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Chapter 9

The Overview of Thermal Decomposition of Cellulose in Lignocellulosic Biomass

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Additional information is available at the end of the chapter

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1. Introduction

Lignocellulosic biomass including wood, logging residue, crops and agricultural wastes) has been widely utilized to produce energy, fuels or chemicals, acting as the potential renewable source for taking place of fossil energies (such as coal, natural gas and petroleum) [1]. Pyrolysis is proved to be, one of the most promising methods to convert biomass into different products (syn-gas, bio-liquid, char and chemicals), which could essentially diversify the energy-supply in many situations [2].

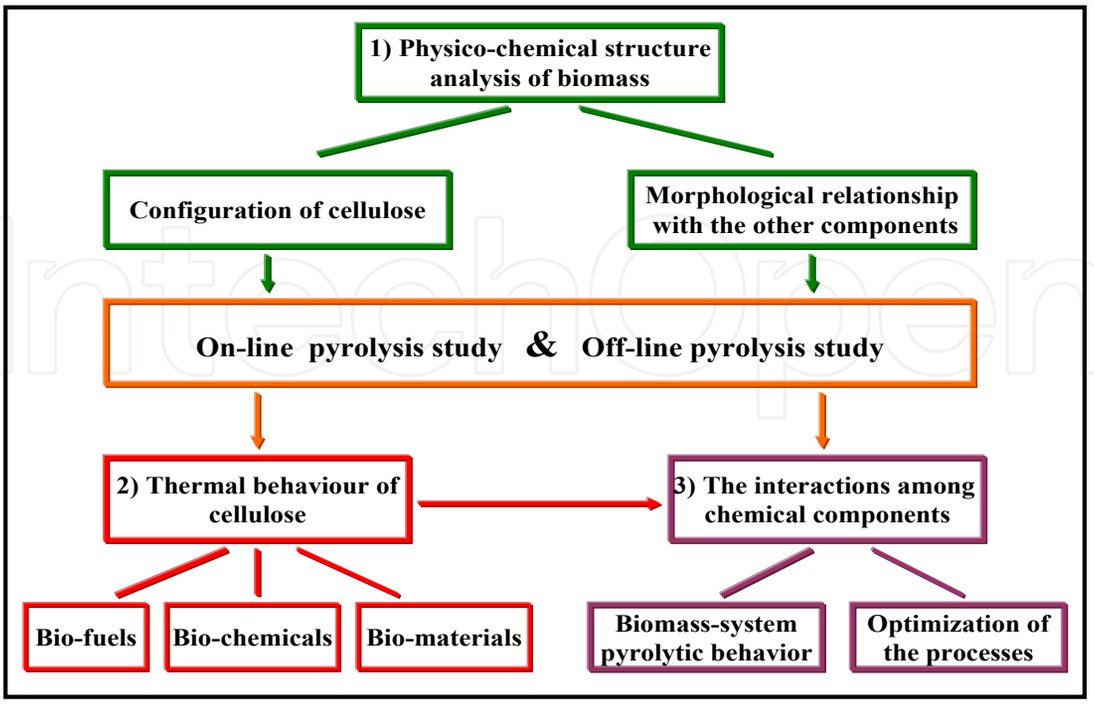


Figure 1. The fundamental issues and targets concerning the pyrolysis of cellulose

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Cellulose, the most principal chemical component in different lignocellulosic biomass (accounting for more than 50% by weight), has a linear homopolymer of glucopyranose residues linked by β-1, 4- glycosidic bond. The study on pyrolysis of cellulose would be particularly benificial for achieving the better understanding of the pyrolytic mechanism of biomass and facilitating its direct applications in terms of fuels, chemicals and bio-materials. This gives rise to substantial studies on pyrolysis of cellulose in lignocellulosic biomass during the past half-century (Fig. 1), which could be categorized into the three following fundamental issues (Fig. 1):

1. The physico-chemical structure analysis of biomass is concerning the morphological analysis of the biomass cell-wall structure, the distribution and configuration of cellulose, which would facilitate not only the direct utilization of biomass as bio-material, but also the improvement of conversion processes of biomass to fuels or chemicals;
2. The thermal behavior of cellulose involving on-line pyrolysis and off-line pyrolysis study. The on-line pyrolysis is concentrated on the solid mass loss versus temperature or time (along with the evolution of the volatiles) and kinetic models, mostly employing isothermal and dynamic thermo-gravimetry analysis coupled with or without Fourier Transformation Infrared Spectrometry (FTIR) or Mass spectrometry (MS); The off-line pyrolysis study is to examine the yield of the main products (gas, liquid and solid), variation of the compositions in gaseous or liquid product influenced by the intrinsic characteristics and experimental conditions, in order to optimize the pyrolysis process for energy and/or chemicals production;
3. The interactions among the three main components under the pyrolytic condition is to introduce the possible interacting mechanism of the components in biomass, in terms of the mass loss process, the evolution of the volatiles and the yield of the specific products. This would help to improve the understanding of pyrolysis of whole biomass system from the pyrolytic behavior of the individual components.

The studies of pyrolysis of cellulose concerning the above four fundamental issues would be vigorously discussed in this work (especially for the works reported during the past 25 years), where the way-forward of this field would also be specified. This would supply the conceptual guide for the improvement of cellulose utilization and optimization of the thermal-conversion process of biomass.

2. The cell-wall structure of biomass and the configuration of cellulose

The morphological structure of lignocellulosic biomass has been studied regarding the distribution and inter-linkages of the chemical components, and their configuration [3, 4]. This facilitates not only the better understanding of the physico-chemical properties of biomass, but also the improvement of conversion processes (such as pyrolysis) of biomass to fuels or chemicals.

With the growing interest on lignocellulosic biomass as a potential substituent for fossil fuels, the pyrolysis of biomass should be dramatically examined. Consequently, the cell-wall model of lignocellulosic biomass, the distribution of the chemical components (especially

cellulose), and the configuration of cellulose would be discussed in the following sections, which would help understand the remarkable characteristics of cellulose pyrolysis and its interactions with the other two main components (hemicellulose and lignin).

2.1. The cell-wall structure of biomass

The model of the cell-wall of woody biomass, firstly proposed by Fengel and Wegener [3], is well-established and further developed by Dumitriu [5], involving cell-wall structure and the distribution of the chemical components in different cell wall layers.

The cell wall could be morphologically divided into three distinct zones: middle lamella, primary cell wall and secondary wall [5]. The middle lamella is shared by two contiguous cells and is composed almost entirely of pectic substances. The primary cell walls are composed of cellulose microfibrils and interpenetrating matrix of hemicelluloses, pectins, and proteins. Cellulose forms the framework of the cell walls, hemicelluloses cross-link noncellulosic and cellulosic polymers, and pectins provide the structural support to the cell wall. The secondary cell walls are derived from the primary walls by thickening and inclusion of lignin into the cell wall matrix and occur inside the primary wall. The transition from primary to secondary cell wall synthesis is marked by the cessation of pectin deposition and a noted increase in the synthesis and deposition of cellulose/hemicellulose and lignin. The cellulose and non-cellulosic polysaccharides of the secondary cell wall are qualitatively distinct from those found in the primary cell walls.

The relevant study [6] evidenced that if cellulose is deposited actively between S1 and S3 developmental stages (especially in the middle part of S2 stage), hemicellulose (xylan) deposition occurs in the S1 to early S2 and again in the S3 developmental layers. Successive deposition of hemicellulose (xylan) onto the cell wall increases the microfibril diameter. The large amounts of hemicellulose (xylan) that accumulated on microfibrils appear globular but are covered with lignin after they are deposited. The information about the distribution of the main components (hemicellulose, cellulose and lignin) in the cell wall layers of lignocellulosic biomass is quantitatively reported in the literature [7].

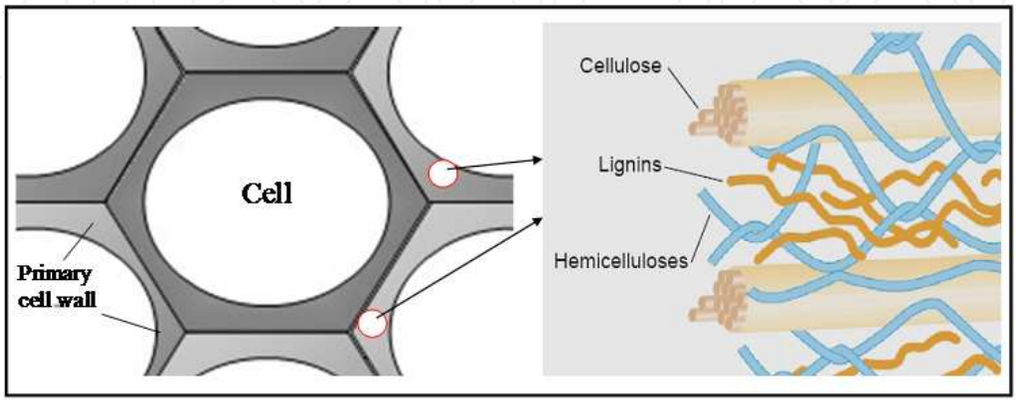


Figure 2. The schematic representation of the proposed cell wall along with the location of the main components in biomass

According to the above discussion, a simplified schematics for the structure of plant cell wall is presented in Fig. 2, where the morphological relationship among the main components in biomass (cellulose, hemicellulose and lignin) is clearly specified. It still needs to be notified that the details concerning the inter-linking/bond relationship (such as the H-bond among the polysaccharide molecules and lignin-carbohydrate coalescence) between the chemical components in the cell walls of wood are not well examined in the literature.

2.2. The configuration of cellulose

As far as the chemical components of biomass were concerned, a distinction should be made between the main macromolecular cell-wall components--cellulose, hemicellulose (polyoses) and lignin [3]. Cellulose is a uniform component in all lignocellulosic biomass, while the proportions and chemical composition of lignin and hemicellulose differ in different biomass. The configuration of cellulose in lignocellulosic biomass would be discussed, with regard to its content, isolation methods, the characterization of the macromolecules and the inter-linkages among the units.

Cellulose is the prominent chemical component in lignocellulosic biomass, accounting for approximately 50% by weight. The methods for isolating and/or determining cellulose from biomass could be summarized as [3]:

1. Separation of the main portions of hemicellulose and residual lignin from cellulose;
2. Direct isolation of cellulose from lignocellulosic biomass, including purification procedures (such as pulping process);
3. Determination of the approximate cellulose content by total hydrolysis of biomass, cellulose with subsequent determination of the resulting sugars.

In any isolation method cellulose cannot be obtained in a pure state, thus the purification always plays an important role in the cellulose isolation process. Through the relevant methylation experimental studies [3, 5], the primary structure of cellulose is evidenced as a linearhomopolymer of glucose having the D configuration and connected by β-(1-4) glycosidic linkages (Fig. 3). It could be found that the units of the cellulose molecular chain are bound by β-(1-4) glycosidic linkages, presenting that the adjacent glucose units are linked by dehydration between their hydroxylic groups at carbon 1 and carbon 4. The β-position of the OH-group at C1 needs a turning of the following glucose unit around the C1-C4 axis of the pyranose ring.

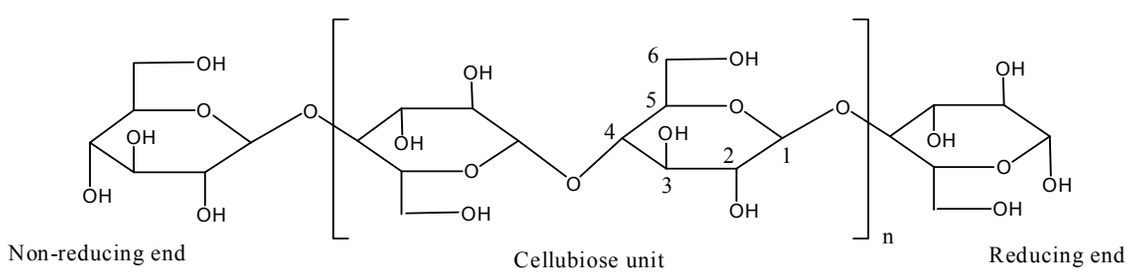


Figure 3. The central part (cellubiose unit) of cellulose molecular chain with the reducing and non-reducing end groups.

The stabilization of the long cellulose molecular chains in order systems originates in the presence of functional groups which are able to interact with each other. The functional groups of the cellulose chains are the hydroxyl groups, three of which are linked to each glucopyranose unit. These OH-groups are not only responsible for the supramolecular structure by also for the chemical and physical behavior of the cellulose through the hydrogen bond (H-bond). The OH-groups of cellulose molecules are able to form two types of hydrogen bonds depending on their site at the glucose unit [3]. The hydrogen bonds between OH-groups of adjacent glucose units in the same cellulose chain are called intramolecular linkages, which give certain stiffness to the single chain. The hydrogen bonds between OH-groups of the adjacent cellulose chains are called intermolecular linkages, which are responsible for the formation of supramolecular structures. The primary structures, consisting of a number of cellulose chains through the hydrogen bonds in a superhelicoidal fashion, are the cellulose microfibrils, which build up the framework of the whole cell walls [5].

Two chain ends of the cellulose chain are chemically different (Fig. 3). One end has a D-glucopyranose unit in which anomeric carbon atom is involved in a glycosidic linkage, whereas the other end has a D-glucopyranose unit in which the anomeric carbon atom is free. This cyclic hemiacetal function is in an equilibrium in which a small proportion is an aldehyde, which gives rise to reducing properties at this end of the chain, so that the cellulose chain has a chemical polarity, while the OH-group at the C4 end of the cellulose chain is an alcoholic hydroxyl and therefore non-reducing. The molecular weight of cellulose varies widely depending on the origin of the sample. As cellulose is a linear polymer with uniform units and bonds the size of the chain molecule is usually defined as degree of polymerization (DP). The degrees of polymerization of the plant-cellulose as well as the technical cellulose products are estimated from 15300 for capsules to 305 for rayon fibers [5].

3. The thermal behavior of cellulose

3.1. On-line pyrolysis of cellulose

The thermogravimetric (TG) analysis method, either dynamic heating process or isothermal heating process, is well-established for on-line pyrolysis of biomass and its components (cellulose, hemicellulose and lignin). The mass loss of the solid sample could be exactly recorded versus temperature/time. The chemical kinetic models for the biomass and its components are proposed from the analysis of the different mass loss stages and validated through the correlation between the predicted data and the experimental mass loss curve. Since the specific chemical phenomena and the prediction of the volatile yields are rarely referred in those models, TGA coupled with FTIR, GC, MS or other advanced analytical equipments is recently employed to investigate the evolution of the volatile along during the pyrolysis process. This facilitates the understanding of the possible chemical reactions for depolymerization of the macromolecules and the secondary cracking of the primary fragments. The development of the kinetics of cellulose pyrolysis would be systematically

overviewed, involving most of recent studies implemented by other groups led by Piskorz, Di Blasi, Banyaz, Agrawal, Wooten, Hosoya and so on. Several controversial points addressed in previous studies would be intensively discussed, concerning the existence of the intermediate anhydrosugars, secondary cracking of the volatiles and the formation of char residue.

Historically, it was perhaps that Broido' s group firstly called attention to the intriguing phenomena of cellulose pyrolysis and proposed the established kinetic scheme in 1960s [25, 26]. As described in **Scheme 1** (Fig. 4) [26, 27], the decomposition of cellulose can be represented through two competing reactions: the first step is estimated to be important at low temperatures and slow heating rates, accounting for the slight endothermic formation of anhydrocellulose below 280 °C detected by DTA. At about 280 °C a competitive, more endothermic unzipping reaction is initiated for the remained cellulose, leading to the tar formation. The third step presents the exothermic decomposition of anhydrocellulose to char and gas.

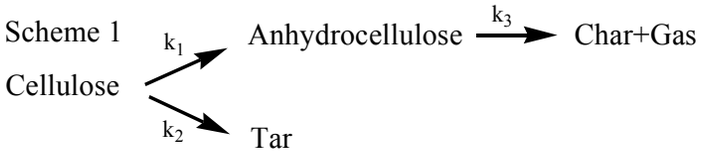


Figure 4. The kinetic model for cellulose pyrolysis proposed by Broido and Weinstein (1971) [27]

This Broido' s kinetic scheme is re-examined by Argawal [13], revealing that the rates of anhydrocellulose formation are comparable to those of the depolymerization process only in one case for temperatures of ~ 270 °C in the isothermal, fixed-bed conditions. Then, the mechanism is approved through the isothermal, fluid-bed experiments in the temperature range 250-300 °C, providing a complete set of kinetic data for the Broido model [13]. It is worthily noting that the formation of the anhydrocellulose as an intermediate product is undetectable in the experiments, and no kinetic data for the char forming reaction are reported in the above publications. These ambiguities stimulated the global researchers' interests in the kinetic studies of cellulose pyrolysis, resulting in a vigorous debate in the following years.

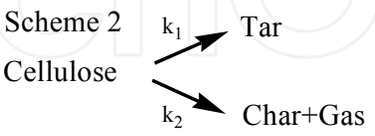


Figure 5. The kinetic model for cellulose pyrolysis proposed by Broido and Nelson (1975) [10]

In 1975, Broido and Nelson examined the effect of thermal pretreatments at 230-275 °C on the cellulose char yields varying from 13% (no thermal pretreatment) to over 27% [10]. They employed the large samples of cellulose (100 mg of shredded cellulose, and 7 cm × 3 cm sheets, individually wrapped several layers deep around a glass rod), which might incur the char formation from solid-vapor interactions during the prolonged thermal pretreatment. The previous kinetic model (Scheme 1) is correspondingly improved as described in **Scheme**

2 (Fig. 5), eliminating the formation of the anhydrocellulose as an intermediate product. The **Scheme 3 (Fig. 6)** is slightly different from those proposed by Broido and the co-workers but largely confirms the previous findings, which is even titled as "Broido-Shafizadeh model" in somewhere [23, 30-32]. At the low temperatures (259-295 ^{o}C), the initiation period (characterized by an accelerating rate of weight loss [33]) has been explained as a formation of "active cellulose" through the depolymerization process (reduction of the DP) with the activation energy of 242.8 kJ/mol. Then, the "active cellulose" undergoes the two competitive reactions to produce either char and gas (activation energy 153.1 kJ/mol) or primary volatiles (197.9 kJ/mol). At high temperatures (above 295 ^{o}C), no initial period of accelerating rate of weight loss was observed in Shafizadeh's study [29]. Thus cellulose degradation mechanism was described simply via two competitive first-order reactions, where the formation of "active cellulose" is eliminated from **Scheme 3**. This mechanism is then confirmed by Antal and Varhegyi' TGA study of cellulose pyrolysis with the heating rate of 40 K/min, attaining the activation energy for the formation of volatiles as 238 kJ/mol and 148 kJ/mol for the formation of char and gas [14].

Scheme 3

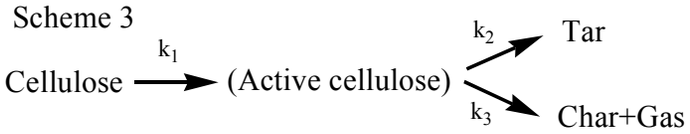


Figure 6. The kinetic model for cellulose pyrolysis proposed by Bradbury et al. (1979) [29]

The argument between Antal-Varhegyi and Broido-Shafezadeh is remarkable, concerning the existence of "active cellulose" during the pyrolysis of cellulose. Antal and Varhegyi presented that no evidence was found to support the inclusion of the initiation step displayed in the **Scheme 5** (titled as "Broido-Schafezadeh model"), whatever this step proceeded at an immeasurably high rate at conditions of interests, or it does not exist [23].

In 2002, Lede et al. directly observed a transient "intermediate liquid compound" in small pellets of cellulose that had been heated by radiant flash pyrolysis in an imaging furnace, which is characterized by HPLC/MS and found to be composed predominantly of anhydro-oligosaccharides (such as levoglucosan, cellobiosan and cellotriosan) [41]. In the slow heating experiments of cellulose, Wooten [32] revealed that intermediate cellulose (IC) is an ephemeral component that appears and ten disappears over the course of 60 min of heating at 300 ^{o}C, while the rapid disappearance of IC in samples that have been heated at only a slightly higher temperature (i.e., 325 ^{o}C) further demonstrates the transient nature of IC. This behavior clearly identifies the compound(s) as a reaction intermediate, and the authors correspondingly associated this intermediate compound with the "active cellulose" in the Broido and Shafezadeh kinetic models (**Scheme 3**) [28, 29]. Thus, some recent researchers have attained the formation of "active cellulose" as an intermediate during cellulose pyrolysis, as presented in **Scheme 4** (Fig. 7) [12, 42]

Previously, Bradbury et al. [29] and Antal [23] suggested that char formation might result from the repolymerization of volatile materials such as levoglucosan. This phenomenon is approved by Hosoya [36], presenting that the secondary char from cellulose is formed from

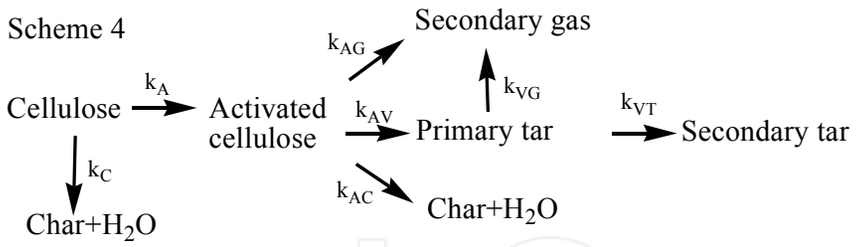


Figure 7. The kinetic model for cellulose pyrolysis proposed by Diebold (1994) [39] and similarly proposed by Wooten et al. (2004) [32]

the repolymerization of anhydrosugars (levoglucosan). The experimental data from the Wooten et al.'s study [32] shows that a precursor-product relationship does exist between intermediate cellulose ("active cellulose") and the aliphatic and aromatic components of the char.

Nowadays, it might be not difficult to evidence the existence of "active cellulose" or other important (intermediate) products with the help of the advanced analytical equipments, but the chemical reaction mechanism for cellulose pyrolysis is still ambiguous and controversial. One of the possible routes to improve the understanding of the structure changes of cellulose molecules and formation of the specific products is to employ the study of thermal decomposition of the relevant derivatives, together with the molecular dynamic simulation (MDS) which is well-established for estimating the specific chemical pathways from the microscopic point of view. Moreover, the identification of intermolecular hydrogen bonding and that between the different molecular chains would be another uncertainty for understanding the pyrolytic behavior of cellulose, especially for the initial stage of the cellulose pyrolysis.

3.2. Off-line pyrolysis of cellulose

Compared to the on-line pyrolysis study of cellulose, the off-line pyrolysis of cellulose is mostly carried out under the relatively high temperature (above 400 ^{o}C) or high heating rate (more than or around 1000 ^{o}C/s) [12, 32, 36, 40, 44-48] and sometimes under low temperature heating (below 400 ^{o}C) [49, 50], concerning the following issues: 1) the distributions of the gas, liquid and solid products; 2) the formation of the specific compounds and the pyrolytic chemical pathways. How these two issues may be influenced by the pyrolytic reactors and the variables like temperature, residence time, heating rate, pressure, particle size, catalytic salts and crystallinity is extensively examined in the literature, in order to promote the product specificity, maximize the yield and improve the understanding of the pyrolytic mechanism.

In this work, the emphasis is on the effects of the predominant factors such as the reactor type, temperature or heating rate, residence time on the distributions of the products (gas, liquid and solid) from cellulose pyrolysis. Considering the complexity of chemical constituents in gas and liquid products, the attention would be confined to those few compounds which have been established to be producible in good yield (such as

levoglucosan, hydroxyacetaldehyde, furfural, CO, CO_2 and so on), in order to meet the interests in potential industrial applications.

Reactor	Liquid yield wt%	Feed size	Input gas	Complexity	Scale-up	Status*
Fluidized bed	75	Small	High	Medium	Easy	Demo
CFB	75	Medium	High	High	Easy	Pilot
Entrained gas flow	65	Small	High	High	Easy	Lab
Vaccum	60	Large	Low	High	Hard	Demo
Rotating cone	65	Very small	Low	High	Hard	Pilot
Ablative	75	Large	Low	High	Hard	Lab
Auger	65	Small	Low	Low	Easy	

*: Demo scale is estimated to be 200-2000 kg/h, pilot scale is 20-200 kg/h and lab scale is <20 kg/h.

Table 1. The characteristics of the fast (off-line) pyrolysis reactors of biomass [51]

3.2.1. The distributions of gas, liquid and solid products

Regarding the commercialization of the pyrolytic technology for bio-energy conversion, the designed pyrolytic reactor involving the variation of the operating parameters (temperature, residence time, pressure and so on) has remarkable effects on the threshold of the specific product yield and the operating cost of the process [52-55]. Most of the reactors for the fast (off-line) pyrolysis of biomass to produce bio-oil or fuel gases is summarized by Bridgewater [51], estimated in terms of product yield, feed size, input gas, complexity and so on (Table 1). It is approved that the fluidized bed reactor is determined to be one of the promising technologies for biomass thermal conversion due to the high-efficient heat transfer and ease of scale-up, which has potential for commercial practice [56-60]. Microwave pyrolysis, termed as a novel thermo-chemical technology for converting biomass to solid, liquid and gas fuels, is of growing interests with thanks to its low requirement on energy input during the process, flexibility of the feedstock size and high quality of products (low oxygen content in char and bio-oil). The yield of the products from cellulose through different pyrolysis reactors would be intensively discussed, with regard to the effect of operating conditions such as temperature, residence time and condensing patterns.

3.2.1.1. Pyrolysis in fluidized-bed reactor

The outstanding contribution on study of cellulose pyrolysis in the fluidized bed reactor was made by the research group led by Scott and Piskorz in the University of Waterloo in Canada [12, 17, 42, 46, 61-63]. A bench scale atmospheric pressure fluidized bed unit using sand as the fluidized solid with the feeding rate of 30 g/h of biomass was designed to investigate the yield of liquid product at different temperatures in an inert nitrogen atmosphere with an apparent vapor residence time of approximately 0.5 s [62]. Piskorz [12] reported the pyrolytic behavior of the two types of cellulose (S&S powdered cellulose with ash content of 0.22% and Baker TLC microcrystalline cellulose with ash content of 0.04%) in

the fluidized bed reactor, giving the distribution of the gas, liquid and solid products at the temperature from 450 to 550 °C summarized in Table 2. The yield of organic products in the liquid phase (except water) from the S&S powdered cellulose ranges from 58.58% to 67.81% of the moisture and ash free feed at the temperature from 450 to 550 °C, reaching the maximum at 500 °C. Comparatively, the yield of organic products from the Baker TLC microcrystalline cellulose at 500 °C is determined to be 90.1%. Moreover, the yield of char for S&S powdered cellulose at 500 °C is 3.4%, compared to 1.0% for Baker TLC microcrystalline cellulose.

These results confirms that the larger amount of the inorganic salts in the ash content promotes the formation of the condensed structure through the catalytic effects, inhibiting the cracking of the macromolecules and enhancing the yield of solid product [21, 30, 31, 34, 46, 64]. Several years later, the pyrolysis of the two further types of cellulose (commercial SS-144 crystalline cellulose and Avicel pH-102 crystalline cellulose) were also studied in the fluidized bed by Piskorz's co-worker (Radlein, et al.) [46], presenting the yield of the products in Table 2. The temperature 500 °C, regarded as the optimal condition for producing bio-oil from cellulose in the fluidized bed reactor, gives the yield of organic products of 72.5% for commercial SS-144 crystalline cellulose and 83.5% for Avicel pH-102 crystalline cellulose. The difference should also be attributed to the catalytic effect of inorganic salts in the ash, since the yield of char for commercial SS-144 crystalline cellulose is 5.4% compared to 1.3% for Avicel pH-102 crystalline cellulose.

Recently, Aho [47] conducted the pyrolysis of softwood carbohydrates under the nitrogen atmosphere in a batch-operating fluidized bed reactor, where the quartz sand was used as bed material and the load of the raw material is approximately 10 g. All sand was kept in the reactor by a net at the upper part of the reactor. The evolved vapors were cooled in the four consecutive coolers with the set point of -20 °C, while between the third and fourth cooler the vapors were passed through a water quench with the pH value of 3 for avoiding the absorption of CO_2. The furnace temperature was kept at 490 °C until the release of non-condensable gases stopped, while the temperature in the reactor is about 460 °C. The vapor residence time was estimated to be less than 1.5 s based on the height of the reactor and the actual fluidizing gas velocity. The distribution of the products from cellulose (microcrystalline cellulose powder) is shown in Table 2, giving the low yield of organic products of 23.1% and high yield of char as 20.1%. The condensation of the vapors was estimated to be insufficient, while the values for gases and char can be considered reliable. It should be mentioned that the mass balance of the experiment could not be satisfactorily completed, due to its current reactor set-up (especially the vapor-cooling and liquid-precipitating system). A similar batch-operating fluidized bed reactor was designed by Shen and Gu, in order to study the fast pyrolysis of biomass and its components with the variation of temperature and vapor residence time under inert atmosphere [21, 65, 66]. No bed material was applied and the load of the raw material is about 5 g. The solid product was captured by the carbon filter, while the evolved hot vapors were cooled through the two U-tubes immersed in ice-water mixture (0 °C) and dry ice-acetone (-30 °C), respectively. The distribution of the products from the pyrolysis of microcrystalline cellulose at

temperatures between 420 and 730 °C with a residence time from 0.44 to 1.32 s is given in Table 2. It is estimated that the yield of liquid product reaches its maximum of 72.2% at the temperature of 580 °C with the residence time of 0.44 s. The higher temperature and long residence time promotes the decomposition of the macromolecules and cracking of the volatile, enhancing the yield of gases and reducing the solid product [21].

3.2.1.2. Pyrolysis in entrained-bed reactor

Graham [69] designed a complicated entrained bed reactor to investigate the fast pyrolysis of cellulose, which had a similar or even higher heating rate than that of fluidized bed. The rapid heat transfer and thorough mixing between the particulate solids and feed are accomplished in two vertical gas-solids contactors: Thermovortactor and Cryovortactor. The biomass or other carbonaceous fuel is rapidly mixed with the hot particulate solids in Thermovortactor. The suspension passed through a downdraft entrained-bed (fluidized) reactor allowing the individual setting of temperatures, and then was quenched by the cold

Author(s)	Sample	Pyrolysis reactor	Conditions		Yield of products (wt%)		
			Temperature (°C)	Residence time (s)	Gas	Liquid [1] (water)	Char
M.R. Hajaligol, et al. (1982) [67]	No. 507 filter paper	Screen-heating Pyrex reactor (fixed bed)	400 ~ 1000	0 ~ 30	5.25 ~ 46.97	16.37 ~ 83.35	3.32 ~ 78.37
W.S.L. Mok and M.J. Antal (1983) [68]	Whatman filter paper	Two-zone tubular micro reactor (fixed bed) [3]	800	1 ~ 18	62 ~ 71	--	15 ~ 23
R.G. Graham, et al. (1984) [69]	Avicel pH-102 crystalline cellulose	Downflow entrained bed (fluidized) reactor	750 ~ 900	< 0.6	74.7 ~ 98.1	0.7 ~ 15.8 [4]	--
J. Piskorz, et al. (1986) [12, 42]	S&S powdered cellulose	Fluidized bed reactor	450 ~ 550	0.53 ~ 0.56	8.49 ~ 17.89	68.75 ~ 75.59 (7.35 ~ 10.17)	4.2 ~ 8.53
	Baker TLC crystalline cellulose		500	0.48	5.1	94.7 (4.6)	1.0
D. Radlein, et al. (1991) [46]	Commercial SS-144 crystalline cellulose	Fluidized bed reactor	500	< 0.5	7.8	83.3 (10.8)	5.4
	Avicel pH-102 crystalline cellulose		500	< 0.5	3.9	89.6 (6.1)	1.3
Y.F. Liao (2003) [31]	Filter paper with ash content of 0.01%	Gravitational feeding reactor (Fixed bed)	300 ~ 1090	0.1 ~ 1.4	1.5 ~ 60.2	6.0 ~ 86.3	1.8 ~ 92.5
Aho, et al. (2008) [47]	Microcrystalline cellulose powder	Batch-operating fluidized bed reactor	460	<1.5	32.3	47.6 (24.5)	20.1
T. Hosoya, et al. (2007) [36]	Cellulose powder from Toyoroshi Co.	Cylindrical furnace and tube reactor (fixed bed)	800	30	12.9	77.1 (5.1)	10
D.K. Shen and S. Gu (2009) [21]	Microcrystalline cellulose powder	Batch-operating fluidized bed reactor	420 ~ 730	0.44 ~ 1.32	20.1 ~ 42.5	30.6 ~ 72.2	1.03 ~ 47.4

1: the yield of liquid product including water;2: the pressure is 5 psig of helium pressure;3: the operating pressure in the furnace is 5 atm;4: including solid product (char);

Table 2. The summary of the studies on fast (off-line) pyrolysis of cellulose

solids in the Cryvortactor and cooled through the cooling coil submerged in a water tank. The solids were then separated in the mass balance filter and the gas was collected in sampling bags. The feeding rate is less than 1 kg/h and the total elapsed time from the Termovortactor inlet to the cryovortactor exit is typically less than 600 ms. The yield of the gas and liquid (heavy fraction including tar and char) products at the temperature from 750 to 900 °C is shown in Table 2. The low yield of liquid product (less than 20%) is mainly due to the high reactor temperature and the inefficient cooling method. Moreover, the mass balance is not convincing, since the heavy fraction of the vapors may condense on the vessels of Cryovortactor and solid separator [69]. It should be noted that the high yield of gases is attributed to the enhanced heat transfer through the pre-mixing between the biomass and solid heat carrier before being fed to the pyolsyis reactor, compared to that of fluidized bed reactor.

The residence time (both solid and vapor) in the fluidized or entrained bed reactors could be narrowly changed (normally less than 1 s), because of the confinement of the minimum gas velocity for the solid fluidization. Therefore, the fixed bed reactors are designed for investigating the effect of not only temperature but also residence time on the yield of products and their specificity [31, 36, 44, 68]. Liao [31] designed a fixed bed reactor (quartz tube with a sample-holder in the middle), the temperature of which could be changed from 0 to 1100 °C. The filter paper shaped as 18*50 mm (about 2 g) is fed gravitationally to the reactor from the top, and the carrier gas (nitrogen) brings the evolved volatiles and some char fragments through the carbon filter. The purified volatiles are then cooled through the three traps consecutively: 1) the mixture of water and ice (0 °C); 2) the mixture of acetone and dry ice (-30 °C); and 3) assisting cooling agent (-45 °C). The yield of the products (gas, liquid and char) at the temperature from 300 to 1090 °C with the (vapor) residence time between 0.1 to 1.4 s determined by the carrier gas velocity is extensively discussed by Liao [31] (shown in Table 2-3), while the mass balance for all the experiments is convincingly located between 96% and 101.5%. With the same vapor residence time (carrier gas velocity), the yield of liquid product complies with a Gaussian distribution with temperature, giving the maximum of 86.29% (including 15.72% water) at around 600 °C with the residence time of 0.1 s. It is estimated that the long residence time promotes the yield of gases, due to the sufficient secondary reactions of the volatiles. The yield of gases is increased from 1.5% to 60.2% monotonously with temperature (from 300 to 1090 °C). It needs to be noted that the duration of each experiment, corresponding to the sample heating-up and holding time, is not specified in the work.

3.2.1.3. Pyrolysis in fixed-bed reactor

The pyrolysis of cellulose in a tube (fixed bed) reactor made of Pyrex glass is investigated by Hosoya et al. [36]. Compared to the study of Liao [31], the cellulose sample is horizontally fed to the furnace and the carrier gas is not employed which means that the vapor residence time could not be set individually. It is estimated that thirty seconds are enough for completing the pyrolysis since no volatile product formation is observed after longer pyrolysis time. The evolved volatiles are retained in the reactor with the solid residue

during the whole pyrolysis process. After 30 s pyrolysis, the reactor is pulled out from the furnace and cooled with air flow for 1 min at the room temperature. The tar (liquid product) condensed on the reactor vessel is extracted by *i*-PrOH and water. The amounts of the gaseous, tar and char fractions are determined gravimetrically after pyrolysis and extraction, giving the result at the temperature of 800 °C in Table 2. It should be mentioned that the temperature of the reactor is not evenly distributed during the pyrolysis process, because the bottom of the tube reactor was placed at the center of the cylindrical furnace. Most of the evolved volatiles are condensed at the upper part of the reactor, but not suffered from the vigorous secondary cracking due to the long (solid) residence time. Thus, the yield of liquid product (77.1% including water) is not visibly different from that of Liao's results at the temperature of 810 °C with the shorter vapor residence time (74.39%) [31].

Another Pyrex cylindrical tube (fixed bed) reactor was made by Hajaligol et al. [44], where the cellulose sample is held and heated by the porous stainless screen connected to the brass electrodes of the reactor. The system allows independent variation of the following reaction conditions: heating rates (100-100 000 °C/s), final temperatures (200-1100 °C), sample residence (holding) time at final temperature (0-∝ s). Similar to the experimental set-up of Hosoya [36], the vapor residence time could not be individually changed while the carrier gas is not employed. Part of the evolved vapors is rapidly diluted and quenched in the reactor vessel during the operation, because most of the gas within the reactor remains close to the room temperature. The other part of the evolved vapors is purged out of reactor vessel with the helium and cooled down through two downstream traps: 1) U-tube packed with glass wool immersed in dry ice/alcohol (-77 °C) and 2) the same trap in liquid nitrogen (-196 °C). The char retained on the screen is determined gravimetrically. The mass balance for each case is around 100%, giving the convincing results of the yield of the products at the temperature 400- 1000 °C with the sample holding time 0-30 s in Table 2. It is concluded [44] that tar yield (liquid product) increases with temperature to a maximum of about 65% at around 700 °C and then decreases with further temperature increases, since the sample residence time is zero. With the long residence time (for example 30 s), the yield of liquid product at 400 °C is remarkably increased to 83.35%, due to the sufficient heating-up time for the complete pyrolysis of cellulose. Comparatively, the yield of liquid product at 500 °C with zero holding time is only 16.37% and the yield of char is 83.63% (where the mass balance is 105%), because of the incomplete decomposition of cellulose.

A two-zone tubular micro reactor (fixed bed) was designed by Mok and Antal [68], to investigate the effect of vapor residence time on the yield of products from cellulose pyrolysis. Zone A is operated for 15 min for complete solid phase pyrolysis, while Zone B is maintained at 700 °C for vapor phase cracking. The char is determined gravimetrically, and the gases are collected by the replacement of water. Unfortunately, the tar collection is not possible with that apparatus. The results of the product distribution at the temperature of 800 °C with the vapor residence time 1-18 s are shown in Table 2. The long vapor residence time and high pressure (5 atm) promote the secondary cracking of volatiles, enhancing the yield of the gas product.

3.2.1.4. Pyrolysis in microwave reactor

The microwaves might be firstly used to activate biomass (cellulose as the feedstock) to solid, liquid and gas products by Allan et al. in 1970s [70]. After 2000, two research groups (one is led by J.H. Clark from University of York in UK and the other by Y. Fernandez and J.J. Pis from National Institute of Carbon in Spain) have published a large number of the remarkable results on microwave pyrolysis **(MWP)** of biomass and its components (such as cellulose and lignin) [49, 50, 71-74].

The studies of the research group led by Fernandez and Pis are mainly concentrated on the **high-temperature** microwave pyrolysis (more than 400 ^{o}C) of biomass [72, 74]. The feedstock sample (coffee hulls) being rich in cellulose, is made to be the cylindrical pellets (approximately 3 mm in diameter and 2 cm in length). The pyrolysis of the sample (15 g of that kind of pellets) was carried out in an electrical furnace (called CP-conventional pyrolysis) and in a single mode microwave oven at 500, 800, and 1000 ^{o}C, regarding the variation of the yield of products (char, oil and gases) and their properties (element content and heating value). The electrical furnace was previously heated to the corresponding pyrolysis temperature, so that the temperature of sample rose quickly. In case of microwave heating, the sample was placed in an identical quartz reactor, which was then placed in the centre of microwave guide [75]. The volatiles evolved passed through five consecutive condensers placed in an ice bath, the last of three of which contained dichloromethane, while the carbonaceous residue was separated from the receptor by sieving. The gas yield was evaluated by difference. It is found that the yield of char, oil and gas from pyrolysis of sample under microwave heating is 30.21%, 7.90% and 65.28% by weight of feedstock at 500 ^{o}C and changed to be 22.70 %, 8.58% and 68.72% at 1000 ^{o}C. Compared to that of conventional pyrolysis by electrical heating, the formation of the gas products (especially syngas CO+H_2) is remarkably enhanced under microwave pyrolysis and the oxygen content in char and oil is significantly reduced increasing their heating value. Most of the above findings on microwave pyrolysis of biomass are also approved by other researchers [48, 76].

Research group led by J.H. Clark has made a remarkable contribution on the microwave pyrolysis of biomass under **low temperature** (less than 350 ^{o}C) [49, 50, 73]. Milestone ROTO SYNTH Rotative Solid Phase Microwave Reactor is used for microwave pyrolysis of wheat straw [49]. Average sample mass was between 150 and 200g. The sample was heated at a rate of 17 ^{o}C/min to a maximum temperature of **180 ^{o}C** as measured by in situ temperature probes. The condensable fraction produced during the process was collected through a vacuum unit. The yield of solid, liquid and gas products is estimated to be 29%, 57% and 14% by weight of feedstock at 180 ^{o}C. Compared to that of conventional pyrolysis under relevantly high temperature [77], the oxygen content of the bio-oil obtained from low-temperature microwave pyrolysis is significantly reduced facilitating the following upgrading processes [49]. The microwave pyrolysis of cellulose was carried out at the temperature between 100 ^{o}C and 300 ^{o}C in a CEM Discovery laboratory microwave, regarding the yield of char and its formation mechanism. The high-quality char, where more energy from feedstock is conserved, could be produced with the adjustment of the low

pyrolysis temperature. The temperature of 180 °C was estimated as a key turning point in the microwave degradation of cellulose, favoring the understanding that the production of fuels is allowed at dramatically lower temperatures than those required under conventional pyrolysis (electrical heating). The energy conserved in solid, oil and gas product is evaluated to be balanced for the whole process. In terms of an industrial process, the low-temperature microwave technology can be easily adapted to a variety of biomass to produce a uniform char which can be handled by the end users.

With regard to the above discussion, the microwave pyrolysis under both high and low temperature is estimated to be one of the promising technologies to achieve high-quality solid (low oxygen content), liquid (low oxygen content and water content) and gas (low energy input and high syngas concentration) fuels with the low cost, helping to achieve sustainable development through the utilization of renewable alternatives (biomass) instead of fossil fuels.

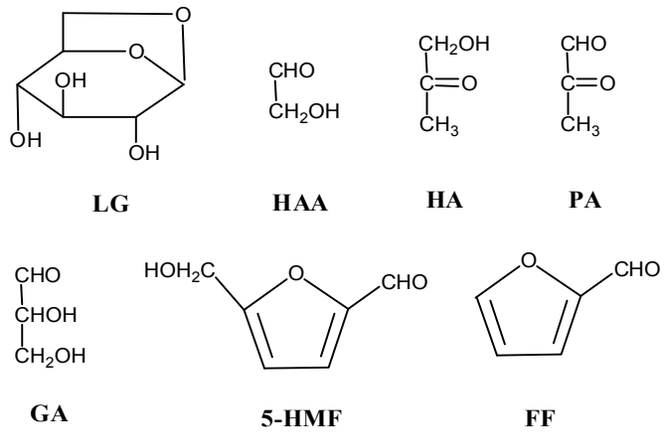


Figure 8. The chemical structures of the typical compounds in bio-oil from cellulose pyrolysis: LG: levoglucosan, HAA: hydroxyacetaldehyde, HA: Hydroxyactone, PA: pyruvic aldehyde, GA: glyceraldehyde, 5-HMF: 5-hydroxymethyl-furfural and FF: furfural

3.2.2. The formation of the specific compounds

The volatiles (both condensable and non-condensable) evolved from cellulose pyrolysis under moderate or high temperatures are very complicated, most of which have been identified by employing the advanced analytical equipments such as FTIR, GC-MS, HPLC, NMR and so on. A variety of pyran and furan derivatives ($C_{5\text{-}6}$ ring-containing compounds), aliphatic oxygenated $C_{2\text{-}4}$ organic compounds and light species/gases (such as light hydrocarbons, CO and CO_2) can be obtained, and the extensive lists together with their spectrometric/chromatograghic patterns and the yields are available in the literature, where the results are remarkably affected by the pyrolytic reactor, operating condition, condensing method and sample sources. Due to the great potential as the feedstock for fuel and chemicals production, some products established in good yields (such as levoglucosan, furfural, hydroxyacetaldehyde, acetol, CO, CO_2 and so on) (Fig. 8) would be vigorously investigated regarding the chemical mechanism for their formation and fractionation.

3.2.2.1. Pyran- and furan- derivatives (C5-6 ring-contained compounds)

The $C_{5\text{-}6}$ ring-containing compounds from cellulose pyrolysis are condensable and mainly composed of a variety of anhydrosugar and furan derivatives, among which levoglucosan (1, 6-anhydro-β-D-glucopyranose) are the outstanding one [12, 18, 21, 23, 31, 36, 41, 78-82]. Shafizadeh et al. [33] confirmed that levoglucosan can be obtained in yields from 20% to 60% by weight in their vacuum pyrolysis study of various cellulose samples, while other anhydrosugars (such as 2,3-anhydro-d-mannose, 1,4:3,6-dianhydro-α-D-glucopyranose, 1,6-anhydro-β-D-glucofuranose and 3,4-altrosan) are slightly produced (less than 1% by weight). Similar results were reported by Piskorz et al. by comparing levoglucosan yields from S & S powdered cellulose (2.1%) and Baker TLC microcrystalline cellulose (25.2%) pyrolysis at the temperature of 500 °C under atmospheric pressure in a fluidized bed reactor [12].

Inasmuch as the cellulose samples have somewhat different ash contents, the different levoglucan yield may be due to the well-known effect of inorganic cations in reducing tar yields by promoting other fragments or char formation [46]. Richards and co-workers established the extraordinary influence of salts and metal ions on the productivity of volatiles (especially levoglucosan and hydroxyacetaldehyde), presenting that the addition of alkali and Ca^{2+} cations to ash-free cellulose reduced the yield of levoglucosan while other metal ions (particularly Fe^{3+} and Cu^{2+}) enhanced the yield of levoglucosan [83, 84]. In accord with the findings of Richards's laboratory, Piskorz et al. observed very dramatic increases in the yields of levoglucosan (more than 30% by weight) from various celluloses after a mild sulfuric acid-wash pretreatment [42]. The profound effects of inorganic substances on the product from carbohydrates were also evidenced by Van der Kaaden through the matrix study on amylase pyrolysis using Curie-point pyrolysis, concluding that carbonyl compounds, acids and lactones are released by alkaline and neutral matrices while furans and anhydrohexoses are favored under neutral and acidic conditions [85].

The experimental conditions as well as the purity of cellulose and inorganic additions appear to have an important effect on the yield of levoglucosan. The yield of levoglucosan produced from the S &S powdered cellulose pyrolysis in a fluidized bed is increased with the temperature, reaches its maximum at the temperature of 500 °C and then decreased with the elevated temperature [46]. This is consistent with the results from Shen's work using fluidized bed reactor, giving the maximum yield of levoglucosan at the temperature of 530 °C [21]. A great deal of specific work studying pyrolysis oils produced from Whatman filter paper at the temperature from 400 °C to 930 °C in the fixed bed reactor confirmed that the formation of levoglucosan is mainly located at the temperature between 450 °C and 650 °C, obtaining the maximum yield at 580 °C (about 58.37% by weight of pyrolysis oil) [31]. Moreover, the yield of levoglucosan is decreased with the long vapor residence time at the temperature of 600 °C, while most of the small fragments (low molecular weight volatiles) are increased notably. These phenomena add the interests in looking inside into the chemical mechanism of the levoglucosan formation and its secondary cracking during the cellulose pyrolysis.

An established standpoint presents that the formation of levoglucosan is initiated by disruption of the cellulose chain, primarily at the 1,4 glucosidic linkage in the macromolecule, followed by intramolecular rearrangement of the cellulosic monomer units [18, 21, 31, 33, 46]. The actual mechanism of levoglucosan formation remains controversial. Golova favors a free-radical mechanism through the successful validation of the data on the effects of free-radical [86]. Shafizadeh arguing by analogy with the reactions of model phenyl glucosides prefers a heterolytic mechanism [33]. Essig and Richards [83] proposed that the hydroxyl group (-OH) of free chain ends further depolymerizes the short chain through transglycosylation accompanying with the release of levoglucosan.

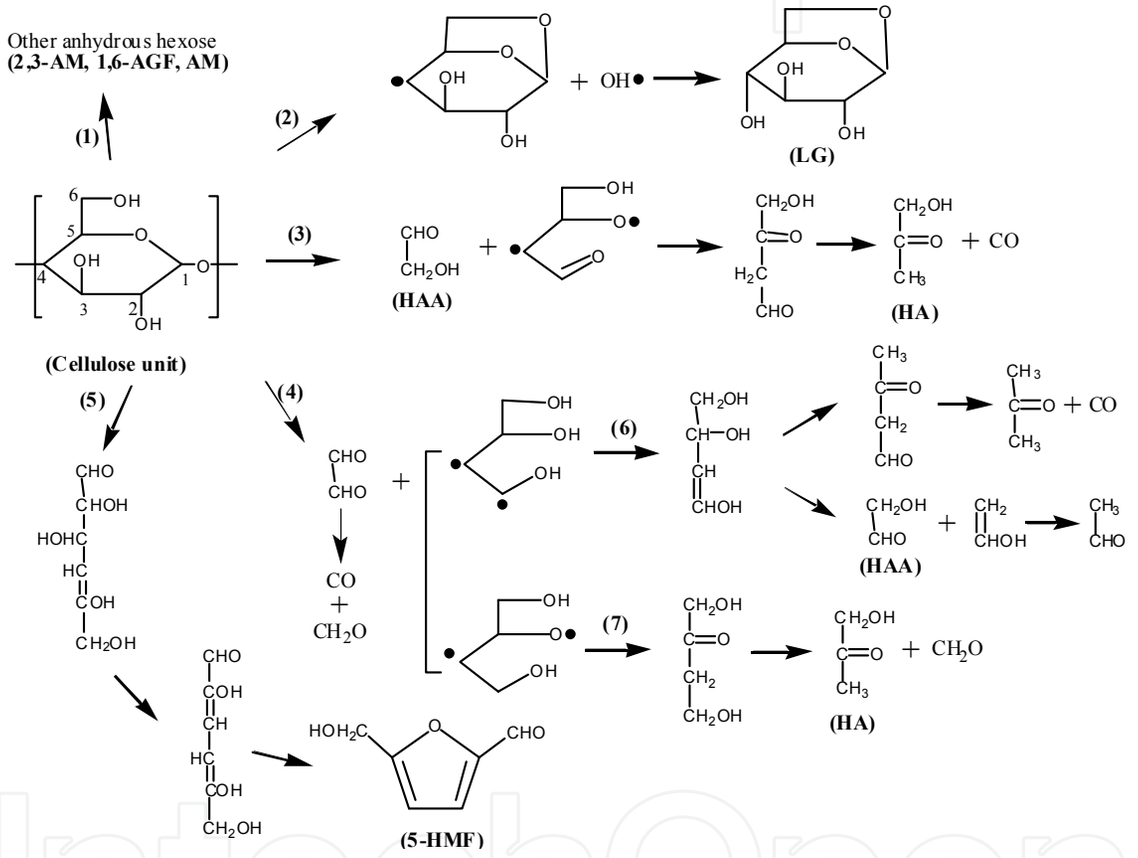


Figure 9. The speculative chemical pathways for the primary decomposition of cellulose monomer [21]

Another unsettled issue is whether depolymerization of macromolecule (disruption of cellulose chain) takes place by a concerted "unzipping" process or by random breaking of the cellulose chain. Briodo et al. [87] found that crystalline cellulose and undergoes a large change in DP before weight loss occurs. Similarly, Basch and Lewin [88] proposed that if cellulose depolymerized by an unzipping process then the number of free chain ends, as reflected by DP, will influence the initiation rate. Radlein [46] presented that one cellulose sample which has been heated to 180 °C for several hours and has a very low DP appears to give an abnormally high yield of levoglucosan. While the unzipping process may well operate at low temperature, there is evidence that it is inapplicable under fast pyrolysis conditions due to the significant amounts of cellobiosan and higher anhydro-oligomers in cellulose pyrolysates [46].

The correlation between the yield of levoglucosan and DP of cellulose sample under fast pyrolysis conditions needs to be specified, attracting the interests for further study.

The possible chemical pathways for primary decomposition of cellulose monomer (Fig. 9) and secondary cracking of levoglucosan and other primary fragments were comprehensively overviewed and developed by Shen and Gu, revealing the possible chemical information of the typical compound formation from cellulose pyrolysis [21] (Fig. 17). The usual view on the mechanism of levoglucosan cracking is that the lower molecular weight products are formed by fragmentation of principal intermediates like levoglucosan and cellobiosan as discussed by Pouwels et al. [81]. Such a scheme is also indicated by the data of Shafizadeh and Lu who showed that similar low molecular weight products (such as furfural, 5-HMF, glycolaldehyde, hydroxyacetone, acetic acid, formic acid and light species) as from cellulose pyrolysis can be formed by direct pyrolysis of levoglucosan [79], which is consistent with the observation by Hosoya et al. through the NMR identification of levoglucosan pyrolysis volatiles [37]. Evans et al. [89] even concluded that both cellulose and levoglucosan were pyrolyzed at various residence times and give similar cracking patterns and products by using a flash pyrolysis-mass spectrometric technique.

However, Richards [45] has argued that it is more likely that hydroxyacetaldehyde, known as one of the prominent products from cellulose pyrolysis (chemical pathway (3) in Fig. 16), forms directly from cellulose by a plausible mechanism involving the dehydration followed by a retro-Diels-Alder reaction but not from the secondary cracking of levoglucosan. Li et al. [18] presented that no detactable hydroxyacetaldehyde is observed by FTIR during levoglucosan pyrolysis in the two-zone pyrolysis reactor, indicating that levoglucosan might not be the major precursor of hydroxyacetaldehyde in cellulose pyrolysis. The two major pathways are then recognized to be active during cellulose pyrolysis: one leading to the formation of levoglucosan as a relatively stable product and the second to yield low molecular products particularly hydroxyacetaldehyde. The experimental studies of cellulose pyrolysis with the addition of inorganic substances show that conditions which result in the selective formation of levoglucosan realize very low yield of hydroxyacetaldehyder and vice versa, confirming the competitive nature of the above two pathways [4, 12, 23, 83, 84, 90].

Regarding to the notable argument on the relationship between levoglucosan and hydroxyacetaldehyde, Liao [31] conducted the pyrolysis of both cellulose and levoglucosan under different temperature and vapor residence time in a fixed bed. For cellulose pyrolysis, the yield of levoglucosan is increased and then decreased with the elevated temperature reaching the maximum at the temperature of 580 ^{o}C, while the yield of hydroxyacetaldehyde is monotoneously increased with the temperature. Under the fixed temperature (610 ^{o}C), the long vapor residence time favors the yield of small fragments (especially hydroxyacetaldehyde) remarkably at the expense of levoglucosan, showing the plausibly "consecutive mechanism" between them. For levoglucosan pyrolysis, no hydroxyacetaldehyde (even some other prevalent volatiles from cellulose pyrolysis) is detected at the temperature of 610 ^{o}C with the short residence time 0.1 s, confirming the "competitive mechanism" between levoglucosan and hydroxyacetaldehyde. But under the same temperature with the long

residence time 1 s, almost all kinds of volatiles from cellulose are released from levoglucosan pyrolysis, enhancing the "consecutive mechanism" between levoglucosan and hydroxyacetaldehyde. The quantitatively similar results are reported by Shen and Gu [91] for cellulose pyrolysis in a fluidized bed reactor at different temperatures and vapor residence times. The published data by Piskorz et al. [42] presenting the variation of levoglucosan and hydroxyacetaldehyde yields with temperature are compatible with either mechanism.

The experimental results summarized above plainly reveal the hybrid relationship between levoglucosan and the low molecular weight fragments (particularly hydroxyacetaldehyde) during cellulose pyrolysis: both competitive and consecutive (Fig. 9 and Fig. 10). However, the predominance of the nominal mechanism during cellulose pyrolysis is still ambiguous for specifying the hydroxyacetaldehyde (or other low molecular weight volatiles) formation and the extent of levoglucosan secondary decomposition, due to the widely varied experimental conditions and inorganic additions.

Furfural and 5-hydroxymethyl-furfural categorized as furan derivatives, are another two important $C_{5\text{-}6}$ ring-contained compounds in the products list of cellulose pyrolysis [12]. Although the yield of these two compounds is less than 1% by weight of fed cellulose, they are notably identified from the pyrolysis oil (GC-MS) spectrum of cellulose [12, 21, 31, 36, 47, 78, 81]. The effect of experimental conditions (temperature and vapor residence time) on yield of furfural and 5-hydroxymethyl-furfural is fully discussed by Liao [31], presenting that the formation of furfural is notably enhanced by the increased temperature and residence time while the yield of 5-hydroxymethyl-furfural is only increased with the elevated temperature. It is observed that these two compounds could be produced from levoglucosan pyrolysis under the suitable vapor residence time, showing the "consecutive mechanism" between them (Fig. 10). Moreover, furfural is found to be one of the important secondary cracking products from 5-hydroxymethyl-furfural pyrolysis. The commonly accepted standpoint concerning the chemical pathway for furfural and 5-hydroxymethyl-furfural is that levoglucosan or cellulose monomer undergoes ring-opening reaction to the C6 aliphatic intermediate, followed by hemiacetal reaction between C-2 and C-5 to form furan-ring structure after the formation of acetone-structure on position C-2 through dehydration reactions (chemical pathway (5) in Fig. 9 and chemical pathway (16) in Fig. 10) [31, 79]. The 5-hydroxymethyl-furfural could be decomposed to furfural together with release of formaldehyde through the de-hydroxylmethyl reaction, furan methanol through de-carbonylation reaction, or 5-methyl-furfural through de-hydroxyl reaction (chemical pathway (24) and (25) in Fig. 10) [21, 31, 92]. It could be concluded that furfural and 5-hydroxymethyl-furfural are both competitively and consecutively produced with levoglucosan, while 5-hydroxymethyl-furfural is another source for the formation of furfural.

3.2.2.2. Aliphatic oxygenated C2-4 organic compounds

Perhaps the most unusual result noticeably in the compounds from cellulose pyrolysis is the abundance of hydroxyacetaldehyde (glycolaldehyde) and acetol (1-hydroxy-2-propanone) [12, 21, 31, 36, 42, 46, 79]. A survey of literature reveals that these compounds were only occasionally reported as pyrolysis products, and have received very little attention in the

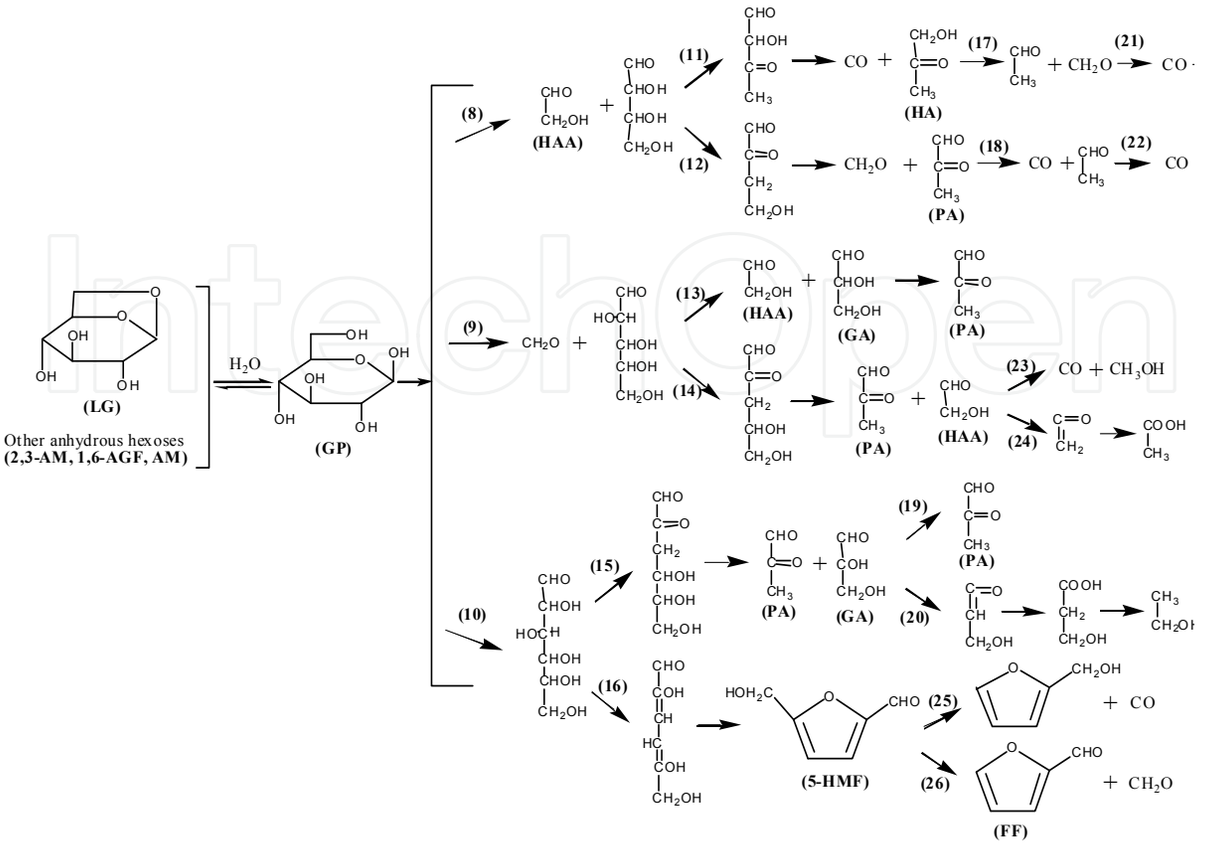


Figure 10. The speculative chemical pathways for secondary decomposition of the anhydrosugars (especially levoglucosan) [21]

sense of being a major product [67-69]. In 1966, Byrne et al. reported hydroxyacetaldehyde as one major components of a group of highly oxygenated products from pyrolysis of cellulose treated with flame retardants, along with glyoxal, pyruvaldehyde and 5-hydroxymethylfurfural [78]. It is perhaps that Pikorz et al. who first called attention to hydroxyacetaldehyde as a major product from rapid pyrolysis of slightly impure cellulose in a fluidized bed reactor, obtaining approximately 18% yield by weight of S & S powdered cellulose (0.22% ash content) and 8% of Baker TLC microcrystalline (0.04% ash content) [12]. The difference of hydroxyacetaldehyde among diverse celluloses is possibly attributed to the catalytic effects of inorganic salts in ash. A great deal of careful work on pyrolysis of cellulose treated with salts, neutral or acidic inorganics by Piskorz et al. and Richards' laboratory proves that the formation of hydroxyacetaldehyde is notably favored by the addition of alkali salts (such as NaCl), but inhibited by the addition of acid (such as H_2SO_4) [42, 46, 83, 84].

Moreover, the study of cellulose (Whatman filter paper) pyrolysis in a fixed bed reactor by Liao [31] indicates that hydroxyacetaldehyde is an important compounds in the condensed liquid product, the yield of which is notably increased from 3% to 19% by weight of liquid product with the elevated temperature (450 to 930 ^{o}C). The quantitatively similar result is reported by Shen and Gu [21] studying the cellulose pyrolysis in a fluidized bed reactor under various temperatures and residence times. But the experimental data published by

Piskorz et al. [42] shows that yield of hydroxyacetaldehyde by weight of fed cellulose is increased with the temperature and starts to decrease at the temperature of 610 °C. Since the yield of liquid product against temperature is changed compatibly with the yield of hydroxyacetaldehyde [12, 21, 31, 42], the apparent yield of hydroxyacetaldehyde by weight of fed cellulose performs a Gaussian distribution with temperature even though its relevant yield by weight of liquid product is monotonously increased with temperature.

Since no other C_2 or C_3 product appears in the same yield as hydroxyacetaldehyde, it is an intermediate or primary products formed early in the decomposition process through monomer ring cleavage (Fig. 9). The most acceptable standpoint for hydroxyacetaldehyde formation is proposed by Shafizadeh and Lai (chemical pathway (3) in Fig. 9), presenting that hydroxyacetaldehyde, assumed as the precursor for glyoxal, was produced mainly from C-1 and C-2 position of the glucopyranose [79]. This scheme is similar to that proposed by Byrne et al. [78].

Through the examination of bond energies in the monomer unit by Frankiewicz [93]and interatomic distance for β-D-glucose by Sutton [94], it was shown that the length for the C-2 to C-3 bond and for C-1 and O-ring linkage is slightly greater than other similar bonds. This finding is confirmed by Madorsky et al. [95] who pointed out that the C-O hemiacetal bond on the ring is thermally less stable than C-C bonds. These information offer support to the hypothesis that initial ring cleavage of cellulose monomer tends to occur frequently at these two locations, yielding a two-carbon fragment and a four-carbon fragment, while the two-carbon fragment is rearranged to a relatively stable product, hydroxyacetaldehyde, and the four-carbon fragment can undergo a number of rearrangement of dehydration, scission and decarbonylation to yield a variety of lower molecular weight products [12]. This chemical pathway for the formation of hydroxyacetaldehyde is well presented in the study of Liao [31] and Shen et al. [21] (Fig. 9). They also suggested that almost all of the positions on the pyran-ring could be contributed to hydroxyacetaldehyde formation, involving the examples on C-2 to C-3 or C-5 to C-6 positions plausibly through the cracking of five carbon fragment from initial cleavage of monomer on the bonds of C-1 to C-2 and hemiacetal C-O (chemical pathway (9) in Fig. 10). However, this suggestion should be evidenced through the bond energy examination and atomic label technology on the model compound.

Acetol (1-hydroxy-2-propanganone), regarded as another major product, is perhaps firstly reported by Lipska and Wodley [96] in their study of isothermal cellulose pyrolysis at 315 °C. Moreover, some of cellulose fast pyrolysis studies have also evidenced the acetol as a major component in the products. For instance, Hosoya et al. [36] obtained the acetol (in the *i*-PrOH-soluble fraction) yield of 1.1% by weight of fed sample from the cellulose pyrolysis at the temperature of 800 °C in a sealed tube. Two cellulose samples pyrolysed at the temperature of 500 °C in a fluidized bed reactor by Piskorz et al. [12] gave the acetol yield of 3.2% for S & S Powdered cellulose and 0.7% for Baker TLC microstalline cellulose by weight of fed sample, which is possibly due to the well-known effect of inorganic salts. Meanwhile, the authors [12] observed that the acetol yield from S & S Powdered cellulose pyrolysis is notably increased with the temperature. This phenomenon is also evidenced by the work of

Liao [31] studying cellulose pyrolysis in the fixed bed reactor and the fluidized bed reactor respectively, obtaining the range of acetol yield by weight of liquid product from 0.8% to 6% at the temperature from 450 °C to 930 °C.

In 1972, Shafizadeh and Lai [79] proposed the possible chemical pathway for acetol formation from levoglucosan decomposition as the rearrangement of the four-carbon fragment from the primary pyran-ring cleavage, while the other two-carbon fragment might be the precursor for hydroxyacetaldehyde. The similar reaction scheme is reported by Byrne et al. in 1966 [78] and proposed again by Piskorz et al. [12] in 1986. Meanwhile, the pyruvaldehyde was also proposed to be formed through the rearrangement of the four-carbon fragment, competing with the formation of acetol (Fig. 10). It could be found that enol-structure from the dehydration between the conjunct carbon is the intermediate for the acetone-structure, while the dehydration is between C-5 and C-6 for acetol formation and between C-4 and C-5 for pyruvaldehyde formation. According to Benson's rules on energy grounds [97], acetol should be favored over the alternative possibility of pyruvaldehyde. This speculation is evidenced by Piskorz [12], Liao [31] and Shen and Gu [21] studying cellulose fast pyrolysis in fixed bed reactor or fluidized bed reactor, obtaining higher yield of acetol over pyruvaldehyde (Fig. 9 and Fig. 10). Moreover, other chemical pathways for acetol and pyruvaldehyde formation from the five-carbon fragment or ring-opened six-carbon intermediate are proposed by Liao [31], which are then summarized in levoglucosan secondary cracking pathways by Shen and Gu [21]. However, the prevalent one for their formation, which might be affected by experimental conditions, is not specified, while their secondary cracking to CO and aldehyde-compounds could be readily determined.

Among a number of the detectable pyrolysis products from cellulose, some products, such as acetic acid, aldehyde, methanol, formaldehyde and so on, are less frequently discussed in the literature due to their low yields [12, 31, 44, 46, 64, 68, 69, 98]. In an investigation of the formation of acidic product, Kang et al. [99] proposed a mechanism of hydration of ketene which is formed from the dehydration of alcohol-aldehyde structure (chemical pathway (24) in Fig. 10). This reaction scheme for carboxyl group formation was well-established by the following researchers [12, 21, 31, 36, 46, 61, 65], most of whom did not specify its position on the pyran-ring. The possible chemical pathways for cellulose primary reactions and volatile secondary cracking are systematically summarized by Shen and Gu [21], giving a number of pathways for the formation of these low molecular weight oxygenated compounds.

3.2.2.3. Light species/gases

CO and CO_2 are regarded as the most dominant gas species in the gaseous product from cellulose pyrolysis, accounting for approximately 90% by weight of total gas products [12, 21, 31, 44, 47, 67-69, 98]. Hajaligol et al. presented that above 750 °C CO (more than 15% by weight of the fed) was the most abundant gaseous product from rapid pyrolysis of cellulose in the screen-heating reactor, while CO_2 (around 3% by weight of fed) was the second abundant species in gaseous product [44]. The result is agreed by Graham [69] that CO is observed as the single most prevalent gas species with the yield of 63% mole percent of the product gas at the reaction temperature of 700 °C in the entrained down-flow reactor.

Comparatively, Aho et al. [47] obtained the higher yield of CO_2 than that of CO from the cellulose fast pyrolysis in a fluidized bed reactor at the temperature of 460 °C. The above phenomena are all evidenced by Piskorz et al. studying cellulose fast pyrolysis under the temperature of 450 °C, 500 °C and 550 °C in a fluidized bed reactor [12], finding that CO_2 is predominant over CO in the gaseous product as the reaction temperature is lower than 500 °C, but above 500 °C CO turns to be dominant over CO_2. The different result is reported by Shen and Gu [21] studying cellulose pyrolysis in a fluidized bed reactor, observing that the yield of CO is dominant over that of CO_2 in spite of the reaction temperature. Although the predominance of CO and CO_2 in gaseous product from cellulose pyrolysis against the variation of temperature is still controversial, the yield of CO is confirmed to be enhanced by the elevated reaction temperature while that of CO_2 is slightly changed [12, 18, 21, 31, 44, 46]. The established explanation is that CO_2 is the primary product mainly formed at the low temperature stage, while CO is produced of large proportion from secondary tar decomposition steadily enhanced by the increased temperature.

Mok and Antal [68] investigated the effect of residence time on the yield of main gas products from cellulose pyrolysis at the pressure of 5 psig, concluding that CO_2 formation was notably enhanced by the longer residence time while CO was inhibited. The different result is reported by Liao [31] that CO is remarkably favored by the longer residence time while CO_2 is changed slightly, which is further confirmed by Shen and Gu [21]. Evans et al. [89] proposed that carboxyl group formed through hydration of ketene structure is the precursor for producing CO_2, while CO is mainly produced through the decarbonylation reaction of aldehyde-type species. Since the ketene structure, which is related to the formation of acidic compounds (containing carboxyl group), is mainly formed during the low temperature stage, CO_2 is approved to be the primary product of cellulose pyrolysis, and thus it is not remarkably influenced by reaction temperature. Comparatively, high reaction temperature favors the vigorous secondary tar cracking reactions, especially the carbonyl-group containing fragments, in order to enhance the formation of CO steadily and rapidly. This reaction mechanism is summarized from the results of the researchers [12, 18, 21, 31, 37, 46, 89], however the preference of the carbon on the pyran-ring for CO and CO_2 formation is not specified. From the study of thermal decomposition of levoglucosan, Shafizadeh and Lai [79] suggested that CO_2 was produced primarily from C-1 and C-2 position as well as hydroxyacetaldehyde, while the production of CO was less specific, but the information for cellulose pyrolysis is not ruled out.

It needs to be noted that the mole fraction of hydrogen (H_2) is also important as well as CO and CO_2 and constitutes approximately 21% of the product gas at the reaction temperature of 900 °C in the study of Garham et al. [69]. Quantitatively similar result is reported by Hajaligol et al. [44], also finding that the yield of H_2 is noticeably increased at the high temperature (more than 800 °C), while no hydrogen is observed at the low reaction temperatures. This implies that high reaction energy is required for the formation of hydrogen through the secondary tar cracking reaction. Li et al. [18] proposed that formaldehyde is precursor for hydrogen formation, together with the evolution of CO through the secondary cracking at around 550 °C. The same chemical scheme is proposed

again by Liao [31], Hosoya [37] and Shen and Gu [21], also giving the possible chemical pathway for hydrocarbons formation through the decarbonylation of aldehyde-type compounds together with the production of CO. It is also observed that both hydrogen and hydrocarbons formation are favored by the elevated temperature, confirming the enhancement of temperature on the secondary tar cracking reactions proposed above together with the evolution of CO. Since hydrogen is the important synthesis gas for methanol and other synthesis, the new methods coupled with thermal technology but with low heating energy input, such as catalytic hydrothermal conversion technology [100-102], are attracting global interests to specify the hydrogen formation from cellulose.

The typical compounds from cellulose pyrolysis are extensively discussed in the above studies, regarding the variation of the yield with experimental conditions (residence time and temperature), and the possible chemical pathways for their formation and cracking. It is commonly accepted that levoglucosan is the most prevalent product in the primary volatiles from cellulose pyrolysis, which could be further decomposed into various low molecular weight compounds (C_{2-4} compounds or light gases). However, the preference of the various primary reactions and secondary tar (especially levoglucosan) cracking reactions under widely varied experimental conditions with or without the catalysts needs to be further determined, in order to identify and promote the specific compound formation. The commonly-accepted chemical pathways need to be essentially estimated through advanced theory and/or technology analysis, such as molecular dynamic simulation (MDS).

4. The interactions among the components in lignocellulosic biomass under pyrolytic conditions

The constituent polymers from lignocellulosic biomass, i.e. polysaccharides (cellulose and hemicellulose) and lignin, are pyrolyzed in different ways [30]. The polysaccharides form anhydraosugars, furans, aldehydes, ketones and carboxylic acids as their primary volatile products, while the volatiles from lignin mainly consist of the low molecular weight aromatic compounds with guaiacyl-units or phenolic-units. To date, many researchers have extensively studied the pyrolysis of the real biomass and proposed reaction models by assuming that pyrolysis of the main chemical components (cellulose, hemicellulose and lignin) takes place independently without interactions among the three components [103-107]. They stated that pyrolysis of biomass can be explained based on a linear superposition of that of the three components. Yang et al. [108] presented that the pyrolysis of the synthesized biomass samples containing two or three of the biomass components indicated negligible interaction among the components. A computational approach was made firstly to predict the weight loss of a synthesized biomass from its composition in cellulose, hemicellulose and lignin, and secondly to predict the proportions of the three components of a biomass. The results calculated for the weight loss of the synthesized biomass are quite consistent with the experimental results. **However, results for predicting the composition of the biomass in terms of cellulose, hemicellulose and lignin were not very satisfactory, possibly due to the ignorance of interactions among the components.** From the

morphological view of the plant cell-wall as discussed in section 2, the main chemical components (cellulose, hemicellulose and lignin) would not perform individually without the intrinsic interactions during the pyrolysis of the whole biomass system [3, 5, 109, 110]. The interactions among the chemical components of woody biomass under pyrolytic conditions are of growing interests during recent years, in order to gain better understanding of the pyrolytic mechanism of the whole biomass system from the pyrolysis of individual component [109, 111-113].

Hosoya et al. [109] investigated cellulose-hemicellulose and cellulose-lignin interactions during pyrolysis at gasification temperature of 800 ^{o}C for 30 s in a tube reactor, while cellulose sample mixed with hemicellulose (2:1, wt/wt) was prepared by grinding cellulose-hemicellulose mixture in mortar and cellulose sample mixed with MWL (milled wood lignin) (2:1, wt/wt) was prepared by adding cellulose to the 1,4-dioxane solution (0.5 ml) of MWL followed by evaporation of the solvent. In the cellulose-hemicellulose pyrolysis, the experimental and estimated yields were not different so much although the tar (total) yield tended to decrease slightly with small increase in the char yields by mixing. The results indicate that cellulose-hemicellulose interaction is not significant in gas, tar and char yields. In the cellulose-MWL pyrolysis, more significant deviations were observed between the experimental and estimated yields of char and tar fractions; char yield decreased with the increasing yield of the tar total fraction by mixing. Tar composition was also substantially affected by mixing cellulose with MWL, presenting that the yield of the i-PrOH-soluble fraction substantially increased from 52.1% to 68% while the yield of water-soluble fractions substantially decreased from 14.5% to 2.8%. These results suggest that nature of the tar fraction is significantly altered from the water-soluble to i-PrOH-soluble products by the mixing of cellulose with MWL.

Moreover, the interactions among the components for the characteristic secondary char-forming were also investigated, involving the photographs of the reactors after pyrolysis and tar extraction [109]. The wood polysaccharide samples form the secondary char at the upper side of the reactor while vapor phase carbonization of the products from lignin leads to the formation of secondary char from the bottom to upper side continuously. In cellulose-hemicellulose pyrolysis, these char-forming behaviors were explainable as combined behaviors of the individual cellulose and hemicellulose pyrolysis. On the other hand, the cellulose –MWL pyrolysis substantially reduced the vapor phase secondary char formation from MWL.

Time profile of evolution rates of gas and tar in steam gasification of model biomass samples at the temperature of 673 K were examined by Fushimi et al. [114] using a continuous craoss-flow moving bed type differential reactor to elucidate the interaction among the major biomass components (cellulose, xylan and lignin) during gas and tar evolution. Two types of model biomass samples (sample A: mixture of cellulose (65%) and lignin (35%) with a ball-mill for 5 h; sample B: mixture of cellulose (50%), xylan (23%) and lignin (27%) with a ball-mill for 5 h) were used for the experiment. In steam gasification of sample A, the evolution of water-soluble tar and gaseous products (CO, H_2, CH_4 and C_2H_4) are

significantly suppressed by the interaction between cellulose and lignin. The primary (initial) decomposition of lignin is hindered by the interaction with pyrolysate of cellulose, which is different from the result from Hosoya et al. [115]. The CO_2 evolution appreciably enhanced and the evolution of water-soluble tar delays. These results may imply that the volatilization of water soluble tar derived from cellulose is suppressed by lignin and then the decomposition of char derived from polymerized saccharides and lignin takes place, emitting mainly CO_2.

In order to establish a link of the pyrolysis gas yield from the biomass and its main compositions, experimental flash pyrolysis of several biomasses and the model compounds (xylan, cellulose and lignin) at a temperature of 950 ^oC with a gas residence time of about 2 s was carried out by Couhert et al. [113] using an entrained flow reactor (EFR). The synthesized biomass by mixing the three components is described as simple mix where the products are mixed in equal mass proportion with a spatula in a container, and intimate mix where the components were mixed and then co-ground to thin elements using a laboratory ball mill. During the pyrolysis of simple mixes, the three components devolatilized separately. Interactions are likely to occur outside the particles. During the pyrolysis of intimate mixes, reactions can occur outside the particles in the same way as during the pyrolysis of simple mixes but additional interactions may occur inside the particles. As one component devolatilizes inside the particle, it is submitted to an atmosphere with very high concentrations in gas and condensable vapors; the gases formed are in close contact with the solids of other components. There are also probably interactions inside the particles because CO_2 yield of intimate mix is higher than CO_2 yield of simple mix. An attempt was then made to predict gas yields of any biomass according to its composition, but an additivity law does not allow the gas yields of a biomass to be correlated with its fractions of cellulose, hemicellulose and lignin. It is concluded that interactions occur between compounds and that mineral matter influences the pyrolysis process.

It is confirmed that the interactions among the components of wood under pyrolysis conditions are insufficiently investigated in the literature. Some issues concerning the interactions among components need to be further addressed for gaining better understanding in this field: 1) the component-mixed sample to simulate/represent the original physico-chemical information among the components in the real biomass; 2) the effect of experimental conditions (temperature, residence time, pressure and so on) and reactor type on the interactions among the components during pyrolysis; 3) specificity of the chemical mechanisms of the interactions among the components in vapor-phase, solid/liquid-phase or morphological-phase. This would be beneficial for expressing pyrolysis of biomass through the pyrolysis of individual components in biomass.

5. Conclusions and the way-forward

The cell-wall model for lingocellulosic biomass, divided into three main zones, is well – established to represent its morphological structure and distribution of the prominent chemical components (hemicellulose, cellulose and lignin) in different zones. This would

facilitate the direct utilization of biomass as bio-material and the improvement of the conversion process of biomass to fuels and chemicals. It needs to be noted that the existed cell-wall model is mostly applicable for woody biomass, while that for other lignocellulosic biomass (such as crops, straws and grass) should be further identified.

For on-line pyrolysis of cellulose, the initial stage of the cellulose pyrolysis, mainly related to the intermolecular hydrogen bonding and that between the different molecular chains, needs to be clarified for gaining better understanding of the whole pyrolytic behavior of cellulose. The kinetic models for the cellulose pyrolysis are improved toward track the mass loss process of solid along with the formation of the typical products with help of the advanced analytic instruments (such as FTIR, GC, NMR and so on). For off-line pyrolysis of cellulose, the yield of the products is tightly allied to the reactor type, temperature, residence time and condensing method. The preference of the various primary reactions and secondary tar (especially levoglucosan) cracking reactions under widely varied experimental conditions with or without the catalysts needs to be further determined, in order to identify and promote the specific compound formation.

The interactions among the main chemical components of lignocellulosic biomass under pyrolytic conditions are remarkably evidenced, regarding the differences between the estimated yield of products and variation of the specific compositions and the experimental data. This proves that the interactions among the components should be significantly considered for gaining better understanding of the pyrolysis of the biomass system. The component-mixed sample representing the original physico-chemical information between the components in real biomass is required for revealing the intrinsic interaction mechanism between them under the pyrolytic condition, favoring to predict the pyrolytic behavior of biomass from pyrolysis of its individual components.

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