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Production of Chemicals from Selective Fast Pyrolysis of Biomass

Xi-feng Zhu and Qiang Lu
University of Science and Technology of China
P.R.China

1. Introduction

With the increasing concern on fossil fuel storage and environmental problems, the utilization of renewable lignocellulosic biomass resources will play an increasing important role in the future. Biomass can be converted to a variety of fuels and chemicals by different technologies, one of them is fast pyrolysis which has received extensive interests in recent years (Bridgwater & Peacocke, 2000; Mohan et al., 2006). Fast pyrolysis of biomass is a thermal decomposition process that occurs in the absence of oxygen, with quickly biomass decomposition and rapid vapor condensation, to convert biomass mainly into a liquid product (know as bio-oil) with the yield as high as 70~80 wt%. The essential principles to obtain high bio-oil yield include moderate pyrolysis temperature (around 500 °C), very high heating rates ($10^3 – 10^5$ °C/s), short vapor residence time (< 2 s) and rapid quenching of pyrolysis vapors. A number of pyrolysis reactors have been developed for the bio-oil production, including bubbling fluidized bed, entrained bed, circulating fluidized bed, rotating cone, screw pyrolysis reactor, vacuum pyrolysis reactor, etc. In recent years, several research institutes (BTG, Dynamotive) have already established demonstration biomass fast pyrolysis plants, suggesting that the fast pyrolysis technique is near commercial.

Crude bio-oils, also referred to as biomass pyrolysis liquids, pyrolysis oils, or bio-crude oils, are dark brown, free flowing liquids with an acrid or smoky odor. Chemically, bio-oils are complex mixtures of water and hundreds of organic compounds that belong to acids, aldehydes, ketones, alcohols, esters, anhydrosugars, furans, phenols, guaiacols, syringols, nitrogen compounds, as well as large molecular oligomers (holocellulose-derived anhydro-oligosaccharides and lignin-derived oligomers). There are many valuable compounds, and thus, bio-oils have the potential for useful chemicals recovery. However, most of the chemicals are in low contents, making their recovery not only technically difficult but also economically unattractive at present. Therefore, the commercialization of bio-oils for value-added chemicals requires the production of specific bio-oils with high contents of target products.

Selective fast pyrolysis, differed from conventional fast pyrolysis which is usually aimed at the maximum bio-oil yield, is to drive the pyrolysis of biomass towards the products of interest. Since the biomass pyrolytic pathways and the subsequent products are influenced by various factors, and thus, selective fast pyrolysis can be performed in different ways, mostly by catalyst utilization, to (1) maximize the yield of target products and (2) obtain target products with high purity. This manuscript is divided into two sections. The first

section reviews the biomass fast pyrolysis reaction pathways and mechanisms, and the second section discusses the methods for the production of several value-added chemicals from selective fast pyrolysis of biomass.

2. Biomass fast pyrolysis reaction pathways and mechanisms

2.1 Cellulose fast pyrolysis

Cellulose is the main component of lignocellulosic biomass and is predominantly located in the cell wall. It is a linear homopolysaccharide of β-D-glucopyranose units linked together by (1→4)-glycosidic bonds. Among the three major components of lignocellulosic biomass, the cellulose has received the most attention in its pyrolytic mechanism study.

Cellulose starts pyrolysis at as low as 150 °C. At temperatures lower than 300 °C, pyrolysis of cellulose mainly involves the reduction in degree of polymerization, the formation of free radicals, elimination of water, formation of carbonyl, carboxyl and hydroperoxide groups, and evolution of carbon monoxide and carbon dioxide, finally leaving a charred residue (Shafizadeh, 1982; Evans & Milne, 1987). The low temperature pyrolysis will produce very low yield of organic liquid products.

At temperatures above 300°C, the pyrolysis of cellulose involves many new reactions, mainly leading to a liquid product with the yield as high as 87 wt% (Piskorz et al., 1989). Generally, cellulose is firstly decomposed to form activated cellulose (Boutin et al., 1998). Afterwards, two major parallel pathways will take place, the depolymerization and the fragmentation (ring scission), as shown in Fig.1. The depolymerization process mainly forms anhydro-oligosaccharides, levoglucosan (LG) and other monomeric anhydrosugars, furans, cyclopentanones, pyrans and other related derivatives. The ring scission process mainly obtains hydroxyacetaldehyde (HAA), acetol (HA), other linear carbonyls, linear alcohols, esters, and other products (Piskorz et al., 1986; Radlein et al., 1991; Lanza et al., 2009; Lin et al., 2009). In a recent study, Shen & Gu (2009) proposed the detailed possible routes for the pyrolytic formation of several major products from cellulose, as shown in Fig.2.
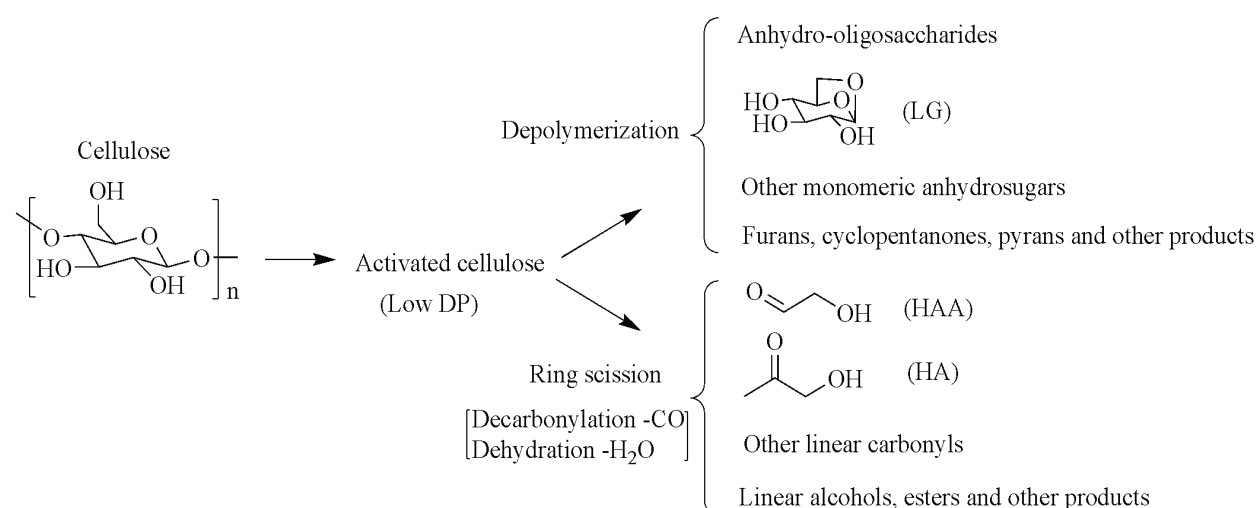

Fig. 1. The two parallel pyrolytic pathways during fast pyrolysis of cellulose at moderate temperatures
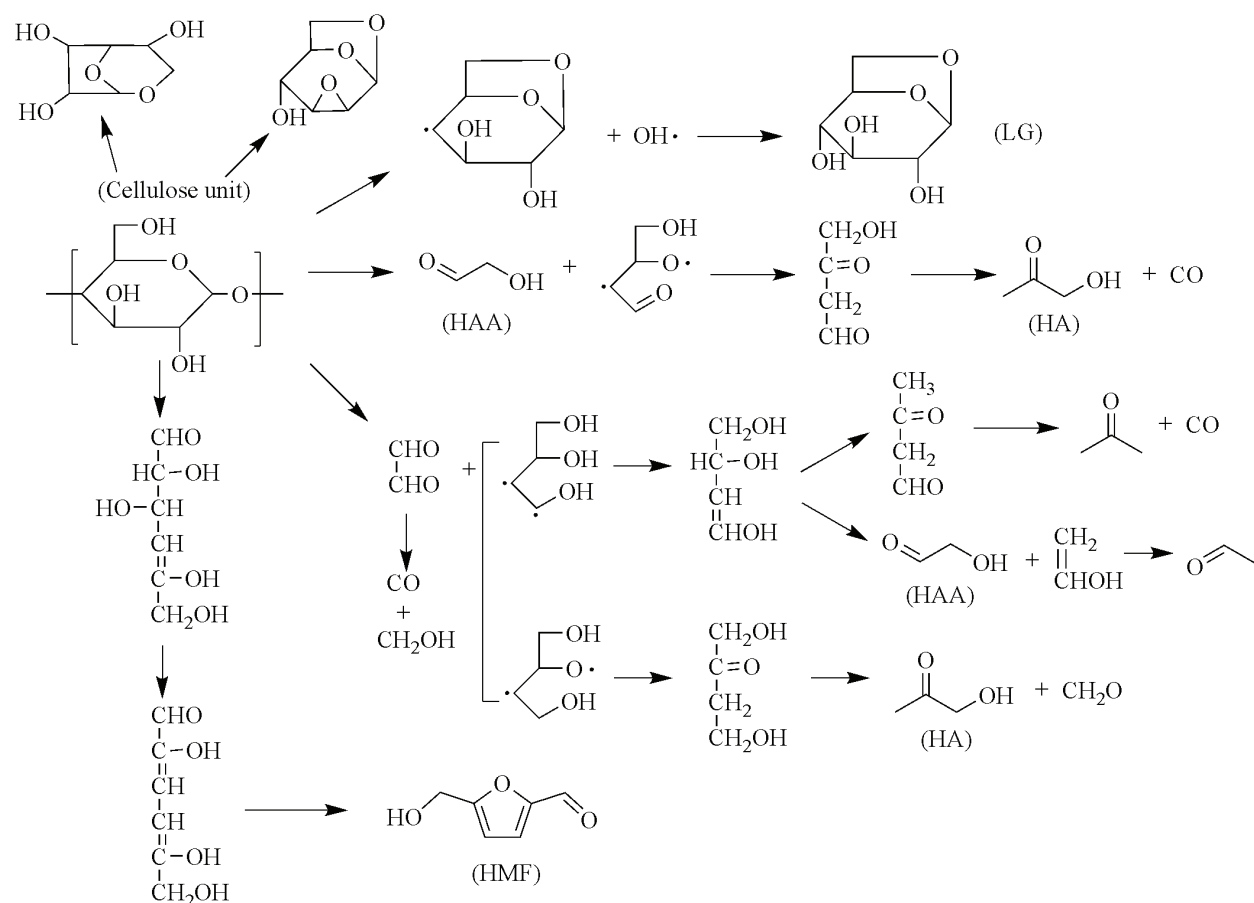
Fig. 2. The major pyrolytic pathways during cellulose fast pyrolysis (proposed by Shen & Gu)

2.2 Hemicellulose fast pyrolysis

Hemicelluloses are closely associated with cellulose in the cell wall as well as to lignin in the middle lamella. They are amorphous polysaccharides with building units belong either to hexoses (mainly D-glucose, D-mannose, and D-galactose) or to pentoses (mainly D-xylose and L-arabinose). The primary hemicellulose components are galactoglucomannans (glucomannans) and arabinoglucuronoxylan (xylan). Compared with cellulose, hemicelluloses have received less attention in their pyrolytic mechanism study.

Hemicelluloses are less thermally stable than cellulose, presumably due to the lack of crystallinity, and their pyrolysis is generally thought to be analogous to cellulose in the reaction mechanisms. Fast pyrolysis of glucomannans generates similar pyrolytic products as the cellulose, while the pyrolytic products from xylan differ more than those from cellulose (Alen et al., 1996). Generally, xylan fast pyrolysis will obtain higher char yield than that from cellulose, and will not form a typical depolymerization product, like the LG from cellulose. A probable cause of this difference was explained by Ponder & Nichards (1991). During cellulose pyrolysis, the glucosyl cation from the scission of the common glucans can readily form a stable 1,6-anhydride with the free primary hydroxyl group at C-6, and finally yields the volatile LG. However, there is no feasible mechanism for intramolecular "stabilization" for the xylosyl cation via anhydride formation, and hence, the xylosyl cation is more likely to enter the non-specific dehydration pathways, resulting in the char formation rather volatiles.

In a recent study, Shen et al. (2010) also proposed the detailed possible routes for the pyrolytic formation of several major products from main xylan chain, as well as the O-acetylxylan and 4-O-methylglucuronic acid unit, as shown in Fig.3.
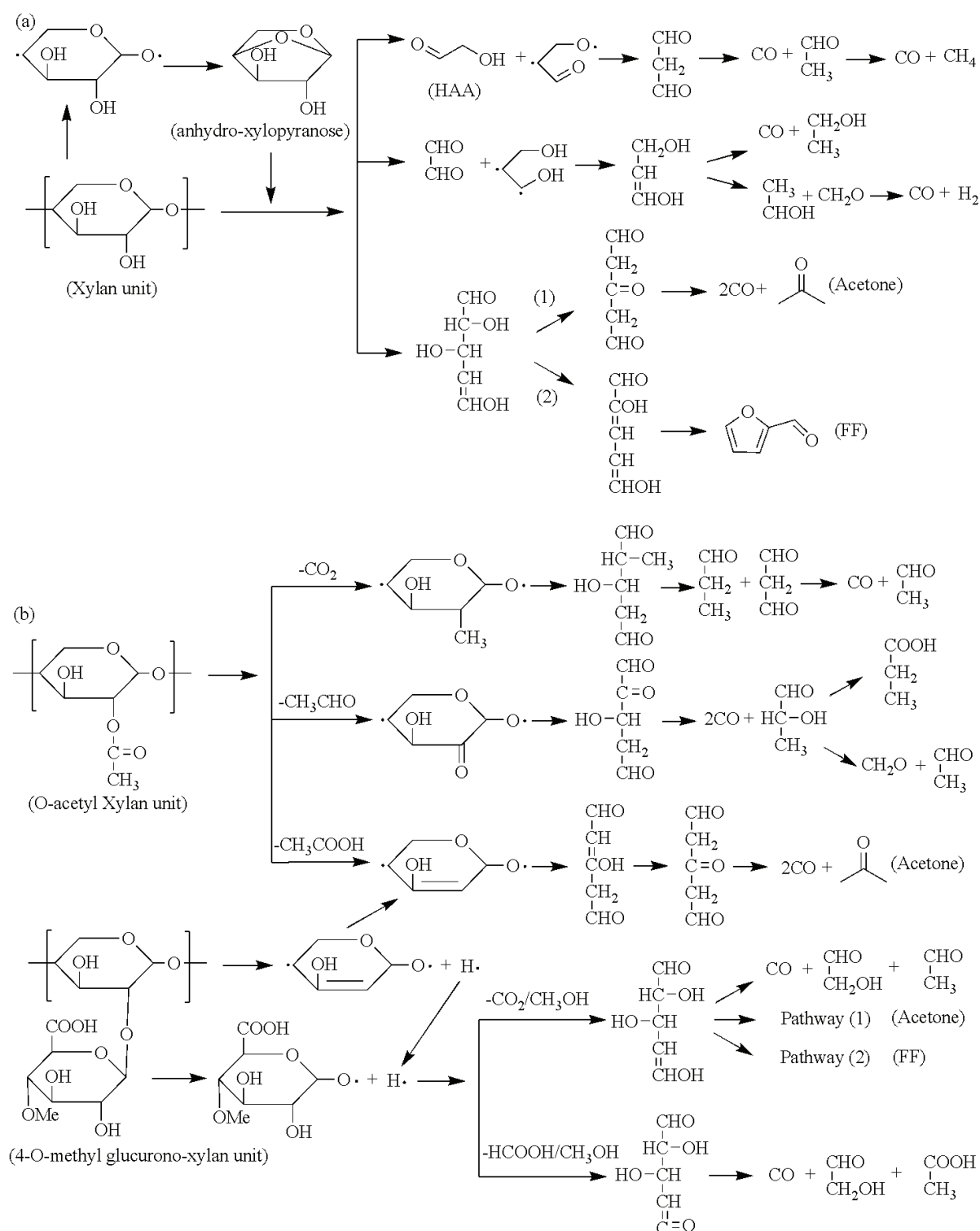

Fig. 3. The major pyrolytic pathways during xylan fast pyrolysis (proposed by Shen et al.) (a) the main chain of O-acetyl-4-methylglucurono-xylan, (b) O-acetylxylan and 4-O-methylglucuronic acid unit

2.3 Lignin fast pyrolysis

Lignin is the amorphous material that surrounds cellulose fibres and cements them together. It is a complex, heterogeneous polymer formed by the polymerization of three phenyl propane monomers, i.e. guaiacyl (4-hydroxy-3-methoxyphenyl), syringyl (3,5-dimethoxy-4-hydroxyphenyl) and *p*-hydroxyphenyl units. Lignin is the most complicated, least understood and most thermally stable component of biomass.

Primary pyrolysis of lignin begins with thermal softening at around 200°C, while most lignin pyrolysis occurs at higher temperatures, higher than the fast decomposition of cellulose. Fast pyrolysis of lignin will obtain higher char yield and lower liquid yield than holocellulose, and the liquid product can be classified into three groups, the large molecular oligomers (known as pyrolytic lignins), the monomeric phenolic compounds, as well as light compounds (such as methanol, HAA, acetic acid). The pyrolytic lignins are formed in much higher yield than the other two classes of products, usually account for 13.5-27.7 wt% of crude bio-oils on a water-free basis (Oasmaa et al., 2003; Garcia-Perez et al., 2007; Garcia-Perez et al., 2008). Several studies have been conducted to analyze them by various wet chemical and spectroscopic methods as well as pyrolysis-gas chromatography/mass spectrometry (Scholze & Meier, 2001; Scholze et al., 2001; Bayerbach et al., 2006; Garcia-Perez et al., 2008; Bayerbach & Meier, 2009), and to find out that their average molecular weight is between 650 and 1300 g/mol, and they are typically characterized by biphenyl, phenyl coumaran, diphenyl ethers, stilbene and resinol structures.

2.4 Biomass fast pyrolysis

Biomass fast pyrolysis is the summation of its major components fast pyrolysis. In addition to the cellulose, hemicellulose and lignin, biomass usually contains some extractives which would also decompose during fast pyrolysis, making the pyrolytic products more complex.

The biomass fast pyrolytic pathways and subsequent product distribution will be influenced by many factors, including biomass composition, feedstock property, pyrolysis temperature, heating rate, pressure, pyrolysis reactor configuration and a combination of these variables. The detailed effects of these factors can be found in previous studies, and will not be shown here.

3. Chemicals production from selective fast pyrolysis of biomass

3.1 Levoglucosan

LG (1,6-anhydro-β-D-glucopyranose) is the most important pyrolytic product of pure cellulose, formed through the depolymerization reaction. The chemistry of LG has long been known, and it can be used as a chiral synthon for the synthesis of stereoregular polysaccharides possessing biological activities (Miftakhov et al., 2001; Bailliez et al., 2004). Moreover, LG can also be hydrolyzed to glucose, providing a potentially rapid route to produce bio-ethanol (Bennett et al., 2009).

Fast pyrolysis of pure cellulose can produce LG with the yield up to 40 wt%, but fast pyrolysis of raw biomass materials would produce much lower LG yield due to the presence of inorganic impurities. Even the minor amounts of alkaline cations would shift the pyrolytic pathways of cellulose, to promote the formation of ring-scission products (such as HAA, HA, etc) and char on the expense of LG (Pan & Richards, 1989; NikAzar et al., 1997). Hence, it is necessary to use pure cellulose or demineralized biomass for the LG production. Furthermore, some studies pointed out that when small amounts of acids or acidic salts

were added to demineralized biomass, the LG yield could be increased. For example, it was reported in an analytical pyrolysis study that, the LG content in the pyrolytic products was 5.3% from raw birch wood, 17.0% from decationized wood, 33.6% from wood impregnated with 1.0% phosphoric acid, and 27.3% from decationized wood adsorbed with iron ions (Dobele et al., 2005).

The main difficulty in LG preparation is not the pyrolysis process, but its isolation from pyrolysis liquids. Due to its high boiling point (386 °C), LG could not be simply recovered by distillation. Currently, several methods have been proposed or patented for the purification of LG (Howard et al., 1993; Moens, 1994; S.Scott et al., 1996).

3.2 Levoglucosenone

Levoglucosenone (LGO, 1,6-anhydro-3,4-dideoxy-β-D-pyranosen-2-one, or 6,8-dioxabicyclo[3.2.1]oct-2-en-4-one) is a sugar enone product of cellulose, formed from the combined depolymerization and dehydration reactions, with the possible pyrolytic pathways shown in Fig.4 (Ohnishi et al., 1975). Its structure was firstly confirmed in 1973 (Halpern et al., 1973), and further confirmed and adopted by other researchers. LGO is an optically active organic compound in which all carbon atoms are different environments and which has easily modifiable functional groups. As a result, LGO can be used in the synthesis of various products (such as tetrodotoxin, thiosugar, ras activation inhibitors). The detailed application ways of the LGO can be found elsewhere (Miftakhov et al., 1994).
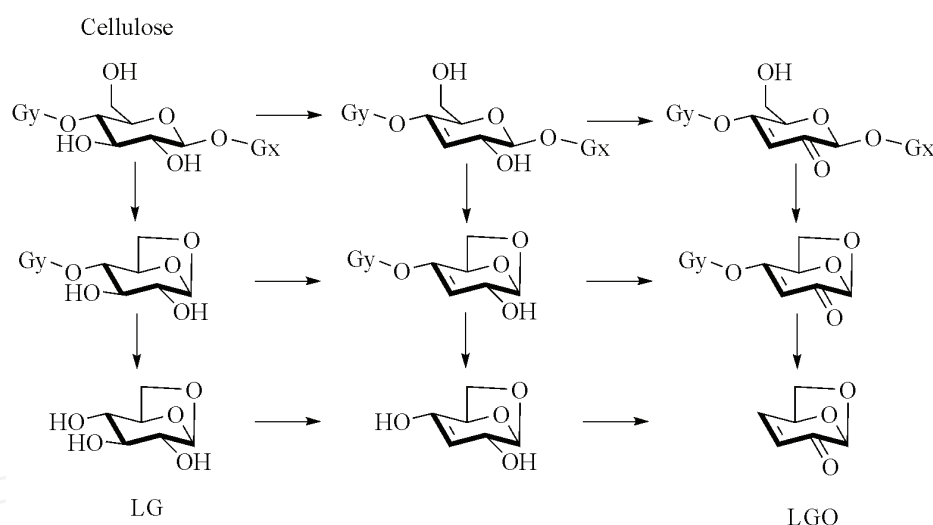

Fig. 4. The pyrolytic pathways for the formation of LGO from pyrolysis of cellulose
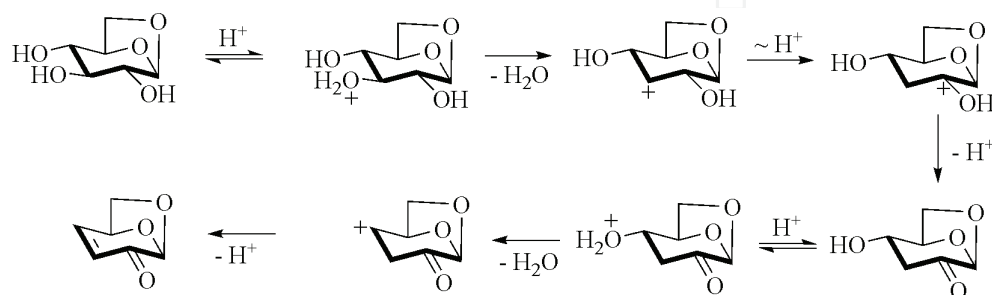

Fig. 5. The formation of LGO from acid-catalyzed decomposition of LG

LGO is formed in very low yield from fast pyrolysis of cellulose or biomass, but can be promoted by the addition of some acid catalysts in the pyrolytic process. A mechanism has been proposed for acid-catalyzed decomposition of LG to form the LGO, as shown in Fig.5 (Halpern et al., 1973).

Various acid catalysts exhibited the capability to promote the LGO formation, such as the $MgCl_2$ and $FeCl_3$ (Klampfl et al., 2006), $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ (Pappa et al., 2006; Di Blasi et al., 2007), CrO_3 and CrO_3+CuSO_4 (Fu et al., 2008a), $ZnCl_2$ (Di Blasi et al., 2008), M/MCM-41(M=Sn, Zr, Ti, Mg, etc.) (Torri et al., 2009a). However, almost all of these catalysts did not show high selectivity on the LGO, because they catalyzed the formation of several dehydrated products (LGO, LAC, DGP, FF, etc.), rather than LGO alone.

According to a series of studies performed by Dobele et al. (1999, 2001, 2003), fast pyrolysis of cellulose/biomass impregnated with phosphoric acid could produce LGO with very high purity. The highest LGO yield reached 34 wt% from microcrystalline cellulose impregnated with 2% phosphoric acid, or 17.5 wt% from birch wood impregnated with 2.5% phosphoric acid. Other studies also confirmed the promising catalytic selectivity of the phosphoric acid on the LGO production (Sarotti et al., 2007; Fu et al., 2008b; Nowakowski et al., 2008). Furthermore, Dobele et al. (2005) reported that the pretreatment of cellulose/biomass with adsorption of $Fe_2(SO_4)_3$ provided another way to prepare LGO with high purity, but the selectivity of the $Fe_2(SO_4)_3$ on the LGO was a little lower than the phosphoric acid.

In a recent study, it was reported that fast pyrolysis of pure cellulose followed with catalytic cracking of the pyrolysis vapors with solid super acids (sulfated metal oxides, SO_4^{2-}/TiO_2, SO_4^{2-}/ZrO_2, SO_4^{2-}/SnO_2, etc.) allowed the production of LGO with the content reaching 40% (peak area% on the GC/MS ion chromatograms) in the pyrolytic products (Lu et al., 2009a). In fact, when the solid super acids were mechanically mixed with cellulose, fast pyrolysis of the mixture also produced LGO with high purity. Compared with the impregnation of catalysts (phosphoric acid or $Fe_2(SO_4)_3$) on the cellulose/biomass, the utilization of solid catalysts avoids the complex pretreatment process, and will offer a significant advantage on catalyst recycles.

Compared with the LG, the LGO can be easily recovered from pyrolytic liquids by distillation, and a detailed purification method was proposed by Marshall (2008).

3.3 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one

The 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one (LAC) is another multifunctional C6-monomer formed from fast pyrolysis of cellulose. It was firstly identified by Fruneaxu et al. (1988), who also proposed its possible pyrolytic formation pathways, as shown in Fig.6. Compared with the LG and LGO, the LAC has received much less attention in either its production or application studies.

Similar as the LGO, the LAC is formed in very low yield during fast pyrolysis of cellulose, but can be promoted in the acid-catalyzed pyrolysis process. Most of the catalysts which could increase the LGO formation, could also promote the LAC formation. Therefore, it is necessary to find out proper catalyst which has high selectivity on the LAC.

According to some previous studies, fast pyrolysis of cellulose mixed with nanopowder aluminium titanate at 350 °C obtained the LGO and LAC as the major products, with the yields reaching 22 wt% and 8.6 wt%, respectively. When the pyrolysis temperature was increased to 500 °C, the LAC was formed as the only predominant product with high purity, but its yield was decreased to 6.2 wt% (the LGO yield was decreased to 0.77 wt%) (Fabbri et
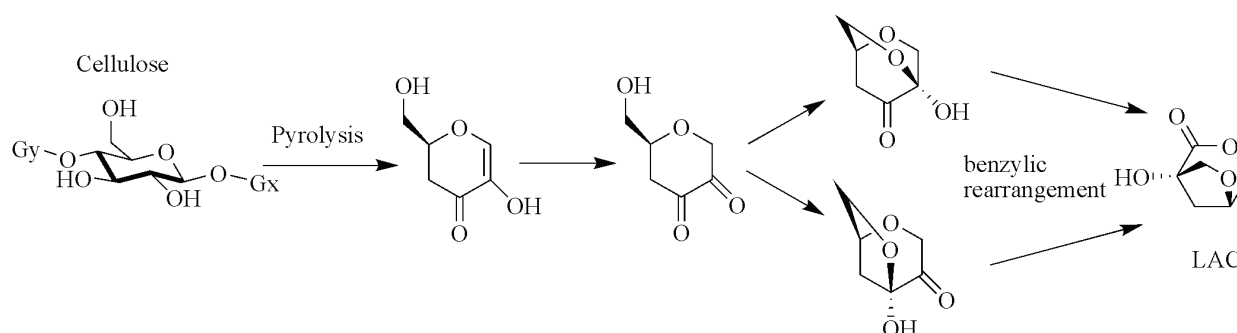
Fig. 6. The pyrolytic pathways for the formation of LAC from pyrolysis of cellulose

al., 2007a; Fabbri et al., 2007b; Torri et al., 2009b). As been indicated above, the utilization of solid catalysts will provide a convenient way for the catalyst recycles. Further studies have also been conducted by them to use the LAC as a possible building block in the synthesis of fine chemicals.

3.4 Anhydro-oligosaccharides

It is clearly demonstrated in previous studies that fast pyrolysis of cellulose will generate a range of anhydro-oligosaccharides, resulting from random cleavage of the polymer chain (Radlein et al., 1987; Pouwels et al., 1989; Lomax et al., 1991; Radlein et al., 1991). Anhydro-oligosaccharides are potential for a number of possible uses, such as the preparation of glycoconjugates, the so-called anti-adhesive drugs, and so on.

Although fast pyrolysis is a known technique to produce anhydro-oligosaccharides from cellulose, very limited studies have been carried out to produce the oligomers as a target product. Piskorz et al. (2000) initiated a flash pyrolysis study on this target product. Compared with conventional fast pyrolysis aiming at the maximum bio-oil yield, the production of anhydro-oligosaccharides required stricter reaction conditions: higher pyrolysis temperature (850~1200 °C) together with shorter residence time (35~75 ms). The short residence time was used to inhibit the conversion of large oligomers to monomer and dimer anhydrosaccharides. Anhydro-oligosaccharides in the range of G2-G7 were successfully produced with the yield up to near 20 wt%. These oligomers could be recovered as water soluble fraction from the reaction solid residues. Moreover, substantial amounts of larger oligomers (> G7) could also be produced but difficult to be identified.

Furthermore, if single anhydro-oligosaccharides can be produced and recovered, they should be more valuable than the mixed anhydro-oligosaccharides, but no reports are available in this research field at present.

3.5 Furfural

Furfural (FF) is a typical pyrolytic product formed from both of cellulose and hemicellulose. It is widely used as an organic solvent or an organic reagent for the production of medicines, resins, food additives, fuel additives and other special chemicals. Currently, FF is industrially produced from agricultural raw materials rich in pentosan. By aqueous acid catalysis (e.g., sulfuric acid or phosphoric acid), the pentosan is firstly hydrolyzed to pentose which is then dehydrated to form FF (Zeitsch, 2000).

Similar as the LGO and LAC, the formation of FF can be promoted in the acid-catalyzed pyrolysis of biomass (Shafizadeh & Lai, 1972; Encinar et al., 1997; Encinar et al., 1998; Adam

et al., 2005; Shimada et al., 2008; Lu et al., 2009b). Zinc chloride ($ZnCl_2$) is one of the promising catalysts to produce FF. It was found that fast pyrolysis of cellulose impregnated with small amounts of $ZnCl_2$ (below 10 wt%) would generate several dehydrated products as the primary pyrolytic products, mainly the FF, LGO, LAC and 1,4:3,6-dianhydro-α-D-glucopyranose (DGP). With the increasing of $ZnCl_2$ impregnation (at least 15 wt% or more), the $ZnCl_2$ catalysis would increase the FF formation, while decrease the anhydrosugars. Moreover, the secondary catalytic cracking of the primary pyrolysis vapors by $ZnCl_2$ could promote the conversion of LGO and other anhydrosugars to FF, leaving the FF as the only predominant product (Fig.7). Compared with the cellulose, the $ZnCl_2$-catalzyed fast pyrolysis of xylan would obtain the FF as the only predominant product, and the FF yield would be higher than that from cellulose, indicating that biomass rich xylan would be suitable for the FF production.
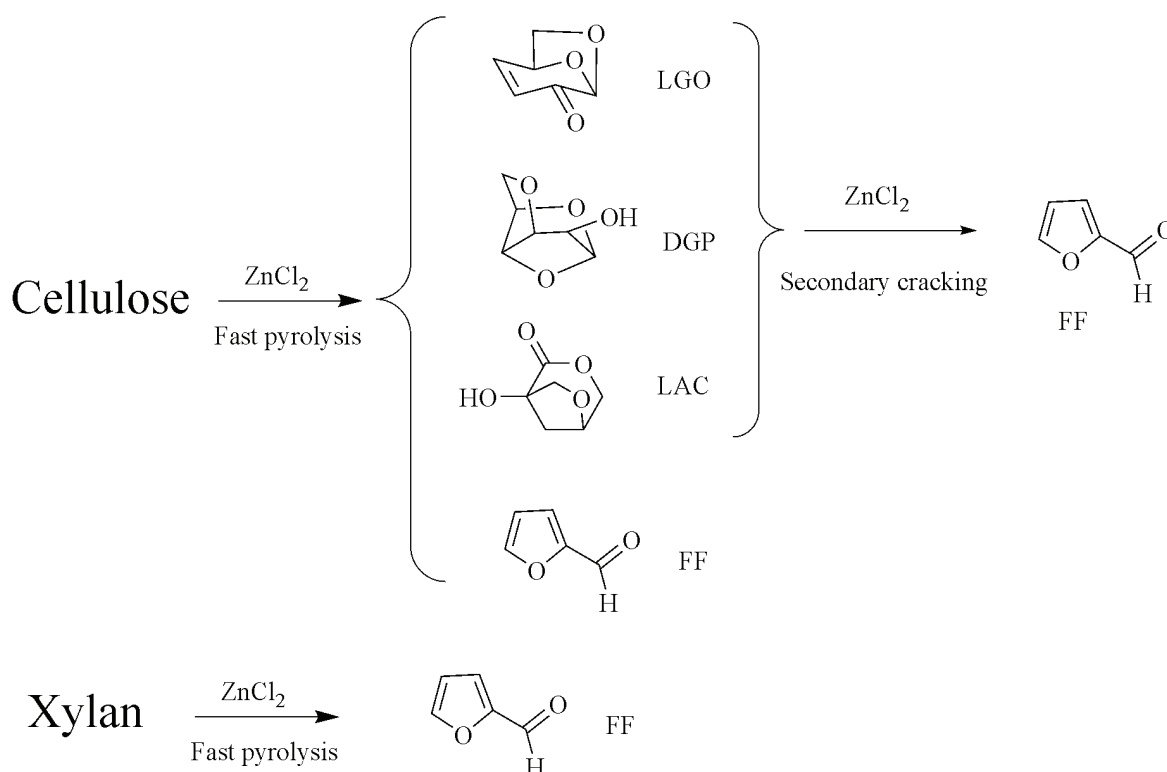

Fig. 7. The formation of FF during $ZnCl_2$-catalyzed fast pyrolysis of biomass

In another study, microwave-assisted fast pyrolysis was applied to treat biomass mixed with various catalysts, and the results revealed that the $MgCl_2$ exhibited high selectivity on the FF production (Wan et al., 2009). The highest FF content was more than 80% (peak area% on the GC/MS ion chromatograms) at the 8 g $MgCl_2$ mixed with 100 g biomass.

In addition, $ZnCl_2$ (or sometimes $MgCl_2$) is an effective chemical activation agent for the production of activated carbons from biomass. Hence, for the biomass pretreated by $ZnCl_2$ (or $MgCl_2$) impregnation, they can be firstly subjected to fast pyrolysis to produce FF. The solid residues which contained char and $ZnCl_2$ (or $MgCl_2$), could be further activated to produce activated carbons, so as to achieve the co-production of FF and activated carbons.

3.6 Hydroxyacetaldehyde

HAA is formed as the most abundant linear carbonyl product from pyrolytic ring scission of holocellulose. It is the simplest aldehyde-alcohol or sugar, and can be used as an active meat-browning agent in food flavoring industry (Garham & Underwood, 1993), or ingredient in cosmetic industry.

As been indicated above, during fast pyrolysis of biomass, the pyrolytic ring scission of holocellulose will be promoted by the small amounts of ash or alkaline cations (Shimada et al., 2008), and hence, HAA can be formed with high yield in these conditions. Moreover, HAA could be further formed from the secondary cracking of the anhydrosugar products. As a result, HAA is usually the most abundant single organic compound in crude bio-oils produced from raw biomass materials.

Similar as the LG, the difficulty for the preparation of HAA mainly lies in its recovery from pyrolysis liquids, due to its high reactivity. An efficient purification method was patented by Stradal & Underwood (1995).

3.7 Acetic acid

During fast pyrolysis of biomass, acetic acid (AA) can be formed from different ways, with a large portion from deacetylation of hemicellulose, and a small portion from pyrolytic ring scission of holocellulose and side-chain cracking of lignin. The content of AA could be over 10 wt% in crude bio-oils produced from biomass rich in acetyl groups, and some preliminary studies have been reported for the recovery of AA (Mahfud et al., 2008). AA is a common chemical, and is less valuable than other chemicals described above. According to its formation characteristics, selective fast pyrolysis of biomass to produce AA with high purity might be achieved in several different ways.

The deacetylation of hemicellulose occurs at relatively low temperature, lower than the fast decomposition of the major biomass components. Hence, AA can be produced from low temperature pyrolysis of biomass. It has already been confirmed that during carbonization or torrefaction of biomass at temperatures lower than 300 °C, a liquid by-product rich in AA could be produced (Prins et al., 2006). In fact, if biomass is subjected to fast pyrolysis at around 300 °C for a short time period, part of the acetyl group would break down to form AA, while the other biomass components would not be greatly influenced. Therefore, a two-step process might be applied to treat biomass, with the first low-temperature fast pyrolysis to produce AA, followed with the moderate-temperature fast pyrolysis to produce bio-oil.

AA can also be prepared by catalytic pyrolysis of biomass. For example, Qi et al. (2006) reported that catalytic pyrolysis of biomass using NaY catalyst produced abundant AA, with the content over 80% (peak area% on the GC/MS ion chromatograms) in the pyrolytic products.

In addition, during the production of FF through fast pyrolysis of biomass impregnated with $ZnCl_2$ (or $MgCl_2$), the catalysis of $ZnCl_2$ (or $MgCl_2$) inhibited most of the pyrolytic pathways, but not the AA formation. As a result, AA would be the second most important product in the catalytic organic products, and thus, it could be recovered as a byproduct during preparation of FF.

3.8 Phenolic compounds

The lignin-derived phenolic compounds (monomeric phenolic compounds and pyrolytic lignins) can be isolated from crude bio-oils by different methods (Achladas, 1991; Amen-

Chen et al., 1997; Deng et al., 2009), and they are known to be used as phenol replacement in production of phenol-formaldehyde resins (Himmelblau, 1991; Chum & Kreibich, 1992; Roy et al., 2000; Giroux et al., 2001).

As indicated above, the monomeric phenolic compounds are usually formed in much lower yield than the pyrolytic lignins. Since the monomers are more reactive than the oligomers for resin production, and thus, it will be attractive to promote the production of monomeric phenolic compounds. According to some previous studies, fast pyrolysis of biomass impregnated with some alkaline compounds (NaOH, KOH) could increase the yield of monomeric phenolic compounds (Nowakowski et al., 2007; Di Blasi et al., 2009a; Di Blasi et al., 2009b). In another study, Pd/SBA-15 catalysts were employed to catalytic crack biomass fast pyrolysis vapors that contained a lot of pyrolytic lignins, and the results indicated that the Pd/SBA-15 catalysts were able to promote the conversion the pyrolytic lignins to monomeric phenolic compounds, and meanwhile to crack and decrease holocellulose-derived products. Hence, the content of the total monomeric phenolic compounds reached 55% (peak area% on the GC/MS ion chromatograms) in the catalytic pyrolytic products (Lu et al., 2010a). Some other catalysts were also confirmed to possess the catalytic capability to increase the yield of monomeric phenolic compounds or their content in the catalytic bio-oils (Adam et al., 2006; Antonakou et al., 2006; Nilsen et al., 2007; Ates & Isikdag, 2009).

Furthermore, if single phenolic compounds could be produced and recovered, they should be much more valuable than the mixed phenolic compounds. According to a previous study done by Murwanashyaka et al. (2001a), the evolution of major monomeric phenolic compounds took place in the following order: methylguaiacol, ethylguaiacol, guaiacol, propenylsyringol, phenol and catechol, which suggested that the production of specific phenolic compounds might be achieved by step-wise pyrolysis of biomass. Catalytic pyrolysis is another promising way. For example, during the catalytic cracking of biomass fast pyrolysis vapors with Pd/SBA-15 catalysts, the 4-ethyl-2-methoxy-phenol was increased greatly, with the content up to 10% (peak area% on the GC/MS ion chromatograms) in the pyrolytic products (Lu et al., 2010a). Some subsequent studies have also been reported for the recovery of pure single phenolic compounds (Murwanashyaka et al., 2001b).

3.9 Light aromatic hydrocarbons

Hydrocarbons are usually formed in very low yields during fast pyrolysis of biomass, but can be greatly increased by using proper cracking catalysts with deoxygenation capability (Bridgwater, 1996). Zeolite catalysts (such as HZSM-5, HY, etc.) are very effective to convert the highly oxygenated crude bio-oils or pyrolysis vapors to hydrocarbons which are dominated by several light aromatic hydrocarbons (benzene, toluene, xylene and naphthalene) (Horne & Williams, 1996; Olazar et al., 2000; Williams & Nugranad, 2000; Pattiya et al., 2008; Zhang et al., 2009). For example, in the studies performed by Adjaye et al. (1995, 1996), catalytic cracking of the crude bio-oil by HZSM-5 catalysts obtained a organic liquid product with up to 90 wt% of aromatic hydrocarbons, and the aromatic hydrocarbons contained abundant toluene (31.8 wt%) and xylene (33.1 wt%).

Other catalysts were also investigated for the production of light aromatic hydrocarbons. For example, Wang et al. (2008) reported that catalytic pyrolysis of biomass using CoMo-S/Al$_2$O$_3$ catalyst produced the four light aromatic hydrocarbons (benzene, toluene, xylene and naphthalene) with the yield reaching 6.3 wt% at 590 °C.

3.10 Other valuable chemicals

In addition to the above chemicals, many other chemicals can be produced by selective fast pyrolysis of biomass. For example, Chen et al. (2008) reported that fast pyrolysis of biomass impregnated with Na_2CO_3 produced HA with high purity. Badri et al. (2008) revealed that catalytic pyrolysis of cotton with reactive dyes favored the formation of 5-hydroxymethyl-furfural (HMF) and 3-(hydroxymethyl)-furan. Lu et al. (2010a) found that fast pyrolysis of cellulose followed with catalytic cracking of the vapors by sulfated metal oxides could obtain high yields of furan and 5-methyl furfural. In another study, Lu et al. (2010b) confirmed that catalytic cracking of the biomass fast pyrolysis vapors using $ZrO_2\&TiO_2$ increased the formation of three light carbonyl products (acetaldehyde, acetone and 2-butanone).

4. Conclusion

Most of the selective fast pyrolysis techniques are only in their early stage of development, and none of the techniques is commercially practical to produce specific chemicals in marketable quantities at present. Three aspects should be considered for the commercialization of the selective fast pyrolysis techniques, including (1) the technique to produce specific chemicals in high yield and purity, (2) the method to recover the target chemicals from pyrolysis liquids, and (3) the ready markets for the chemicals.

Among the above indicated chemicals, the LG, HAA and AA can be produced without catalyst utilization, and thus, their large scale production might be relatively easy to achieve through slight modification of the conventional fast pyrolysis technique. While the production of other chemicals requires catalysts, which will add difficulty to their scale up. Various methods have been proposed for the chemicals recovery, and further studies should be conducted to reduce the purification cost. Finally, it is important to note that ready markets do not exist for the LG, LGO, LAC, anhydro-oligosaccharides, and some other chemicals at present. Corresponding markets should be developed by manufacturers who would incorporate these chemicals into various products.

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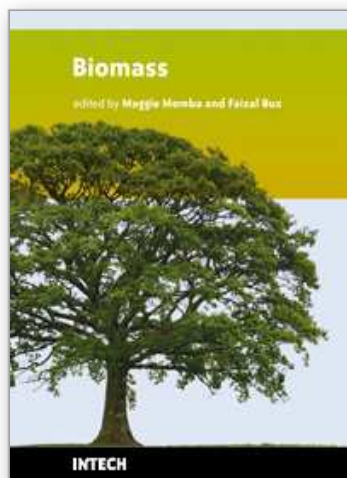
Biomass

Edited by Maggy Ndombo Benteke Momba

Due to demands placed on natural resources globally and subsequent deterioration of the environment, there is a need to source and develop appropriate technology to satisfy this requirement. For decades mankind has largely depended on natural resources such as fossil fuels to meet the ever increasing energy demands. Realizing the finite nature of these resources, emphasis is now shifting to investigating alternate energy source governed by environmentally friendly principles. The abundance of biomass and associated favorable techno-economics has recently changed global perceptions of harnessing biomass as a valuable resource rather than a waste. To this end this book aims to make a contribution to exploring further this area of biomass research and development in the form of a compilation of chapters and covering areas of ecological status of different types of biomass and the roles they play in ecosystems, current status of biomass utilization and deriving energy and other value added products from biomass. In this context biomass can be defined as large plants and trees and different groups of microorganisms. This book will serve as an invaluable resource for scientists and environmental managers in planning solutions for sustainable development.

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