

# FAST PYROLYSIS CHARACTERISTICS OF SUGARCANE BAGASSE HEMICELLULOSE

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The pyrolysis characteristics of sugarcane bagasse hemicellulose were investigated using a tubular furnace. The total gas yield and the releasing behavior of the main gas products were measured by GC analysis. The liquid products were analyzed by GC-MS and ion chromatography. The chars were investigated by elemental analysis and proximate analysis. The volatile remaining in the char extracted by isopropanol was observed by GC-MS analysis. The main gas products from hemicellulose mainly consisted of H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>. It was observed that the yield of CO<sub>2</sub> and CO was higher at lower temperatures, such as 550 °C, as well as that of H<sub>2</sub> and CH<sub>4</sub> at higher temperatures. The liquid products mainly contained furfural, cyclopentene-1 (2-methyl-2-cyclopentene-1, 2-cyclopentene-1, 3-methyl-2-cyclopentene), alcohols (1-butanol), organic acids (acetic acid, 4-hydroxy-butanoic acid, propanoic acid), aromatic series (phenol, ethylbenzene), besides some amounts of sugars. The products remaining in the char were mainly alcohols, cyclopentenones and complex aromatic char.

**Keywords:** sugarcane bagasse, hemicellulose, pyrolysis, gas products, char, tar

## INTRODUCTION

Since biomass materials provide abundant, inexpensive and renewable resources, their conversion into synthetic fuels and chemical feedstock has emerged as an attractive alternative in the past decade.<sup>1</sup> As a first stage of gasification and liquefaction of straw and other agricultural materials, pyrolysis is the key technology of the thermo-chemical processes. Pyrolysis of biomass generates three different energy products in different quantities: coke, gas and oils. Many studies<sup>2-4</sup> showed that fast pyrolysis gives high oil yields, at a pyrolysis temperature around 500 °C, gas being the main product at a temperature over 700 °C. Consequently, pyrolysis of biomass has received increased interest since the process conditions can be optimized to maximize the production of chars, liquids or gases.

As biomass contains varying amounts of cellulose, hemicellulose, lignin and a small amount of extractives, its pyrolysis is a very complex process. The overall rate of biomass pyrolysis was considered as a sum of the individual rates of the three components.<sup>5-7</sup>

The ratio of the three components in a biomass, which is closely related to biomass conversion, differs greatly with the source of the biomass, so that the study of the fundamentals of biomass components pyrolysis is essential. Several studies have been reported on the pyrolysis of lignin and cellulose,<sup>8-12</sup> but fewer on that of hemicellulose.

Various agricultural residues, such as corn fiber, wheat straw and sugarcane bagasse, contain about 20-40% hemicellulose, the second most abundant polysaccharide in nature. Hemicelluloses are heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and uronic acids.<sup>13</sup> As hemicelluloses are the most complex fiber components of straws, difficult to obtain from natural sources, numerous studies used xylan or 4-O-methyl-D-glucurono-D-xylan (Sigma from Birchwood) as a substitute of the hemicellulose component in pyrolysis processes.<sup>5,14,15</sup> Ivan *et al.*<sup>15</sup> used a thermogravimetric/mass spectrometric

(TG/MS) system to characterize the thermal reaction of 4-O-methyl-D-glucurono-D-xylan, at atmospheric pressure, in an inert environment. Glenn *et al.*<sup>16</sup> synthesized xylan, to investigate the effects of neutral inorganic salts on pyrolysis. However, the real hemicellulose is a matrix of different polysaccharides, containing glucuronic and galacturonic acid. It might have different physical and chemical properties in different biomass materials, so that improved isolation procedures and their detailed characterization are necessary. Shafizadeh *et al.*<sup>17</sup> studied the pyrolysis of D-xylose and methyl- $\beta$ -D-xylopyranoside (selected as model compounds), as well as that of 4-O-methylglucuroxylan and O-acetyl-4-O-methylglucuroxylan extracted from cotton wood. The main pyrolysis products were char, carbon monoxide, carbon dioxide, water and a tar fraction. Investigations<sup>18</sup> have been carried out on the chemical structure of hemicellulose isolated from the sugarcane bagasse and wheat straw, including a preliminary study on the characteristics of hemicellulose pyrolysis by TGA and TG-FTIR. Thermogravimetric analysis had demonstrated that the main temperature range required for the thermal decomposition of hemicellulose (200-315 °C) was significantly lower than that required for the decomposition of cellulose (300-415 °C) and lignin (200-600 °C). The released gas products from hemicellulose pyrolysis measured by TG-FTIR were mainly CO<sub>2</sub>, CO,

H<sub>2</sub>O and CH<sub>4</sub>. H<sub>2</sub> had no IR absorption and could not be detected by FTIR.

As part of a continuing study on hemicellulose pyrolysis, in the present investigation, sugarcane bagasse hemicellulose was pyrolyzed at temperatures of 550, 600, 650, 700, 750, 800 and 900 °C, in a home-made tubular furnace. The main objective of the present research was to investigate the effect of pyrolysis temperature on product distribution, and to characterize all pyrolysis products by different analytical techniques, in order to better understand the fast pyrolysis characteristics of hemicellulose at higher temperatures, which will be the basics for the research on biomass gasification and liquefaction.

## EXPERIMENTAL

### Sample preparation

The sugarcane bagasses were provided by the Jiangmen sugar mill in the Guangdong province, China. The procedure for the isolation of hemicellulose was discussed elsewhere.<sup>18</sup>

### Experimental methods

Pyrolysis experiments were carried out under nitrogen atmosphere, at temperatures of 550, 600, 650, 700, 750, 800 and 850 °C. The pyrolysis reactor was a tubular furnace equipped with a quartz tube, tubular furnace and a temperature control system (Fig. 1), externally heated by an electrical furnace. Pyrolysis temperature was measured with an internal thermocouple placed in the center of the pyrolysis reactor.

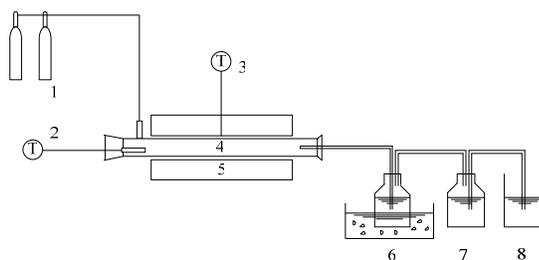


Figure 1: Scheme of tubular pyrolyser (1 – N<sub>2</sub> gas bottle; 2 – thermocouple with a porcelain boat; 3 – thermocouple; 4 – quartz tube; 5 – tubular furnace; 6 – ice-bath; 7 – gas bottle; 8 – breaker

Before the experiments, 2 g of hemicellulose (on a dry base) were loaded and the reactor was purged by nitrogen gas for 10 min, at a flow rate of 300 mL/min, to remove the air from inside. The sample was pushed to the center of the furnace and pyrolysis began when the tubular furnace was heated to the desired pyrolysis

temperature, being pulled out when the sample reached the same temperature as the furnace. The gas carried all volatile products from the reactor into the collection traps. The liquid products were condensed in three traps containing isopropanol, by cooling in an ice bath. The non-condensable volatiles were passed through the last trap,

containing salt-saturated fluids, after which the remaining gases were collected by the displacement method.

#### Analysis procedure

The analyses consisted of three stages: gas product analysis, liquid product analysis and solid product analysis. The volume of the released gas was measured by the displacement method and then converted into the mass. The mass of residual solid products was measured after they were cooled to ambient temperature and stored over dry silica gel until analysis. The weight of gas was calculated with the volume measured by the displacement method. The yields of gas and solid products were calculated based on the initial mass of the sample, and the yield of liquid products was calculated according to the conservation of mass, since the mass of tar was difficult to measure directly.

#### Gas product analyses

The gas products were analyzed by gas chromatography, with a thermal conductivity detector (GC-20B, Shimadzu, Japan). The C-RID area method was used to measure the gas component ratio. Argon gas was used as a carrier gas, at a flow rate of 77.5 mL/min.

#### Liquid product analyses

The liquid products from the pyrolysis of sugarcane bagasse hemicellulose were analyzed on a gas chromatograph equipped with a mass selective detector [GC-MSD: 6890N-5975 MSD, Agilent, America; column: HP-INNOWax, crosslinked polyethylene glycol, 30 m×0.25 mm, *i.d.* 0.25  $\mu\text{m}$  film thickness; oven temperature: from 40 °C (maintained for 5 min) to 220 °C (rate 5 °C  $\text{min}^{-1}$ , maintained for 5 min; flow: 1 mL  $\text{min}^{-1}$ ; split ratio: 20:1].

The aqueous phase of the liquid was first filtered, then detected by ion chromatography (ICS-3000, DIONEX, America) for the identification of sugars. Qualitative analysis of sugars was conducted with two series-wound columns of CarborPac PA1 (analytical, 2×250 mm) and CarborPac PA1 (guard, 2×50 mm). The eluents were 0.001 mol/L sodium hydroxide and 0.05 mol/L sodium acetate. Flow rate of eluent: 0.650 mL/min; injection volume: 10  $\mu\text{L}$ ; column temperature: 30 °C.

#### Solid product analyses

The solid products were analyzed with an elemental analyzer (Vario-I element analyzer, Elementar, France). The analysis of bio-char was done according to GB2001-91, China, for ash, volatile matter and fixed carbon analysis.

The bio-char was extracted with isopropanol, for 24 h, at room temperature. The extract was analyzed by GC-MS.

## RESULTS AND DISCUSSION

### Fast pyrolysis of hemicellulose and product distribution

The distributions of products resulted from the pyrolysis of sugarcane bagasse hemicellulose at different temperatures in the tubular furnace are shown in Figure 2. As seen, the product distributions of hemicellulose changed with increasing temperature. The gas yield was the highest in the three phase products. By increasing the pyrolysis temperature from 550 to 850 °C, gas yield increased, while char yield decreased. This result was expected, since it could be seen from the TG-DTG curves of hemicellulose that the main mass loss of hemicellulose occurred between 200 and 315 °C. Hemicellulose, consisting of various saccharides (xylose, glucose, galactose, etc.), appears as a random, amorphous structure, with numerous branches, which are very easy to remove from the main chain and to degrade by the released volatiles.<sup>19</sup>

### Composition of gas products

The gas evolving profiles resulted from hemicellulose pyrolysis in the tubular furnace are plotted in Figure 3. The gas products released from the pyrolysis of hemicellulose were composed of CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, the major gas being CO<sub>2</sub>, as also shown by other researchers. According to Figure 3, CO<sub>2</sub> was the predominant component of the gas products at relatively lower temperatures, decreasing considerably with the temperature increase. The relative yield of CO first decreased, from 35.7% at 550 °C to 24.0% at 750 °C, and then increased to 30.12% at 850 °C. The release of CH<sub>4</sub> and H<sub>2</sub> showed a contrary pattern to that of CO<sub>2</sub>. Yang *et al.*<sup>17</sup> suggested that releasing of CO<sub>2</sub> was mainly caused by cracking and reforming of the functional groups of carboxyl (C=O), while COOH and CO were mainly released with the cracking of carbonyl (C–O–C) and carboxyl (C=O). Possibly, their high yield was attributed to cracking and abscission of the C–C and C–O bonds connected to the main branch of hemicellulose, thus leading to a high pyrolysis reactivity of hemicellulose. However, they may have been released during the second pyrolysis of volatiles.

### Composition of liquid products

The characterization of the liquid products resulted from hemicellulose pyrolysis was carried out by GC-MS analysis and ion chromatography. Ion chromatography was used for the identification of sugars generated from the depolymerization of polysaccharides.

The aqueous phase of the liquid products was investigated by ion chromatography, the results showing that xylose and glucose were found in the liquid products at 550 °C, together with a small amount of glucose at 600, 650, 700 °C, and no sugar at 750 °C or above. Xylose (76.14%) was the predominant sugar, and glucose (10.72%) appeared as the second major sugar

constituent in the hemicellulosic fraction. Additionally, arabinose (9.06%), galactose (2.37%), uronic acids (1.71%) were observed as minor constituents.<sup>18</sup> Thermogravimetric analysis demonstrated that the temperature required for the onset of thermal decomposition of xylose (218 °C) was higher than that of D-glucose (230-240 °C),<sup>22,23</sup> so that glucose was more likely to survive the pyrolysis condition than xylose.

The characterization of the liquid products was also carried out by GC-MS analysis. The total ion current programs of the liquid products at 550 and 750 °C are shown in Figure 4, and the identification of the main peaks in the total ion current program is shown in Table 1.

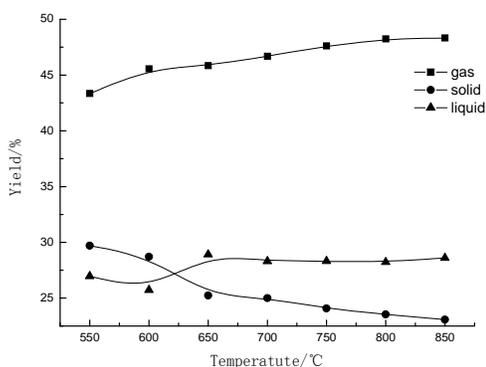


Figure 2: Distribution and yield of products from hemicellulose pyrolysis

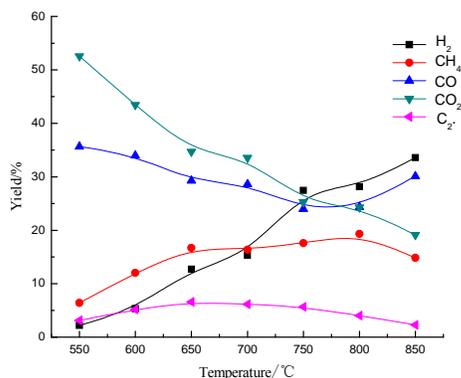
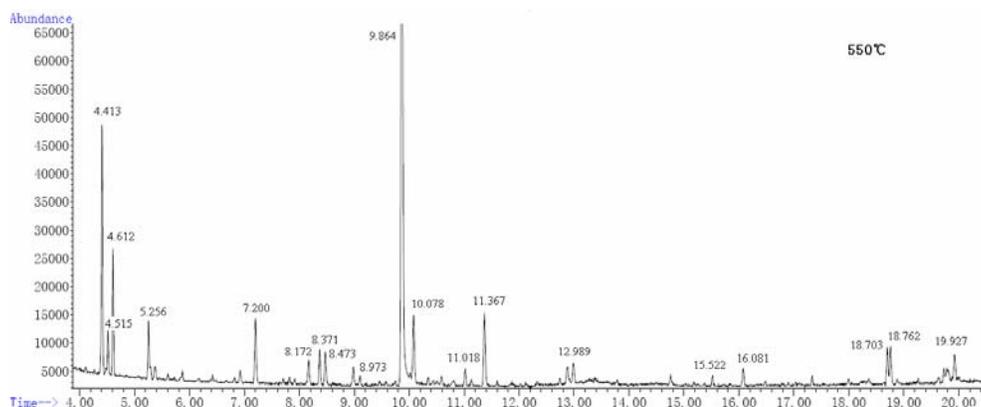


Figure 3: Releasing profiles of the main gas products from hemicellulose (C<sub>2</sub> means C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>)



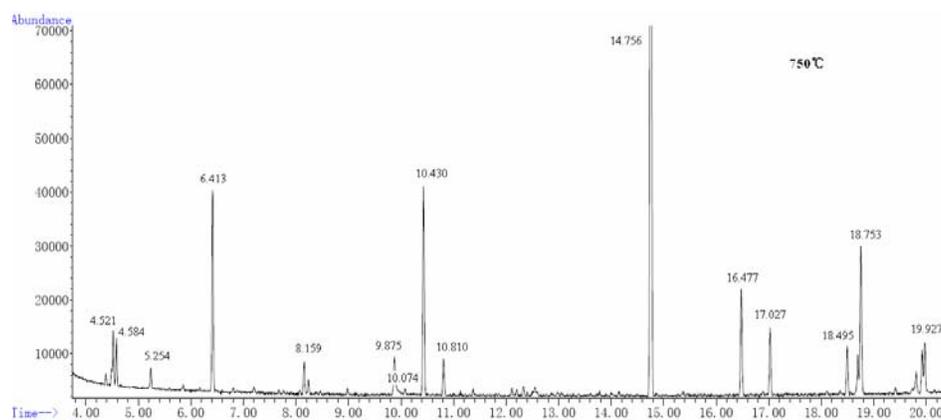


Figure 4: Total ion current (TIC) program of liquid products at different temperatures

The liquid products of hemicellulose pyrolysis at different temperatures are listed in Table 1. Most peaks of the chromatograms were identified by comparing the mass spectra of the degradation products with the spectra given in literature.

In all cases, the main pyrolysis products were classified into the following groups of compounds: furans [2-furancarboxaldehyde]; cyclopentanes [2-methyl-2-cyclopentene-1, 2-cyclopentene, 3-methyl-2-cyclopentene, 3-methyl-2-cyclopentanedione, 2-hydroxy-3,4-dimethyl-2-cyclopentene]; alcohols [tetrahydro-3-furanol, 1-butanol]; saturated fatty acids [acetic acid, 4-hydroxy-butanoic acid, propanoic acid]; cyclohexanes [phenol] and aromatic series [ethylbenzene, p-xylene, naphthalene, indene]. Mainly alcohols, cyclopentanes and fatty acids were present in the liquid products at lower pyrolysis temperatures, as well as aromatic compounds, such as naphthalene, at higher temperatures.

Acetic acid showed the highest peak at lower temperatures, such as 550 °C, its relative content decreasing with the increase of pyrolysis temperature. Upon pyrolysis, D-xylose and other sugars with intact

furanose rings could directly form furans.<sup>24</sup> 2-Furancarboxaldehyde, the typical product of hemicellulose, was found in the pyrolysis of xylan and 4-O-methylglucuro-D-xylan.<sup>25</sup> Organ and Mackie considered that furan consumption was ruled by (1, 2)-H transfers, which resulted in the formation of cyclic carbene intermediates whose successive decomposition forms either CO and propyne or C<sub>2</sub>H<sub>2</sub> and ketene.<sup>26</sup> However, some aromatic compounds were also found in the tar. At lower temperatures (300-600 °C), the pyrolysis of polysaccharides typically led to low molecular weight oxygenated compounds, including anhydrosugars and simple aromatic compounds,<sup>27</sup> at higher temperatures (over 800 °C), the pyrolysis of polysaccharides led to many phenolic and polynuclear aromatic compounds, observable at temperatures as low as 550 °C. Of course, the early stage pyrolysis products can themselves participate in pyrosynthesis, to generate larger molecules and more condensed ring systems. Benzofuran, indene and other complex aromatic compounds may be generated by cyclizative condensation of products at low temperatures.

Table 1  
Composition of liquid products from hemicellulose pyrolysis at different temperatures

No	R.T., min	Compounds	Area, %						
			550 °C	600 °C	650 °C	700 °C	750 °C	800 °C	850 °C
1	4.41	ethylbenzene	10.32	7.12	9.06	8.69	-	-	1.78
2	4.52	p-xylene	2.06	-	1.95	1.82	-	-	-
3	4.521	1-butanol	-	-	-	-	2.11	1.95	6.13
4	4.61	p-xylene	4.88	3.87	4.98	5.21	-	1.34	2.4
5	5.25	p-xylene	3.03	2.40	3.13	2.94	-	0.73	1.16

6	6.42	styrene	-	0.78	1.71	3.21	7.16	6.70	5.17
7	7.20	1-hydroxy-2-propanone	3.60	3.53	2.63	1.81	-	-	-
8	8.17	2-cyclopenten-1-one	1.19	1.58	-	1.96	-	-	-
9	8.36	2-methyl-2-cyclopenten-1-one	1.75	1.46	-	1.02	-	-	-
10	8.47	tetrahydro-3-furanol	1.68	1.49	1.28	-	-	-	-
11	9.86	acetic acid	41.18	52.55	36.24	24.31	2.03	1.94	5.91
12	10.08	2-furancarboxaldehyde	3.56	3.21	3.19	1.55	0.18	-	0.56
13	10.81	benzofuran	-	-	-	1.83	1.42	-	1.66
14	10.43	indene	-	-	-	-	8.55	9.05	5.32
15	11.02	3-methyl-2-cyclopenten-1-one	0.96	0.95	-	-	-	-	-
16	11.36	propanoic acid	4.20	5.55	4.86	3.24	-	-	0.78
17	12.98	4-hydroxy-butanoic acid	1.22	1.45	1.04	1.02	-	-	-
18	14.76	naphthalene	-	-	-	-	43.76	42.63	28.58
19	15.52	2-hydroxy-3,4-dimethyl-2-cyclopenten-1-one	0.49	-	-	-	-	-	-
20	16.08	3-methyl-2-cyclopentanedi- one	1.04	0.64	-	-	-	-	-
21	16.48	2-methyl-naphthalene	-	-	1.46	3.29	4.50	4.58	5.35
22	17.03	1-methyl-naphthalene	-	-	1.04	2.22	2.63	2.82	3.56
23	18.69	2-methyl-phenol	4.06	7.85	8.76	-	-	-	-
24	18.75	phenol	4.06	-	-	13.39	8.07	8.74	13.99
25	19.92	3-methyl-phenol	1.45	3.00	3.14	4.40	-	-	6.15

### Composition of solid products

Some physico-chemical properties of bio-chars resulting from the pyrolysis of hemicellulose at 550, 600, 750 and 850 °C are shown in Table 2. As expected, the amount of volatile matter in bio-char was the highest at 550 °C, besides other pyrolysis temperatures. By increasing temperature from 550 to 850 °C, the amount of fixed carbon of bio-char increased from 16.52 to 22.98 wt%, while the ash content of bio-chars increased only slightly. The ultimate analyses of bio-chars showed that the carbon amounts were first increased and

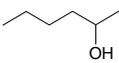
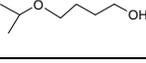
then decreased with increasing the pyrolysis temperature. The molar ratio of C/H and C/O decreased when the pyrolysis temperatures were over 650 °C, which was caused by the secondary cracking of primary volatiles. The condensation and polymerization reaction of the primary volatile took place at higher temperatures, leading to the generation of more thermostable compounds, such as benzene and naphthalene.

During pyrolysis, volatile components were released and absorbed by the condensation trips, however, some residual organics still remained in the solid char.

Table 2  
Properties of bio-chars from pyrolysis of hemicellulose at different temperatures

Pyrolysis temperature	550 °C	600 °C	750 °C	850 °C
Proximate analysis				
Volatile matter	37.04	30.23	28.33	26.46
Fixed carbon	16.52	18.01	20.32	22.98
Ash	18.50	19.44	21.01	22.96
Ultimate analysis (dry wt%)				
C	47.80	50.90	51.47	40.48
H	3.76	3.49	2.25	2.35
O	48.27	45.55	46.20	57.10
N	0.0055	0.0040	0.0090	0.0085
S	0.0895	0.0535	0.0731	0.0691
C/H molar ratio	12.72	14.57	22.87	17.24
C/O molar ratio	0.99	1.12	1.11	0.71

Table 3  
Chemical composition of the iso-propanol soluble fraction in char hemicellulose at 550 °C

No	R.T., min	Compounds	Structure	No	R.T., min	Compounds	Structure
1	3.184	1-methylethyl ester formic acid		8	4.650	2-hexanol	
2	3.221	methyl isobutyl ketone		9	4.961	tetrahydro-6,6-dimethyl-2H-pyran-2-one	
3	3.500	1-propanol		10	5.160	2-methyl-3-pentanol	
4	3.597	toluene		11	10.626	2-methyl-2-cyclopentane-one	
5	4.134	2,3-dimethyl-2-butanol		12	10.965	furfural	
6	4.258	2-methyl-2-pentanol		13	11.249	1,6 ;3,4-dianhydro-2-deoxy-beta-d-lyxo-hexopyranose	
7	4.488	3-methyl-3-pentanol		14	21.382	4-(1-methylethoxy)-1-butanol	

The chemical composition of the isopropanol-soluble fraction in char was detected by GC-MS analysis. The chemical structure and molecular weights of these compounds are listed in Table 3.

As shown in Table 3, the isopropanol-extracted fractions in the char at 550 °C included alcohols, anhydrosugars, acids and furfural, besides complex aromatic compounds. Some kinds of alcohols were also detected, because of the isopropanol used as a solvent. However, the complex aromatic compounds were the predominant components remaining in the char of higher temperatures, and only a few low molecular weights were detected. Indeed, polynuclear aromatic compounds were the kinetically and thermodynamically preferred final products of high temperature pyrolysis of carbohydrates.<sup>24</sup>

## CONCLUSIONS

The products distribution and yields of hemicellulose pyrolysis in the tubular furnace were studied at different temperatures. The yield of gas was the highest of the three-phase products, decreasing gradually with the increase of pyrolysis temperature, while the char yield was contrary to that of the gas products. The incondensable gas products were CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>, and some light hydrocarbon (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>). CO<sub>2</sub> was the predominant

component of the gas products at relatively lower temperatures, decreasing considerably with the increase of temperatures. The relative yield of CO first decreased and then slightly increased. The release of CH<sub>4</sub> and H<sub>2</sub> showed a contrary pattern to that of CO<sub>2</sub>. CO was not released only from primary pyrolysis, but also from the second pyrolysis of the volatile products, whereas CH<sub>4</sub> and H<sub>2</sub> resulted mainly from the latter process. The liquid products included sugars (glucose, xylose), furfural, cyclopentene derivatives, alcohols, saturated fatty acids (acetic acid, 4-hydroxy-butanoic acid, propanoic acid), phenol, phenol methyl-/dimethyl- derivatives and other aromatic compounds. Aromatic compounds, such as naphthalene, increased obviously with increasing temperature. The ultimate and proximate analysis of char showed that the amount of volatile matter decreased, while that of fixed carbon and ash increased by increasing temperature from 550 to 850 °C. The isopropanol-extracted fractions of volatile compounds remaining in the char were mainly alcohols, cyclopentene, and other complex compounds.

According to the analysis of three-phase products resulting from hemicellulose pyrolysis, dehydration and decomposition of the side chain of hemicellulose took place in the beginning of pyrolysis, after which cleavage of the glycosidic, carbon-carbon, carbon-hydrogen and carbon-oxygen bonds

of the sugar units, depolymerization, decarboxylation and decarbonylation reactions took place in the main pyrolysis stage, while the C-C, C=C, C-O bonds, as well as the carbonyl and carboxyl groups were reformed by the free radical reaction and the energy of high temperature. Low molecular weight aldehydes, alcohols, furan and polynuclear aromatic compounds were the observable end-products.

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