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Mechanism of Xylan Pyrolysis by Py-GC/MS

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Abstract In order to investigate the decomposition behavior of hemicellulose, xylan was chosen as the representative of hemicellulose to study the fast pyrolysis on the combination system of analytical pyrolyzer and gas chromatograph coupled with mass spectrometer(Py-GC/MS). The main condensable products of xylan pyrolysis consisted of acids, aldehydes, and ketones; while gas products contained CO_2, CO, CH_4 and H_2. Acetic acid and furfural were the most abundant products with the highest contents of 20.11% and 20.24% respectively. While furfural and acetic acid were formed competitively with residence time and temperature increases, the distribution of xylan pyrolysis products did not vary with the residence time and temperature, while the total content of several kinds of products changed a lot. According to the analysis of experimental data, a reaction pathway of xylan decomposition was deduced so as to illustrate the formation mechanism of main products.

Keywords Xylan; Pyrolysis; Py-GC/MS; Acetic acid; Furfural

1 Introduction

Hemicellulose is the second important component of biomass after cellulose, which has a proportion of 10%—15% in softwood, 18%—23% in hardwood and 20%—25% in herbaceous plant[1]. In contrast to cellulose that is crystalline with a strong strength, hemicellulose has a random and amorphous structure with little strength and cross-links to cellulose and lignin. The saccharides contained in hemicellulose are pentose, hexose, including xylose, mannose, galactose, glucose, and arabinose and so on[2]. Other sugars such as rhamnose and frucose may also be present in small amounts and the hydroxyl groups of sugars can be partially substituted with acetyl groups. Besides, there may be some uronic acids contained in hemicellulose[3].

Recently, thermochemical process has become a very important method for converting the biomass to energy[4]. Fast pyrolysis of biomass and its three major components, *viz.*, cellulose, hemicellulose and lignin have been widely studied to investigate the possibility of direct production of high-quality fuels from biomass[5—7]. The content and chemical structure of hemicellulose vary with material type and extraction method. Hemicellulose, which can be easily decomposed in acid-base circumstances, has a higher activity than cellulose. Its decomposition temperature is around 200 °C, which is lower than those of cellulose and lignin. Moreover, hemicellulose has significant influence on the pyrolysis of biomass[8—10] *via* its interactions with cellulose and lignin[11,12]. It was observed that hemicellulose enhanced the formation of 2,6-dimethoxy phenol from lignin, and the production of acetic acid and furfural(FF) from hemicellulose was promoted by cellulose and lignin in a temperature range of 350—500 °C[13]. To further study the mechanism of biomass pyrolysis, it is very important to investigate hemicellulose pyrolysis and further to get an insight into the mechanism of hemicellulose pyrolysis.

Xylan is the most relevant and abundant in hemicellulose[14], and *O*-acetyl xylan and 4-*O*-methylglucuronoxylan are primary units in hardwood species, while arabinose and 4-*O*-methylglucuronoxylan are rich in softwood plant[3]. As a result, xylan is usually chosen as the model compound of hemicellulose pyrolysis mechanism study. The weight loss of xylan mainly happened at 220—315 °C exothermically with a rapid weight loss rate to produce more CO_2 at a slow heating rate of 10 °C/min[10]. The distribution of the main products, such as bio-oil, gas and char, were also investigated. The yields (mass fraction) of gas, tar, water and char from xylan pyrolysis at gasification temperature 800 °C were 14.1%, 54.3%, 11.5% and 20.1% respectively, and furans compounds, mostly of furfural, were the most abundant compounds in tar constitutes[15]. However, the char from the slow pyrolysis of xylan at 700 °C had unobvious BET-surface area of pores, which was caused by the amorphous nature of adopted xylan and the fragments hardly undergo graphitization like cellulose[16].

Previous studies on xylan pyrolysis have usually been carried out on a thermogravimetric analyzer coupled with a Fourier-transform infrared spectrometer(TG-FTIR), by which the weight loss and pyrolysis product released can be detected[17,18]. Recently, pyrolysis-gas chromatography-mass spectrometry(Py-GC/MS) technology, which has an ultrafast heating speed, has been developed for the mechanism study of

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biomass pyrolysis[19,20]. In the present study, xylan was selected as model compound of hemicellulose and then fast pyrolysis of xylan was carried out on Py-GC/MS. A reaction pathway was deduced to further illustrate the formation mechanism of major products based on the product identification and the chemical structure analysis of xylan.

2 Materials and Methods

2.1 Materials

Xylan as the model compound of hemicellulose was purchased from Sigma Co. It was poly(*β*-*D*-xylopyranose [1→4]) extracted from the beech wood. The chemical structure of xylan was measured on an FTIR spectrometer. Samples were prepared using the KBr pellet technique and FTIR spectra were measured on a Nicolet Impact 830D spectrometer manufactured by Thermo Fisher Scientific Inc. in USA. The chemical structure of xylan is shown in Fig.1 and its FTIR spectrum is described in previous research[21]. Based on the analysis of FTIR spectrum of xylan, it is concluded that xylan contains *O*-acetyl and 4-*O*-methylglucurono units mainly, which is conformed to chemical structure of xylan as shown in Fig.1.

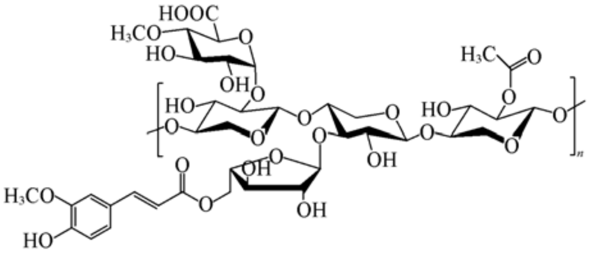

Fig.1 Chemical structure of xylan

2.2 Methods

Fast pyrolysis of xylan was carried out on an analytical pyrolyzer(CDS5200 Pyroprobe) with a platinum filament to heat the micro-reactor of quartz tube up to 1400 °C, the heating rate of the filament was set in 10000 °C/s. Xylan was filled in the pyrolysis tube, and some quartz wool was put at both sides of xylan to fix the sample. About 5 mg of xylan was adopted in all the tests by the control of filled tube length. A series of fast pyrolyses of xylan was carried out at different temperatures (450, 500, 550, 600, 650 and 700 °C) for 10 s and kept at 600 °C for different residence time(2, 5, 10 and 20 s).

The condensable products of xylan pyrolysis desorbed from the trap were immediately analyzed by GC/MS(Thermo scientific, Trace DSQII). The injector temperature was kept at 250 °C. The chromatographic separation was performed on a DB-WAX capillary column(30 m×0.25 m×0.25 μm). Helium (99.999%) was used as the carrier gas with a constant flow rate of 1 mL/min and a 1:50 split ratio was used for pyrolysis volatiles injection to GC. The oven temperature was programmed from 40 °C(1 min) to 240 °C(24 min) at a heating rate of 8 °C/min. And the temperature of the GC/MS interface was held at 250 °C and the mass spectrometer was operated on EI mode at 70 eV. The mass spectra were obtained from *m*/*z* 35 to 450 with the scan rate of 3.9×10^{-24} kg/s. Identification of chromatographic peaks was achieved according to the NIST MS library.

Analysis of gas products was carried out in separate experiments done under the same conditions as those above mentioned. GC analysis was performed on a carbon molecular sieves packed column(Huaai, GC 9560) with the following program: 5 min at 50 °C to 120 °C at a heating rate of 10 °C/min for a total time of 25 min. To quantify the gas yields, calibration curves were worked out with a standard gas mixture comprising CO, CO_2, CH_4, H_2, C_2H_6, C_2H_4, C_3H_8 in nitrogen.

Moreover, the pyrolysis tube was equipped with quartz wool and xylan was weighed before and after pyrolysis by a mass balance with an accuracy of 0.01 mg in order to calculate the mass loss of xylan by subtraction. All the experiments were conducted at least three times to confirm the reproducibility of each test and to obtain an accurate result. The relative standard deviations(RSD) of the rate of mass loss were all less than 5%(*n*=3), and the relative content of product was the average value of all the repeated experiments under the same conditions.

3 Results and Discussion

3.1 Main Condensable Products from Fast Pyrolysis of Xylan

Fast pyrolysis of xylan happened easily at a temperature of 600 °C held for 10 s, a final mass loss of 79.84% was obtained. The GC/MS spectrum of the pyrolysis is shown in Fig.2. As Fig.2 shows, the main products of xylan pyrolysis were furfural, acetic acid, 1-hydroxy-2-propanone, levoglucosenone, 5-hydroxymethyl furfural and 2(3*H*)-furanone, dihydro-4-hydroxy—, among which furfural had the most relative abundance and it was detected at 10.88 min. Compared to pyrolysis of cellulose and lignin under the same conditions, that of hemicellulose is the easiest to take place[11]. Xylan could decompose with a high conversion rate at a low temperature, which agrees well with the results from the slow pyrolysis of xylan[13].

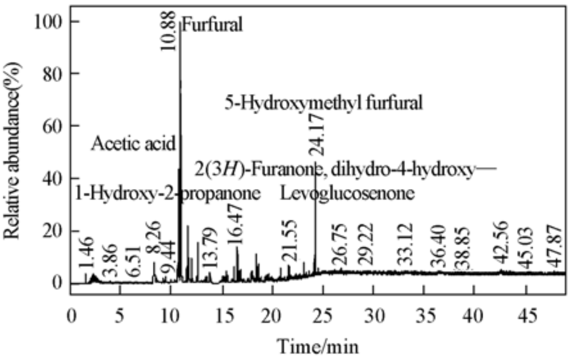

Fig.2 GC/MS spectrum of xylan pyrolysis

The main products are shown in Table 1, which consist of acids, aldehydes, ketones and sugars, etc. Acidic compounds were mainly composed of acetic acid, formic acid and propanoic acid with a total content of 29.87%. Aldehydes were primarily furfural, 5-hydroxymethyl furfural, and small amounts of glycollic aldehyde with a total content of 32.44%. Ketones were divided into linear ketones such as 1-hydroxy-2-propanone, furanone and cyclopentenone, which had the contents of 4.91%, 4.98% and 3.04%, respectively. In addition, there was small amounts of levoglucosan, levoglucosenone (LGO), and 1,4:3,6-dianhydro-α-d-glucopyranose, which were most probably produced from the pyrolysis of cellulose, and classified as pyrans to confirm the cross linking between hemicellulose and cellulose during extraction. Nowakowski *et al.*[22] also found that the main products from the fast pyrolysis of xylan were composed of 1-hydroxy-2-propanone, acetic acid, 3-methyl-2-hydroxy-2-cyclopenten-1-one, and furfural, etc. Acetic acid and furfural were the most abundant products with the contents of 20.11% and 20.24%, which agreed well with the previous studies[15,23].

Table 1 Main products from fast pyrolysis of xylan

Residence time/min	*m*/*z*	Compound	Formula	Area(%)
8.26	74	1-Hydroxy-2-propanone	$C_3H_6O_2$	3.31
8.54	60	Glycollic aldehyde	$C_2H_4O_2$	0.68
9.15	78	2-Cyclopenten-1-one	C_5H_6O	0.65
10.64	60	Acetic acid	$C_2H_4O_2$	20.11
10.88	96	Furfural	$C_5H_4O_2$	20.24
11.60	46	Formic acid	CH_2O_2	7.60
11.99	74	Propanoic acid	$C_3H_6O_2$	2.16
12.57	110	5-Methyl furfural	$C_6H_6O_2$	3.37
15.40	98	1,2-Cyclopentanedione	$C_5H_6O_2$	0.86
16.47	102	2(3*H*)-Furanone, dihydro-4-hydroxy—	$C_4H_6O_3$	3.56
18.39	126	Levoglucosenone	$C_6H_6O_3$	2.12
23.13	144	1,4:3,6-Dianhydro-α-d-glucopyranose	$C_6H_8O_4$	1.23
24.17	126	5-Hydroxymethyl furfural	$C_6H_6O_3$	6.39
42.56	162	Levoglucosan	$C_6H_{10}O_5$	1.07

3.2 Effect of Residence Time on the Xylan Pyrolysis

Mass loss rate of xylan changed with residence time. At a temperature of 600 °C, the mass loss of xylan was increased from 78.28% to 82.93% as the residence time prolonged. It was found that xylan got a high conversion rate in a very short residence time, and longer residence time helped xylan to decompose deeply.

Xylan is easy to decompose into various compounds with the content change of the main products with residence time shown in Fig.3. Generally speaking, the distribution of xylan pyrolysis products did not vary with the residence time, while the total content of several kinds of products changed a lot. With residence time increase, the total content of acids increased, and the total content of aldehydes inversely decreased. For ketones and pyrans, they both increased first and then decreased in content with residence time increase, and their contents were kept about 12% and 5% all along.

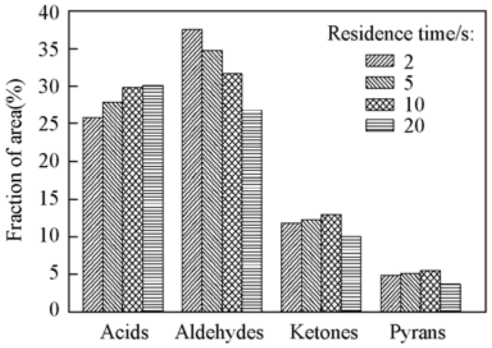

Fig.3 Product distribution at different residence time

The contents of typical products changed with residence time increase regularly, which was confirmed with different kinds of products. As Fig.4(A) shows, the contents of acetic acid, furfural, 1-hydroxy-2-propanone, and LGO were investigated as representative of different kinds of products to study the influence of residence time on xylan pyrolysis. As one of the main products, acetic acid increased with residence time increase, which came from the elimination of acetyl groups originally linked to the xylose unit, the ring-scission of xylose and the break of uronic acid residues[24]. However, shorter residence time contributed to the formation of furfural, which obtained the maximum contents of 24.24% at 600 °C held for 2 s. In addition, the formation of 1-hydroxy-2-propanone and that of LGO were first increased and then decreased, which suggests that longer residence time led to the deeper pyrolysis of 1-hydroxy-2-propanone and LGO. It can also be concluded that longer residence time helped the elimination of acetyl groups to produce acetic acid and the products with carbon ring such as LGO and furfural could be decomposed into small molecular products.

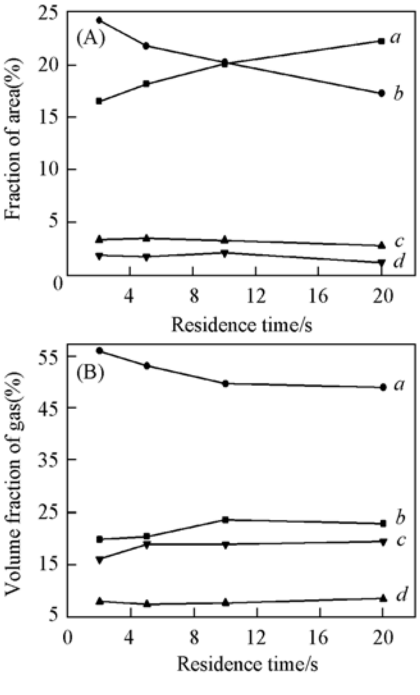

Fig.4 Change trend of typical condensable(A) and gas(B) products at different residence time

(A) *a*. Acetic acid; *b*. FF; *c*. 1-hydroxy-2-propanone; *d*. LGO;
(B) *a*. CO_2; *b*. CO; *c*. H_2; *d*. CH_4.

Gas products of xylan pyrolysis detected by GC mainly consisted of CO_2, CO, CH_4 and H_2, which came from xylan primary pyrolysis as well as secondary pyrolysis. As Fig.4(B) shows, the volume fractions of typical gas products changed with residence time increased. Xylan structure contains plenty of uronic acid side chains that may easily lead to decarboxylation to produce CO_2 at the primary stage of xylan pyrolysis. As a result, CO_2 already had a much higher yield than other gas in a short residence time. As residence time increased, the volume fraction of CO_2 decreased, while those of CO and H_2 increased slightly. CO mainly came from the breakage of unstable carbonyls and other gas products came from the secondary pyrolysis of xylan. It is concluded that longer residence time contributed to the breakage of carbonyls and deep pyrolysis.

3.3 Effect of Temperature on the Xylan Pyrolysis

Unlike residence time, temperature had a negligible effect on the mass loss of xylan pyrolysis. Xylan had already gotten a high mass loss rate of 80% at a low temperature and it kept a stable conversion rate as the temperature increased. The phenomenon that residence time had a more significant influence than temperature in the present study may be due to the more ultrafast heating speed of Py-GC/MS technology than that of previous equipment.

Temperature had a different influence from residence time on the product distribution, as shown in Fig.5. With temperature increasing, the total content of acids slightly changed irregularly, whereas the total content of aldehydes increased first and then decreased with the maximum value of 31.76% at 600 °C held for 10 s. Like aldehydes, ketones and pyrans both increased firstly then decreased with temperature increase. They also had the highest content of 12.93% and 5.5% at 600 °C for 10 s, which were lower than that of aldehydes. It was concluded that main organic products of xylan pyrolysis at 600 °C for 10 s had a great yield.

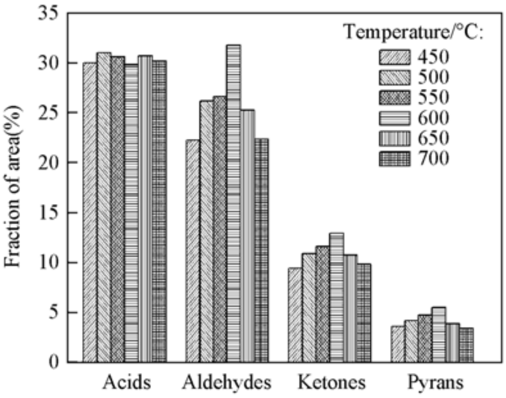

Fig.5 Product distribution at different temperatures

As for typical products, the content change of acetic acid was reverse to that of furfural, as shown in Fig.6(A). Acetic acid decreased firstly and then increased with temperature increase. And higher temperature was conductive to the production of acetic acid, with the maximum content of 23.25% at 700 °C held for 10 s. Furfural was the typical product of xylan pyrolysis the content change of which had an opposite trend with that of acetic acid with a maximum content of 20.24% at 600 °C for 10 s when temperature increased. The ring of furfural opened to form more small molecules at higher temperature. In addition, 1-hydroxy-2-propanone and LGO had a similar change with temperature increase. Their relative contents increased firstly then decreased with a maximum value at 600 °C for 10 s. 1-Hydroxy-2-propanone was formed from the decomposition of sugar units and recombination of opened bonding[25]. It was concluded that the cleavages of glycosidic, carbon-carbon, carbon-hydrogen and carbon-oxygen bonds of sugar units, and decarboxylation and decarbonylation reactions took place at the main pyrolysis stage, while the C—C, C═C, C—O bonds as well as carbonyl and carboxyl groups were formed *via* free radical reaction at a higher temperature[26].

As Fig.6(B) shows, temperature had an unobvious influence on gas products like CH_4 and H_2. However, the content of CO_2 was influenced greatly by temperature with a decrease and then an increase changes, while CO has a reverse change trend. It was deduced that xylan mostly decomposed into CO_2 when the temperature was lower than 600 °C, while further decomposition led to more organic compounds containing oxygen at higher temperatures. As temperature increased, volatile products had deep pyrolysis to produce more CO. At the same time, CH_4 increased weakly because some unstable acids and aldehydes got further decomposition.

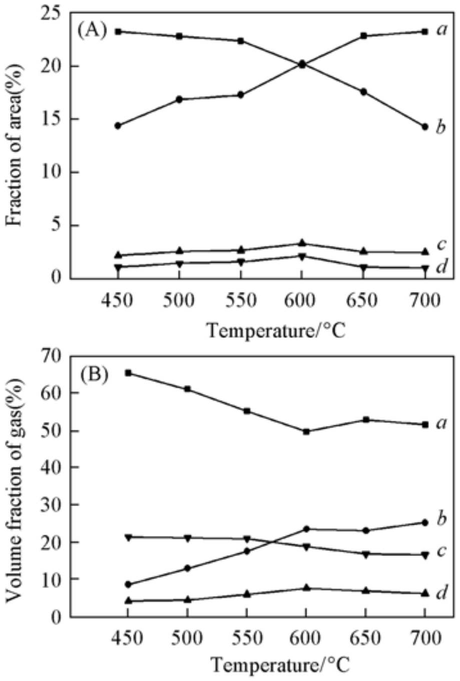

Fig.6 Change trend of typical condensable(A) and gas(B) products at different temperatures

(A) *a*. Acetic acid; *b*. FF; *c*. 1-hydroxy-2-propanone; *d*. LGO; (B) *a*. CO_2; *b*. CO; *c*.H_2; *d*. CH_4.

3.4 Discussion

The formation of main products was closely related to the structure of xylan. Based on the above experimental analysis, the chemical pathway of xylan decomposition was deduced as Fig.7. First of all, the main chain unit was decomposed and the *O*-acetyl xylan was cracked to form intermediates with a hexatomic ring. The 4-*O*-methylglucuronic xylan was also decomposed due to the cracking of carboxyl group.

Then the intermediates with hexatomic rings converted into linear carbon chain *via* the opening of the hexatomic ring. At last, ultimate products were produced by the cyclization and fragmentation of linear carbon chains.

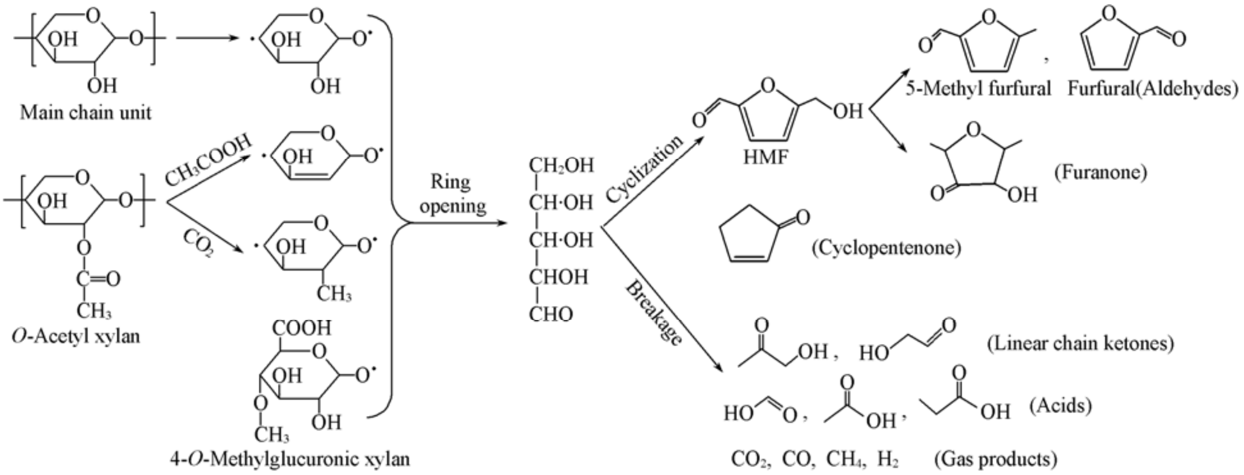

Fig.7 A deduced pathway of xylan decomposition

As Table 1 shows, acetic acid and furfural were both typical products and they formed competitively with each other. When xylan started to decompose, the active *O*-acetyl groups in the side chain was initially cracked from the main chain[27]. It was involved with the formation of a large amount of acetic acid at a low temperature and short residence time. However, acetic acid was still produced intensively with the reaction proceeding deeply. It was caused by the fragmentation of intermediates along with the formation of CO_2, which was the main reaction for acetic acid production. And furfural and furanone were mostly formed *via* the degradation of 5-hydroxymethyl furfural(HMF), which was obtained by the ring open reaction of pyran ring followed by the cyclization reaction. This explanation agreed well with the previous study[28]. In addition, the formation of formic acid was similar to that of acetic acid, including two pathways, one was the cracking of carboxyl group from 4-*O*-methylglucuronic xylan unit, and the other was the fragmentation of intermediates. The linear chain ketones were also produced by the fragmentation of the intermediates.

As for the gas products, CO_2 was mainly attributed to the decomposition of *O*-acetyl groups in the primary pyrolysis, while it might partially come from the decomposition of 4-*O*-methylglucuronic xylan[28]. Unlike CO_2, other gas products were evolved at further pyrolysis. CO was produced by decarbonylation reactions of unstable intermediate products, coupled with the production of H_2. The primary C2—C3 oxygenated products such as acetone, 1-hydroxy-2-propanone, glycolaldehyde would undergo a deep deoxygenation to produce CH_4[21].

Moreover, some common products such as levoglucosan and 5-hydroxymethyl furfural were produced from the fast pyrolysis of both xylan and cellulose. This shows that transglycosylation could occur under the condition of no primary hydroxyl group on the skeleton carbon[29].

4 Conclusions

Fast pyrolysis of hemicellulose was carried out on the Py-GC/MS to investigate the composition of main products. They were composed of acids such as acetic acid, formic acid and propanoic acid, aldehydes such as 5-hydroxymethyl furfural and furfural, ketones namely linear ketones, furanones and cyclopentenones. What's more, gas products mainly contained CO_2, CO, CH_4 and H_2. Acetic acid and furfural were the most abundant products with the highest contents of 20.11% and 20.24% obtained at 600 °C for 10 s. And they formed competitively with the residence time and temperature increasing. Acetic acid was produced from the initial cracking of *O*-acetyl unit and subsequent fragmentation of intermediates accompanied by the formation of CO_2. Meanwhile the formation of furfural was caused by the ring open reaction of pyran ring followed by the cyclization reaction of C—C bond. Finally, a reaction pathway of xylan decomposition was deduced to illustrate the formation mechanism of main products.

References

[1] Jin Z. Y., *Carbohydrate Chemistry,* Chemical Industry Press, Beijing, **2008**

[2] Lavarack B. P., Griffin G. J., Rodman D., *Biomass Bioenerg.*, **2002**, *23*(5), 367

[3] Girio F. M., Fonseca C., Carvalheiro F., Duarte L. C., Marques S., Bogel-Lukasik R., *Bioresource Technol.*, **2010**, *101*(13), 4775

[4] Xiong W. M., Fu Y., Lai D. M., Guo Q. X., *Chem. J. Chinese Universities*, **2009**, *30*(9), 1754

[5] Bridgwater A. V., *Catal. Today*, **1996**, *29*, 285

[6] Dodd D., Cann I. K. O., *Glob. Change Biol. Bioenerg.*, **2009**, *1*, 2

[7] Guo X. J., Wang S. R., Wang K. G., Luo Z. Y., *Chem. Res. Chinese Universities*, **2011**, *27*(3), 426

[8] Orfao J. J. M., Antunes F. J. A., Figueiredo J. L., *Fuel*, **1999**, *78*, 349

[9] Worasuwannarak N., Sonobe T., Tanthapanichakoon W., *J. Anal. Appl. Pyrol.*, **2007**, *78*, 265

[10] Yang H. P., Yan R., Chen H. P., Lee D. H., Zheng C. G., *Fuel*, **2007**, *86*, 1781

[11] Yang H. P., Yan R., Chen H. P., Zheng C. G., Lee D. H., Liang D. T., *Energ. Fuel*, **2006**, *20*, 388

[12] Couhert C., Commandre J. M., Salvador S., *Fuel*, **2009**, *88*, 408

[13] Wang S. R., Guo X. J., Wang K. G., Luo Z. Y., *J. Anal. Appl. Pyrol.*, **2011**, *91*, 183

[14] Bendahou A., Dufresne A., Kaddami H., Habibi Y., *Carbohyd. Polym.*, **2007**, *68*, 601

[15] Hosoya T., Kawamoto H., Saka S., *J. Anal. Appl. Pyrol.*, **2007**, *78*, 328

[16] Khezami L., Chetouani A., Taouk B., Capart R., *Powder Technol.*, **2005**, *157*, 48

[17] Wang S. R., Tan H., Luo Z. Y., Wang L., Cen K. F., *J. Zhejiang Univ.(Eng. Sci.)*, **2006**, *40*(3), 419

[18] Yang C., Lu X., Lin W., Yang X., Yao J., *Chem. Res. Chinese Universities*, **2006**, *22*(4), 524

[19] Wang S. R., Guo X. J., Liang T., Zhou Y., Luo Z. Y., *Bioresource Technol.*, **2012**, *104*, 722

[20] Lu Q., Li W. Z., Dong Z., Zhu X. F., *J. Anal. Appl. Pyrol.*, **2009**, *84*, 131

[21] Guo X. J., Wang S. R., Zhou Y., Luo Z. Y., *Int. J. Energ. Environ.*, **2011**, *5*(4), 524

[22] Nowakowski D. J., Woodbridge C. R., Jones J. M., *J. Anal. Appl. Pyrol.*, **2008**, *83*, 197

[23] Alén R., Kuoppala E., Oesch P., *J. Anal. Appl. Pyrol.*, **1996**, *36*, 137

[24] Beall F. C., *Wood Fiber Sci.*, **1969**, *1*(3), 215

[25] Peng Y. J., Wang S. R., *J. Anal. Appl. Pyrol.*, **2010**, *88*, 134

[26] Saha B. C., *J. Ind. Microbiol. Biotechnol.*, **2003**, *30*, 79

[27] Ponder G. R., Richard G. N., *Carbohyd. Res.*, **1991**, *218*, 143

[28] Shen D. K., Gu S., Bridgwater A. V., *J. Anal. Appl. Pyrol.*, **2010**, *87*, 199

[29] Evans R. J., Milne T. A., *Energ. Fuel*, **1987**, *1*, 123