Catalytic pyrolysis of xylan-based hemicellulose over zeolites

Xiujuan Guo, Shurong Wang, Yan Zhou, Zhongyang Luo

Abstract**—**Xylan, poly (β-D-xylopyranose [1→4]) extracted from the beechwood, was selected as the model compound of hemicellulose to investigate its thermal behavior over zeolites by using the thermogravimetric analyzer coupled with Fourier transform infrared spectrometer (TG-FTIR), and an analytical pyrolyzer coupled with gas chromatography and mass spectrometer (Py-GC/MS). The chemical structure of xylan and characterization of catalysts were first studied. All the three catalysts, HZSM-5, H-β and USY, had obvious influence on deoxygenation and fragmentation reactions during xylan pyrolysis. The dehydration in the initial stage was enhanced and the char formation was suppressed. USY had the best effect on dehydration with the consumption of oxygenated compounds, such as acids and furans. The presence of HZSM-5 and H-β catalyzed the formation of water, CO_2 and alkanes, with the degradation of char residues.

Keywords**—**catalytic pyrolysis, hemicellulose, xylan, zeolites

I. INTRODUCTION

HEMICELLULOSE is a group of polysaccharides found in plant cell walls and can be extracted from different plant sources with heterogeneity [1]. In contrast to cellulose that is crystalline and strong, hemicellulose has a random and amorphous structure with little strength and cross-link to cellulose and lignin. As the major component of biomass, the content of hemicellulose is 10-15 % in softwood, 18-23 % in hardwood and 20-25 % in herbaceous plant. The saccharides contained in hemicellulose are pentose, hexose, and/or uronic acids, including xylose, mannose, galactose, glucose, and arabinose *etc*. [2]. Other sugars such as rhamnose and fucose may also be present in small amounts and the hydroxyl groups of sugars can be partially substituted with acetyl groups. Xylan is the most relevant component in hemicellulose, and being the most abundant [3]. Its dominant structure is shown in Fig.1, in which O-acetyl xylan and 4-O-methylglucuronoxylan are primary units in hardwood species, while arabinose and 4-O-methylglucuronoxylan are rich in softwood plant [4], [5].

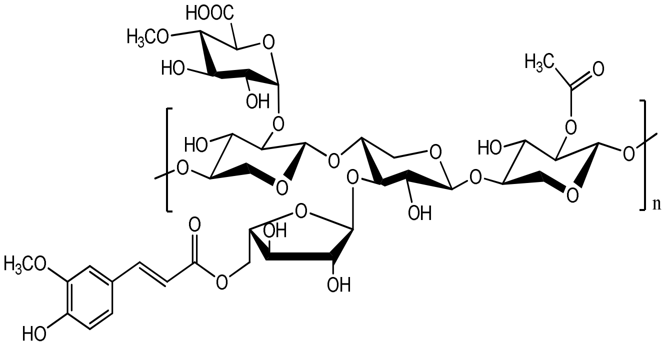


Fig.1 Chemical structure of xylan

The decomposition of xylan mainly occurred at the range of 220-315 °C with a rapid weight loss rate to produce more CO_2 [6]. The successive reactions model and independent parallel reactions model were deduced to obtain the kinetic parameters respectively, and the former had a better fit at 10 and 80 °C /min [7]. The distribution of the main products (bio-oil, gas and char) generated by degradation of xylan were investigated in the studies [8]-[10]. The yields of gas, tar, water and char from xylan gasification at 800 °C are 14.1 wt%, 54.3 wt%, 11.5 wt% and 20.1 wt% respectively, and furans are the most abundant compounds in tar [8]. Meanwhile, hemicellulose has significant influence on pyrolysis behaviors of biomass [6], [11], [12], through the interactions between cellulose and lignin [13]-[15].

Recently, catalytic pyrolysis of biomass and its components are widely studied to investigate the possibility of direct production of high-quality fuels from biomass, with both green and renewable characteristics [16]. Bridgwater [17] proposed that the pyrolysis vapors of biomass could be cracked into aromatics and other hydrocarbon products over zeolites, and then further converted into gasoline or diesel. Bio-gas, with increased hydrogen content, could be produced by pyrolysis & gasification process with catalysts effectively [18]-[20]. The quality of syngas was highly improved with the cogeneration process, the conducted processes with low, medium and high pyrolysis temperature (500, 600, and 800 °C) and high vapor-gasification temperature of wood char (800-1000 °C) [20].In the presence of zeolites, the volatiles released from

Manuscript received November 20, 2010: Revised version received January 9, 2011. This work was supported by the International Science and Technology Cooperation Program of China (2009DFA61050), the National High Technology Research and Development Program of China (2009AA05Z407 & 2007AA05Z334-3), the National Basic Research Program of China (2007CB210200), Doctoral Foundation of Ministry of Education of China (20090101110034), the Key Science and Technology Innovation Team Program of Zhejiang Province (2009R50012).

Xiujuan Guo is with the state key laboratory of clean energy utilization, Zhejiang University, Hangzhou 310027 China. She is now a PhD student in the Department of Energy Engineering (e-mail: guoxiujuan@zju.edu.cn)

Shurong Wang, corresponding author, is with the state key laboratory of clean energy utilization, Zhejiang University, Hangzhou 310027 China. (Phone: 86-571-87952801, fax: 86-571-87951616, e-mail: srwang@zju.edu.cn)

Yan Zhou is with the state key laboratory of clean energy utilization, Zhejiang University, Hangzhou 310027 China.

Zhongyang Luo is also with the state key laboratory of clean energy utilization, Zhejiang University, Hangzhou 310027 China.

cellulose pyrolysis underwent various deoxygenation reactions including dehydration, decarboxylation, and decarbonylation, resulting in the production of hydrocarbons and carbonaceous solids-coke [21]. The conversion of lignin to phenols was also optimized over zeolites with an increased octane number [22]. Various treatments were used to produce sugars from hemicellulose hydrolysis such as acid hydrolysis, hydrothermal treatments, ionic liquids, supercritical fluids *etc.* [5], but the report on catalytic pyrolysis of hemicellulose was rarely.

To further understanding the thermal behaviors of hemicellulose and biomass, xylan was selected as the model compound of hemicellulose to study the decomposition of xylan over zeolites by using the thermogravimetric analyzer coupled with Fourier transform infrared spectrometer (TG-FTIR). An analytical pyrolyzer coupled with gas chromatography and mass spectrometer (Py-GC/MS) was also adopted to study the rapid pyrolysis behavior of xylan, which was complementary to results obtained form TG-FTIR. And the decomposition model was deduced in combination with structure analysis of xylan and catalysts.

II. EXPERIMENTAL METHODS

A. Materials

Xylan as the model compound of hemicellulose was purchased from Sigma Corporation. It was Poly (β-D-xylopyranose [1→4]) extracted from the beechwood. The three zeolite catalysts, HZSM-5 (SiO_2/Al_2O_3=25), H-β and USY, were representative of zeolites. Each catalyst and xylan was well ground and screened to less than 200 μm, and then dried at 105 °C in an oven to remove the absorbed water before experiments.

B. Methods

The chemical structure of xylan was measured by FTIR first. The sample was prepared using the KBr pellet and FTIR spectra were measured using a Nicolet Impact 830D spectrometer manufactured by Thermo Fisher Scientific Inc. in USA. Measurements were taken at wave numbers from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}, and each spectrum was based on the average of 36 scans. BET surface area and other textural properties of zeolites were measured by N_2 adsorption-desorption isotherms at 77 K on a Micromeritics TriStar 3000 apparatus. And surface topography was analyzed by the scanning electron microscope (SEM), SIRION-100 type manufactured by FEI Corporation in USA.

A Mettler–Toledo TGA/SDTA851e thermo-balance coupled with a Nicolet NETXUS 670 FTIR spectrometer was used to study the pyrolysis behaviors of xylan. Nitrogen was as carrier gas with the purity over 99.99 % to ensure the inert atmosphere. Experiments were operated on the TGA at a linear heating rate of 20 °C/min within the temperature range from 30 °C to 800 °C at a steady nitrogen flow rate of 30 ml/min. The volatiles released during pyrolysis would be swept into FTIR gas cell quickly. For the detection of volatiles, a deuterated triglycine sulfate pyroelectric detector was adopted for its quick response and low noise. The spectral range was covered from 400 to 4000 cm^{-1}, and the resolution factor was selected as 1 cm^{-1}. In order to reduce the influence of sample amount on the intensity of IR absorption, the weight of each sample without catalysts was about 10±0.05 mg, the total weight was controlled at 20±0.05 mg. so the mass ratio of mixed catalyst and sample was 1:1

Rapid pyrolysis behavior was studied with the analytical pyrolyzer (CDS Analytical Pyroprobe 5250). Each sample with about 2-5 mg was loaded into quartz tube, which was placed vertically in a carousel. And the quartz tube was dropped sequentially into the pyrolysis zone to pyrolyze, and then the spent tubes were dropped out the bottom into a collection tray. The initial temperature was set to 30 °C for 0.2 s, heated at 10 °C /ms to final temperature of 350 °C, which corresponded to the maximal weight loss temperature in thermal decomposition. Communication among the autosampler, the Pyroprobe controller and the gas chromatography permitted complete automation of the pyrolysis-GC process, with remote-start of the GC, and wait-for-ready intelligence. Therefore, volatiles released from the pyrolyzer were analyzed on a GC-MS system (Thermo Scientific). The gas chromatography was equipped with a 30m×0.25mm×0.25mm Agilent DB-WAXetr capillary column. The oven temperature was maintained at 40 °C for 1min, heated at 8 °C /min to 240 °C, and then held at 240 °C for 14 min. The confirmation of volatiles releasing from pyrolysis of xylan was used to deduce the decomposition route of xylan and made a complementary comparison with FTIR results

III. STRUCTURAL ANALYSIS OF XYLAN

The chemical structure of xylan is shown in Fig.1 and its FTIR spectrum is described in Fig.2. The characteristic functional groups are all identified in the xylan spectrum, corresponding to the chemical structure. For example, the strong (s) bond vibrations of O-H at 3600-3200 cm^{-1} and C-O at 1320-1210 cm^{-1} represent alcoholic hydroxyl, which is carboxyl combined with middle (m) bond stretch of C=O at 1725-1705 cm^{-1}; the strong stretch at 1150-1070 cm^{-1} corresponds to C-O-C linkage; the middle unsymmetrical shrinkage of $-CH_2$-cyclopentane is at 3000-2800 cm^{-1}; and the weak (w) bond vibration at 2250 cm^{-1} is related to -O-Ac structure. Therefore, it is concluded that xylan contains O-acetyl and 4-O-methylglucurono units.

In addition, Xie et al. [23] proposed that hydrogen bonding between the protein and the surface-bound polysaccharide made a modest contribution to the overall binding. Although hydrogen bonds had favorable enthalpy, they restricted the residual motion of the ligand and thus reduced the entropy of the whole system. Further investigation about xylan structure with different advanced technique is very necessary for various researches. So it should be illustrated that the present paper was just related to the simple analysis of basic structure of xylan.

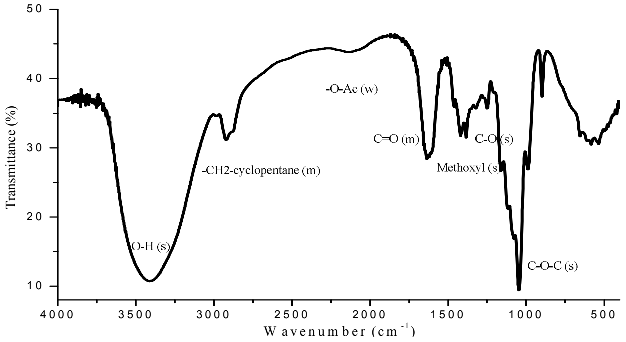


Fig.2 FTIR spectra of xylan

IV. CHARACTERIZATION OF THE CATALYSTS

Zeolite has most of the acid sites located within the micro porous crystal structure, thus the acid sites are an integral part of their structure not at the surface terminating the individual crystallites [24]. Fig.3 shows the surface topography of zeolite catalysts, and also identifies their porous crystal structure.

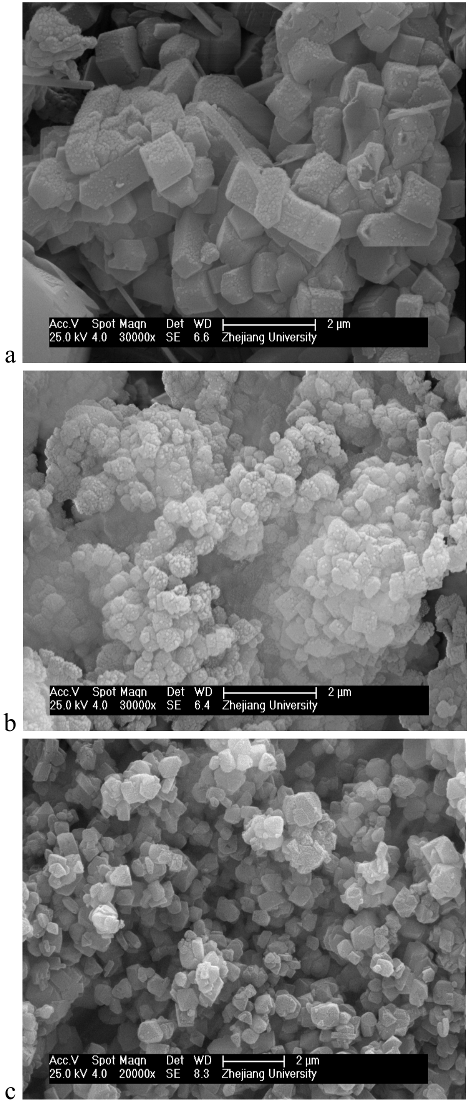


Fig.3 Surface topography of (a) HZSM-5, (b) H-β, and (c) USY

The physical property of zeolite is shown in Table 1. It is found that all the three catalysts have similar high BET surface area and large pore volume, which provide large amount of acid sites to the reactants. The results calculated by using BET method are in the range of previous analysis [25], [26], in spite of little difference due to the unique of each catalyst.

Table 1 Physical property of the catalysts

Sample	**BET surface area (m^2/g)**	**Total pore volume (cm^3/g)**	**Average pore diameter (nm)**
HZSM-5	484.45	0.3567	2.87
H-β	497.54	0.3981	3.20
USY	476.54	0.3040	2.55

V. KINETIC ANALYSIS OF XYLAN PYROLYSIS

A. Thermal degradation

Fig. 4 shows the TG/DTG curves of xylan pyrolysis with zeolites. The decomposition of all samples is divided into four stages, which are the initial stage in the temperature range 30-200 °C, the main stage in 200-350 °C, the third stage in 350-500 °C, and the final stage after 500 °C. The maximal weight loss rate is observed at 260 °C. The initial stage is attributed to water release by evaporation and dehydration [27], so it can be concluded that the three zeolites all catalyze the dehydration of xylan. The main stage is ascribed to the cleavage of the glycosidic bonds and the decomposition of side-chain structure and even the fragmentation of other depolymerized units. It is found that the presence of USY inhibits the further degradation of xylan, which results in a low yield of volatiles. In the third stage, the weight loss of pure xylan and xylan with HZSM-5 or USY was a smooth shoulder, but xylan with H-β was a peak due to the secondary cracking of monomeric residues. It may be caused by the special catalytic effect on4-*O*-methyl-α-d-glucopyranosyluronic acid linkage and acetyl groups, which are both thermal stable linkage in native xylan [28]. In the final stage, pure xylan and xylan with USY retained a char yield of 26 %, and xylan with HZSM-5 and H-β kept a char yield 16 %.

The three main components of biomass, cellulose, lignin, and hemicellulose, were all studied combined with our previous researches. Pyrolysis of cellulose was divided into three stages, the initial stage 30-300 °C, the main weight loss stage 300-400 °C, and the final stage in 400-800 °C. The temperature to maxima weight loss is 350 °C. And the presence of zeolite catalysts, HZSM-5, H-β, and USY, all inhibits the main decomposition of cellulose [29]. Unlike the behavior of cellulose, pyrolysis of lignin had a continuous weight loss from the initial to the end, and the final residue yield was about 40 wt% [30]. Moreover, the interaction between three components also had obvious influence on pyrolysis behavior of biomass. Kinetic analysis showed that the thermal decomposition of levoglucosan was extended over a wider temperature range according to the interaction of hemicellulose or lignin upon the pyrolysis of cellulose; the formation of 2-furfural and acetic acid was enhanced by the presence of cellulose and lignin in the range 350–500 °C; and the amount of phenol, 2, 6-dimethoxy was enhanced by the integrated influence of cellulose and hemicellulose. The components do not act independently during pyrolysis [31].

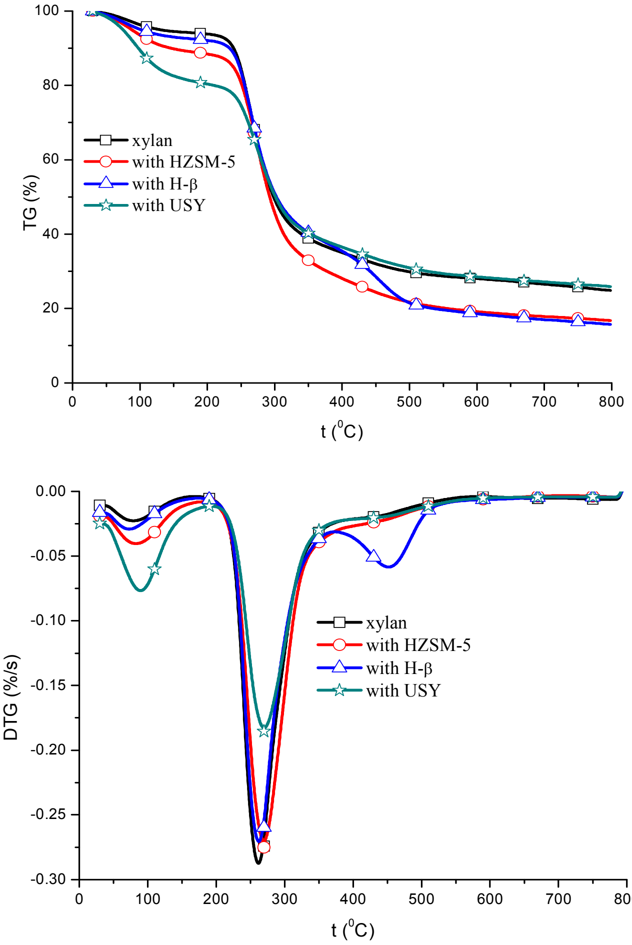


Fig.4 TG/DTG curves of xylan pyrolysis with zeolites

B. *Product release analyzed by FTIR*

The characteristic release from xylan pyrolysis with zeolites is shown in Fig.5. The unique peak release of xylan with or without zeolites is all at 262 °C, which is similar to the tendency of DTG curves. Based on the comparison of standard spectrum of certain compound (shown in Table 2) with the original spectra of xylan, the major products are identified by the appearance of characteristic absorption bonds, such as CO with two continuous peaks at 2280-2144 cm^{-1} and 2144-1950 cm^{-1}. The main products from xylan pyrolysis include water, CO_2, CO, benzene, methanol, formic acid, acetic acid, 2-furaldehyde and furan, 2-methyl *etc.* at 262 °C. The major products from xylan pyrolysis with zeolites are similar to pure xylan just with different release intensity.

The weight loss peak of xylan with H-β appeared in 350-500 °C corresponds to the largely formation of ethylene unexpectedly. The detailed evolution of the typical products can be investigated by their unique infrared spectrum peak (shown in Table 2), as the intensity of absorbance reflects the concentration of the products [30].

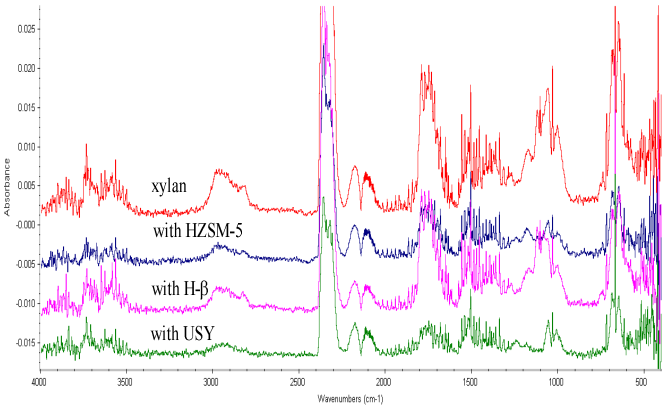


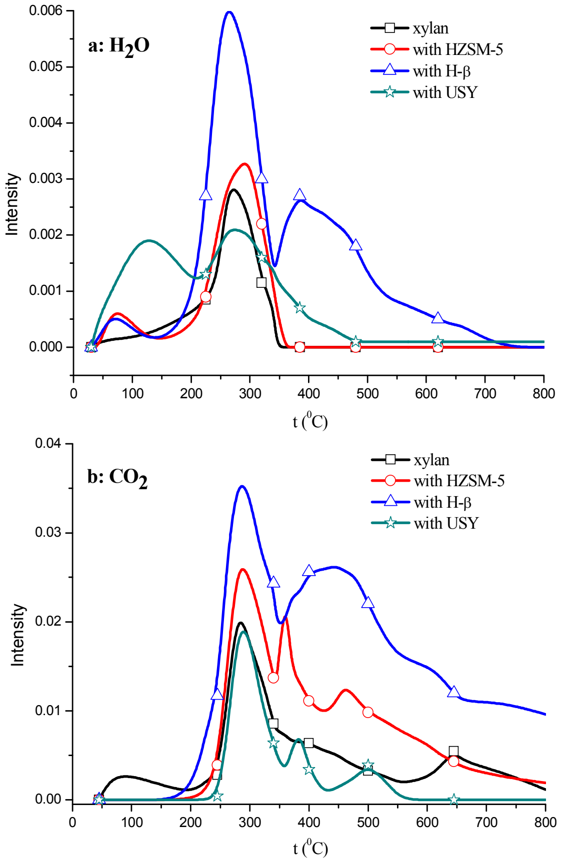
Fig.5 FTIR spectra of xylan pyrolysis with zeolites at maximal volatile release

Table 2 Typical products characterized by FTIR

Wavenumber (cm^{-1})	**Compounds**	**Characterized peak (cm^{-1})**
3964-3038, 2098-1593-1233 (**2**)	H_2O	3735
2406-2215	CO_2	2366
2280-2144-1950 (**2**)	CO	2178
3280-2901,1960-1812, 1523-1360,1153-803	Ethylene	950
3138-2987,2000-1961, 1843-1756,1550-1443, 1076-990,720-615	Benzene	1036
3683-3461, 3055-2840, 1861-1670, 1163-990, 763-483	Formic acid	1123
3630-3513, 1858-1658, 1483-1329-1236-1113-1043-920 (**5**), 741-464	Acetic acid	1184
3100-2600, 1600-1313-1178-929-830 (**4**)	Methanol	1061
3036-2787, 1646-556 (**12**)	Furan, 2-methyl	720
2898-2676, 1812-547 (**13**)	2-Furaldehyde	747

C. *Evolution of the typical products*

By the integration of intensity and temperature, the yield of certain compound can be approximately evaluated. Fig.6 shows the evolution of typical products from xylan pyrolysis. The intensity of acids is the sum of formic acid and acetic acid, and the intensity of furans corresponds to 2-furaldehyde and furan, 2-methyl. The release of water and CO_2 is more complex and is divided into three stages: the initial stage in 30-200 °C, the main stage in 200-350 °C and the last stage in 350-800 °C, which agrees well with the tendency of DTG curves. Pyrolysis of xylan with USY yields the most of water in the initial stage, but the subsequent maximal values are all obtained from pyrolysis of xylan with H-β. The formation of oxygenated compounds is concentrated in 200-500 °C, except for xylan with H-β in 100-500 °C. Pyrolysis of pure xylan produces more acids and furans, and less water and CO_2 than xylan pyrolysis with zeolites. After the addition of HZSM-5, H-β, and USY, the yield of water increases by 29.06 %, 289.69 %, and 116.42 % respectively; the yield of CO_2 increased by 58.11 % and 226.15 %, and decreases by 47.80 %; the yield of acid compounds decreased by 67.39 %, 47.16 % and 94.39 %; and the yield of furans decreased by 60.09 %, 12.94 % and 83.19 % respectively. A large amount of ethylene is produced from xylan pyrolysis with H-β in 400-550 °C. Therefore, it can be concluded that the presence of H-β efficiently promotes the decomposition of xylan to form small molecular gases, such as water, CO_2 and alkanes. The catalytic effect of USY is primarily related to the deoxygenation of oxygenated compounds, which has been identified by Wang [32]. The three catalysts, HZSM-5, H-β, and USY, all catalyzed the dehydration reaction of Manchurian ash pyrolysis, restrained the release of volatiles, and obviously promoted the final residue yields. Y-type catalysts showed the most evident catalytic effect, such as restraining the formation of aldehydes, acids, and ethers, and promoting that of and aromatics.



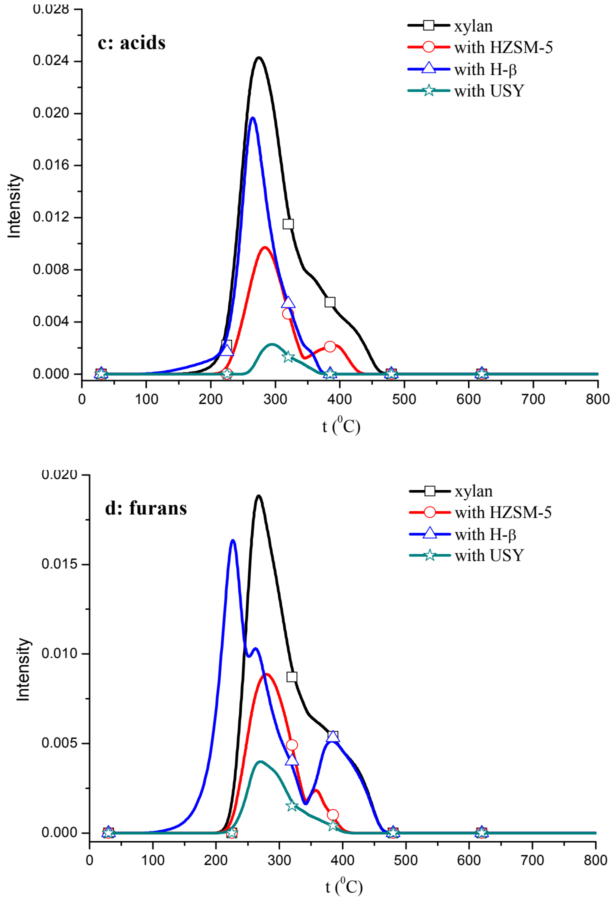


Fig.6 Evolution of typical products

VI. RAPID PYROLYSIS OF XYLAN

Volatiles released from pyrolysis of pure xylan at 350 °C were recorded in Fig.7, which was analyzed by GC/MS. This temperature corresponds to the maximal temperature of weight loss in thermal decomposition with the consideration of error component of temperature measurement in the pyrolyzer. There are several peaks, such as times at 1.40, 3.61, 9.47, 12.14, and 16.58. The relationship of retention time (RT) and compounds was summarized in Table 3.

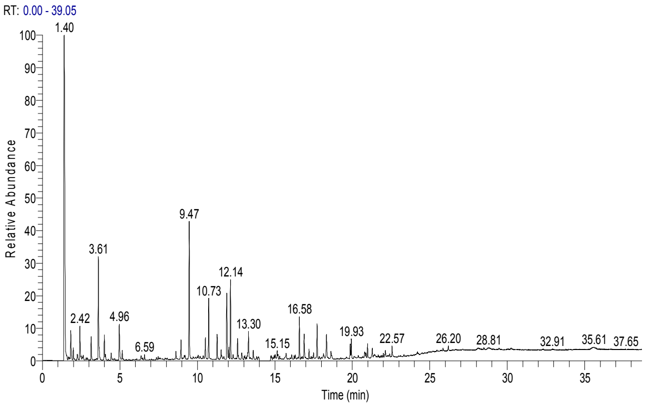


Fig.7 GC/MS spectrum of xylan pyrolysis at 350 °C

Table 3 Identification of pyrolysis volatiles

RT (min)	Compound	Area (%)
1.40	Carbon dioxide	36.56
1.83	Acetaldehyde	2.02
2.42	Acetone	2.31
3.15	2-butanone	1.47
3.61	Benzene	6.67
4.00	2,3-butanedione	1.45
4.96	Toluene	2.47
9.47	1-hydroxy-propanone	8.35
10.52	2-cyclopenten-1-one	1.50
10.73	1-hydroxy-2-butanone	4.04
11.27	2-propenoic, anhydride	1.55
11.90	Acetic acid	5.34
12.13	Furfural	5.29
12.60	Indene	1.44
13.30	Propanoic acid	2.31
16.58	Naphthalene	2.52
16.89	2-hydroxy-2-cyclopenten-1-one	1.69
17.73	2-hydroxy-3-methyl-2-cyclopenten	2.33
19.86	m-cresol	1.75
19.93	Phenol	1.17

Pyrolytic volatiles were composed of acids, aldehydes, ketones, phenols, and aromatics *etc*. Though the probability of peak at 1.40 was not too high to confirm it, carbon dioxide was considered as the most released product during xylan pyrolysis from the analysis by using exclusive method. It might be produced from the degradation of carbon bonds located at side chains. Acetic acid and furfural were the representative compounds of xylan pyrolysis, which had been proved by many researches [33]-[35]. Acetic acid came from the elimination of acetyl groups originally linked to the xylose unit, and furfural was formed by degradation of xylose unit. The yield of aromatic alkanes was about 13.10, contributed by the formation of benzene, toluene, indene, and naphthalene. They might be produced from the cyclization of iso-alkanes due to the absence of benzene ring structures in xylan. In addition, the yield of 1-hydroxy-propanone and 1-hydroxy-2-butanone was higher than that of acetone and 2-butanone, which confirmed that the hydroxyl groups linked to carbon in skeleton directly, was more stable than that in side chains.

VII. DISCUSSION ON DECOMPOSITION MODEL

The thermal decomposition of typical xylan units is proposed and summarized in Fig.8. It starts with the depolymerization of polymer first. The formation of acetic acid is involved with the primary elimination reaction of the active O-Ac groups in the side chain of O-acetyl xylan [36], and furfural is obtained through the cleavage of the bond between O-C_5 and ring forming between C_2-C_5 positions on the main chain of xylan [37]. The other pathway for furfural formation is related to the decomposition of 4-O-methylglucuronic xylan along with the release of CO_2 and methanol. Moreover, alkanes are obvious obtained from the depth deoxygenation of C_2 or C_3 oxygenated compounds, such as acetaldehyde, acetone, ethanol, and glycolaldehyde *etc*. It is observed that the cleavage of chemical bonds in the side chains is easier than these in the sugar ring. In the presence of zeolites, the formation of furfural is restrained and the fragmentation reaction becomes intense to produce more water, CO_2, CO and alkanes.

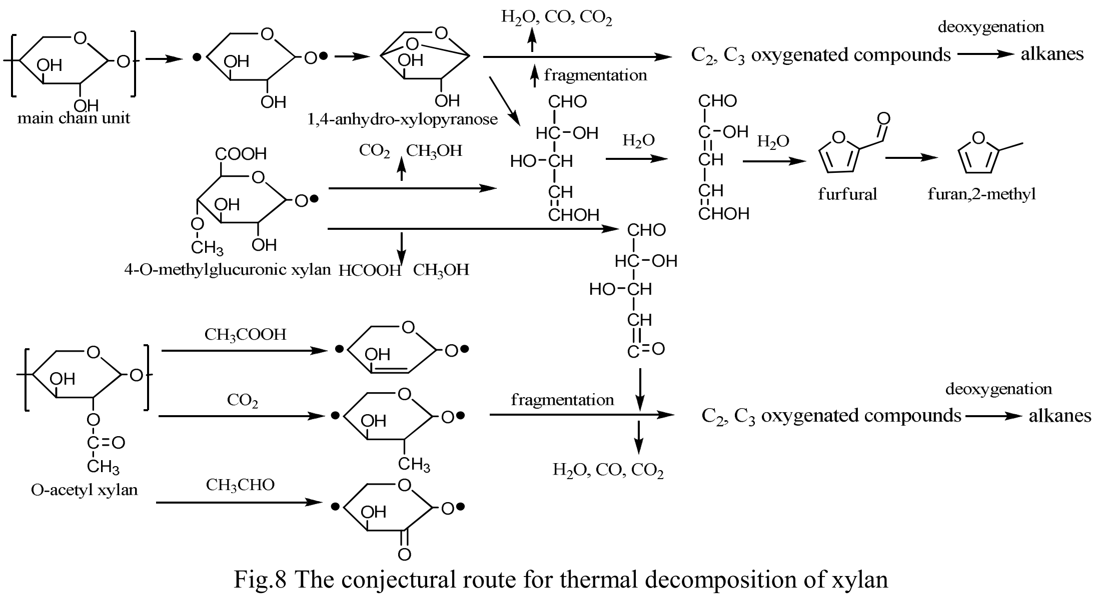


Fig.8 The conjectural route for thermal decomposition of xylan

Meanwhile, the cleavage of O-acetyl group is affected by the zeolites significantly, as acetic acid is mainly formed from it. USY is best for acidic oxygenated compounds removal and H-β prefers to thorough deoxygenation at higher temperature.

VIII. CONCLUSION

In the present study, TG-FTIR technique was used to study the catalytic effect of zeolites on hemicellulose pyrolysis. Xylan was selected as model compound of hemicellulose. It was observed that xylan contained the characteristic 4-O-methylglucurono and O-acetyl units from the FTIR analysis. The decomposition of xylan was complex, as it was divided into four stages respectively. The maximal weight loss rate of xylan with and without catalysts all occurred at 262 °C. All the three zeolites, HZSM-5, H-β and USY, catalyzed the dehydration in the initial stage and inhibited the formation of char residues. The proposed order was USY>HZSM-5>H-β related to the enhancement of dehydration, and inverse to the suppression of char residues.

It was also found that the presence of catalysts decreased the yield of oxygenated compounds and increased the formation of small molecular gaseous products such as water, CO_2 and alkanes. USY had the best effect on deoxygenation in xylan pyrolysis. H-β induced a formation peak of ethylene at 350-510 °C, caused by the secondary cracking of depolymerized compounds.

REFERENCES

[1] A. Aho, N. Kumar, K. Eränen, T. Salmi, M, Hupa, and D. Y. Murzin, "Catalytic Pyrolysis of Biomass in a Fluidized Bed Reactor: Influence of the Acidity of H-Beta Zeolite," *Process Saf. Environ.*, vol. 85, no. 5, pp. 473-480, 2007.

[2] B.P. Lavarack, G.J. Griffin, and D. Rodman, "The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products," *Biomass Bioenergy*, vol. 23, no. 5, pp. 367-380, 2002.

[3] A. Bendahou, A. Dufresne, H. Kaddami, Y. Habibi, "Isolation and structural characterization of hemicelluloses from palm of Phoenix dactylifera L," *Carbohyd. Polym.*, vol. 68, pp. 601-608, 2007.

[4] Z.Y. Jin, Z.B. Gu, Q.Y. Tong, R.J. Yang, "Carbohydrate Chemistry,"Y.Q. Zhao, Ed. Beijing: Chemical industry press, 2007, pp. 243-247.

[5] F.M. Gírio, C. Fonseca, F. Carvalheiro, L.C. Duarte, S. Marques, R. Bogel-Lukasik, "Hemicelluloses for fuel ethanol: A review," *Bioresource Technol.*, vol. 101, no.13, pp. 4775-4800, 2010.

[6] H.P. Yang, R. Yan, H.P. Chen, D.H. Lee, C.G. Zheng, "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel*, vol. 86, no. 12-13, pp. 1781-1788, 2007.

[7] G. Várhegyi, M.J. Antal, E. Jakab, P. Szab, "Kinetic modeling of biomass pyrolysis," *J Anal. Appl. Pyrolysis*, vol. 42, pp. 73-87, 1997.

[8] T. Hosoya, H. Kawamoto, and S. Saka, "Pyrolysis behaviors of wood and its constituent polymers at gasification temperature," *J Anal. Appl. Pyrolysis*, vol. 78, no. 2, pp. 328-336, 2007.

[9] L. Khezami, A. Chetouani, B. Taouk, R. Capart, "Production and characterisation of activated carbon from wood components in powder: Cellulose, lignin, xylan," *Powder Technol.*, vol. 157, no. 1-3, pp. 48-56, 2005.

[10] R. Alén, E. Kuoppala, and P. Oesch, "Formation of the main degradation compound groups from wood and its components during pyrolysis," *J Anal. Appl. Pyrolysis*, vol. 36, no. 2, pp. 137-148, 1996.

[11] J.J.M. Órfão, F.J.A. Antunes, and J.L. Figueiredo, "Pyrolysis kinetics of lignocellulosic materials-three independent reactions model," *Fuel*, vol. 78, no. 3, pp. 349-358, 1999.

[12] N. Worasuwannarak, T. Sonobe, and W. Tanthapanichakoon, "Pyrolysis behaviors of rice straw, rice husk, and corncob by TG-MS technique," *J Anal. Appl. Pyrolysis*, vol. 78, no. 2, pp. 265-271, 2007.

[13] T. Hosoya, H. Kawamoto, and S. Saka, "Cellulose-hemicellulose and cellulose-lignin interactions in wood pyrolysis at gasification temperature," *J Anal. Appl. Pyrolysis*, vol. 80, no. 1, pp. 118-125, 2007.

[14] H.P. Yang, R. Yan, H.P. Chen, C.G, Zheng, D.H. Lee, D.T. Liang, "In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin," *Energy Fuel*, vol. 20, pp. 388-393, 2006.

[15] C. Couhert, J.-M. Commandre, and S. Salvador, "Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicellulose and lignin?" *Fuel*, vol. 88, no. 3, pp. 408-417, 2009.

[16] N. Abatzoglou, A. Dalai, F. Gitzhofer, "Green diesel from Fiecher-Tropsch synthesis: challenges and hurdles," Proc. of the 3rd IASME/WSEAS Int. Conf. on energy, enviroment, ecosystems and sustainable development, 2007.

[17] A.V. Bridgwater, "Production of high grade fuels and chemicals from catalytic pyrolysis of biomass," *Catal, Today*, vol. 29, no. 1-4, pp. 285-295, 1996.

[18] M. Balas, M. Lisy, J. Moskalik, "Gas from biomass gasification in cogeneration," 6th IASME/WSEAS Int. Conf. on heat transfer, thermal engineering and environment (HTE08), 2008.

[19] C. Arapatsalos, and P. Lefakis, "The three way catalyst efficiency and the gas temperature difference," Proc. of the 4th IASME/WSEAS Int. Conf. on energy & environment (EE'09), 2009.

[20] C. Marculescu, A. Badea, C. Dinca, C. Gheorghe, "Biomass to syngas conversion by pyro-gasification process," Proc. of the 3rd WSEAS Int. Conf. on waste management, water pollution, air pollution, indoor climate, 2010.

[21] R. French and S. Czernik, "Catalytic pyrolysis of biomass for biofuels production," *Fuel Process. Technol.*, vol. 91, no. 1, pp. 25-32, 2010.

[22] D. Meier, J. Berns, O. Faix, U. Balfanz, W. Baldauf, "Hydrocracking of organocell lignin for phenol production," *Biomass Bioenergy*, vol. 7, no. 1-6, pp. 99-105, 1994.

[23] H.F. Xie, D.N. Bolam, T. Nagy et al, "Role of hydrogen bonding in the interaction between a xylan binding module and xylan," *Biochem.*, vol. 40, pp. 5700-5707, 2001.

[24] J.A. Lercher, C. Gründling, and G. Eder-Mirth, "Infrared studies of the surface acidity of oxides and zeolites using adsorbed probe molecules," *Catal. Today*, vol. 27, no. 3-4, pp. 353-376, 1996.

[25] C. Zhang, X.W. Guo, C.S. Song, S.Q. Zhao, X.S. Wang, "Effects of steam and TEOS modification on HZSM-5 zeolite for 2,6-dimethylnaphthalene synthesis by methylation of 2-methylnaphthalene with methanol," *Catal. Today*, vol. 149, no. 1-2, pp. 196-201, 2010.

[26] R. Dimitrova, G. Gündüz, and M. Spassova, "A comparative study on the structural and catalytic properties of zeolites type ZSM-5, mordenite, Beta and MCM-41," *J Mol. Catal. A: Chem.*, vol. 243, no. 1, pp. 17-23, 2006.

[27] J. Scheirs, G. Camino, and W. Tumiatti, "Overview of water evolution during the thermal degradation of cellulose," *Eur. Polym. Jl*, vol. 37, pp. 933-942, 2001.

[28] M. Košík, V. Reiser, and P. Kováč, "Thermal decomposition of model compounds related to branched 4-O-methylglucuronoxylans," *Carbohyd. Res.*, vol. 70, no. 2, pp. 199-207, 1979.

[29] X.J. Guo, S.R. Wang, Z.Y. Luo, "Catalytic pyrolysis of cellulose with zeolites," unpublished.

[30] Q. Liu, S.R. Wang, Y. Zheng, Z.Y. Luo, K.F. Cen, "Mechanism study of wood lignin pyrolysis by using TG-FTIR analysis," *J Anal. Appl. Pyrolysis,* vol. 82, no. 1, pp. 170-177, 2008.

[31] S.R. Wang, X.J. Guo, K.G. Wang, Z.Y. Luo, "Influence of the interaction of components on the pyrolysis behavior of biomass," *J Anal. Appl. Pyrolysis*, to be published.

[32] S.R. Wang, Q. Liu, K.G. Wang, X.J. Guo, et al, "Study on catalytic pyrolysis of Manchurian ash for production of bio-oil," *Int. J Green Energy*, vol. 7, no. 3, pp. 300-309, 2010.

[33] X.F. Zhu, Q. Lu, W.Z. Li, D. Zhang, "Fast and catalytic pyrolysis of xylan: effects of temperature and M/HZEM-S (M=Fe, Ze) catalysts on pyrolytic products," *Frontiers of energy and power engineering in China*, vol. 4, no. 3, pp. 424-429, 2009.

[34] X.F. Zhu, and Q. Lu, “Production of chemicals from selective fast pyrolysis of biomass,” in Biomass, edited by M. Momba and F. Bux. Croatia, 2010, pp. 148-153.

[35] A. Demirbas, “The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis.” *Fuel Process. Technol.*, vol. 88, no. 6, 591-597, 2007.

[36] G.R. Ponder and G.N. Richards, “Thermal synthesis and pyrolysis of a xylan,” *Carbohyd. Res.*, vol. 218, pp. 143-155, 1991.

[37] D.K. Shen, S. Gu, and A.V. Bridgwater, “Study on the pyrolytic behaviour of xylan-based hemicellulose using TG-FTIR and Py-GC-FTIR.” *J Anal. Appl. Pyrolysis,* vol. 87, no. 2, pp. 199-206, 2010.