Co which merged with Ru/ γ -Al₂O₃ on the property of bio-oil and the result exhibited that Co-Ru/ γ -Al₂O₃ increased esters in upgrading bio-oil by 2-fold than that in raw bio-oil. In the catalytic process, Co-Ru/ γ -Al₂O₃ slightly improved the property of bio-oil by hydrotreating as well as esterifying reactions[64]. In another research, Mo-Ni/ γ -Al₂O₃ catalysts were tested[65]. However, considering the catalysts with limitation of hydrotreating reaction, to add ethanol into bio-oil can pronouncedly

increases the degree of esterification. In the research of Song *et al*, after adding ethanol/acetic acid into the bio-oil, $\text{SO}_4^{2-}/\text{SiO}_2\text{-TiO}_2$ catalyst increased drastically catalytic performance by increasing the yield of esters and alkane compounds, as well as decreasing organic acids, phenolic, aldehyde compounds. Interaction between SiO_2 and Ti promoted the formation of firm bond of Ti-O-Si so that improved the activity of catalysts[66]. What is more, from another study, when ethanol was added, the solid acid catalysts Amberlyst-70 not only transformed the organic acids into stable esters, but also converted sugar oligomers into stabilized methyl- α -D-glucopyranoside[67].

6. State-of-art of Biomass Pyrolysis

For the sake of biomass pyrolysis products which could be used for fuels and chemicals, biomass pyrolysis has been conducted at commercial scales. By now the reactor of biomass pyrolysis mainly includes fixed bed, fluidized bed, rotating cone, scrow feeder and vacuum pyrolyser. Kan *et al* reviewed the characteristics and current status of pyrolysis reactors and bubbling, fluidized bed, rotating cone have been applied in market commercially[15]. Table 5 lists pyrolysis facilities at commercial scales.

Table 5. Pyrolysis facilities at commercial scales.

| Company | Location | Pyrolysis reactor | Feed | Capacity (t/day) | Primary product | Ref |
|--|-----------------------------|---------------------------------|--|------------------|------------------|------|
| Dynamotive | West Lorne, Ontario, Canada | Bubbling fluidized bed | Waste sawdust and woodchips | 100-130 (dry) | Bio-oil | [68] |
| Mitsubishi Heavy Industries/ Mie Chuo Kaihatsu | Mie Prefecture, Japan | Indirect heating rotary kiln | Woodchips | 100 | Syngas | [68] |
| Ensyn | Rhineland, Wisconsin | Circulating fluidised bed | Hardwood wastes | 40(dry) | Bio-oil | [68] |
| BTG | Malaysia | Rotating cone | Palm oil waste | 50(dry) | Bio-oil | [68] |
| Choren | Germany | Slow pyrolysis and gasification | Woody biomass and agricultural residue | 180(dry) | Syngas | [68] |
| Power China Hubei Electric Engineering Corporation | Hubei province, China | | Cotton stalk, wheat straw, rape stalk | 132 | Syngas | [69] |
| Anyang biomass carbonization Co | Henan province, China | | Straw | 49 | Syngas; Bio-char | [70] |
| Xinjiang development of agriculture and forestry renewable resources company | Xinjiang province, China | | Cotton stalk, branch | 41 | Bio-char | [71] |

7. Conclusion and Prospect

The whole world consumes vast energy and chemicals mainly derived from fossil fuel. Biomass pyrolysis is a promising way to yield bio-oil which contains phenols, sugars, furans and acids. The

phenols, sugars and furans are valuable chemicals that could be extracted from bio-oil. The yield and composition of bio-oil both are strongly depended on the feed, pyrolysis parameters including pyrolysis temperature, heating rate and sweep gases. By controlling the various parameters the desire bio-oil is obtained.

The raw bio-oil is incompetent to used directly as liquid fuels because of its high oxygen content and high acidity. Catalysts could change the composition of bio-oil highly. Metals supported on the Al_2O_3 increase the content of esters, improving the stability of bio-oil. Hydrocarbons could replace a large percentage of fossil fuels in a variety of applications[72]. So far ZSM-5 is considered as the most efficient catalyst to convert oxygenated chemicals in bio-oil to hydrocarbons. By loading metal on the ZSM-5 or enlarging the pore size of ZSM-5 could improve the catalytic performance.

However, by now the mechanism of pyrolysis and catalytic pyrolysis is not clear because of the complicate composition of biomass. For the better using the bio-oil for chemicals and fuels, further researches should focus on the following aspects:

- For the regulation for optimal liquid products during biomass pyrolysis: pretreatment of feedstock containing more cellulose and hemicelluloses, pyrolysis temperature within 450-600°C, high heating rate, high-speed sweeping gas decreasing residence time of vapor in reactor, steam as sweeping gas, medium particle size of feedstock and rapid quenching of the vapor could increase the content of liquid, while the catalysts, especially ZSM-5, upgrade the quality of bio-oil. Therefore, both aspects should be considered simultaneously during biomass pyrolysis.
- The single component and model compound should be used for the studies of mechanism of pyrolysis and catalytic pyrolysis;
- The others biomass or chemicals could be introduced for biomass pyrolysis and the co-pyrolysis is recommended;
- The novel catalysts should be explored, for instance, metal-supported ZSM-5 and enlarging pore size ZSM-5.

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