CHARACTERISTICS OF CORN STALK HEMICELLULOSE PYROLYSIS IN A TUBULAR REACTOR

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Pyrolysis characteristics of corn stalk hemicellulose were investigated in a tubular reactor at different temperatures, with focus mainly on the releasing profiles and forming behaviors of pyrolysis products (gas, char, and tar). The products obtained were further identified using various approaches (including GC, SEM, and GC-MS) to understand the influence of temperature on product properties and compositions. It was found that the devolatilization of hemicellulose mainly occurred at low temperatures (<500°C), and produced large amounts of tar. A higher reactor temperature was conducive to the yield of gas products, accompanied by a reduction of tar because of the secondary cracking of volatiles. The gas components mainly consisted of CO_2, CO, H_2, and CH_4, together with trace C_2H_4 and C_2H_6. The CO_2 evolved easily and reached a relatively large yield of 129.2ml/g at 550°C, while CO and H_2 were mainly released at higher temperatures (700-900°C). The tar was mainly composed of a range of oxygenated compounds, including ketones, furans, carboxylic acids, and alcohols, and their contents were influenced by the final temperature. An in-depth analysis of the properties of the products generated at different temperatures is favorable for a better understanding of the mechanism of hemicellulose pyrolysis.

INTRODUCTION

Energy is an important basis for national economic development, and the basic material necessities of human production and life. Currently, the energy supply relies mainly on coal and other fossil fuels. The limited fossil energy resources, together with environmental pollution and greenhouse gas emissions caused by exploitation and utilization of fossil energy, are all seriously constraining economic and social sustainable development (Thomas et al. 2009). Therefore, the question of how to improve the energy structure, and ensure energy security, thereby promoting economic and social sustainable development, has become a major strategic issue faced by all countries.

Biomass, including agricultural residues, represents a renewable and alternative source available especially in an agricultural country such as China. The conversion of biomass into char, bio-oils, and gaseous products using pyrolysis technologies is one of the most promising alternatives under study today to convert biomass into useful products

and energy (Mohan et al. 2006; Perez et al. 2007). Previous reviews on the thermochemical conversion of biomass have dealt with many aspects, for example, thermal analysis and analytical pyrolysis studies (Mangut et al. 2006; Li et al. 2001), wood and agricultural residue pyrolysis kinetics (Morten et al. 2002; Hu et al. 2007), pyrolysis reactor technologies (Wei et al. 2006; Shen and Gu 2009), catalytic upgrading of pyrolysis products (Adjaye and Bakhshi 1994), and characterization of pyrolysis oils (Sholze and Meier 2001; Bayerbach et al. 2007). However, the chemical structure and major organic components in biomass are extremely important in biomass pyrolysis processes for producing derived fuels and chemicals. The major organic components of biomass can be classified as cellulose, hemicellulose, and lignin, which have very different thermal behaviours (Serdar 2004; Shen et al. 2010). Therefore, in-depth study the pyrolysis characteristics of each component in different biomasses, such as reaction kinetics, products distribution, with a focus on the governing factors, is necessary for a better understanding of biomass pyrolysis processes.

Hemicelluloses, the second most abundant renewable polymers in nature, are plant cell wall polysaccharides closely associated with cellulose and lignin (Badal 2003). Unlike cellulose, which is chemically homogeneous, hemicelluloses are heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids. In particular, in contrast to wood hemicelluloses, there are a great variety of linkages and abundance of branching types in graminaceous hemicelluloses, depending on the species and the tissue within a single species, as well as on the age of the tissue (Sun et al. 2005; Xu et al. 2006). Because of its structural complexity and the varying physical and chemical properties, pyrolysis behaviors of hemicellulose have been less elucidated compared with those of cellulose and lignin. Several previous works have been inclined to use model compounds such as xylan or 4-O-methyl-D-glucurono-D-xylan for hemicellulose pyrolysis study (Di Blasi and Lanceta 1997; Várhegyi et al. 1997; Órfão et al. 1999). Taking into account of the differences between actual hemicellulose and its model compounds, hemicellulose isolated from corn stalk using an optimal chemical process was employed for thermogravimetric analysis in our previous work (Lv et al. 2010). In spite of this, previous research efforts in the area of hemicellulose pyrolysis have concentrated on relatively basic aspects such as thermal analysis and kinetic models, while limited information is available in the literature concerning the products distribution and composition from hemicellulose pyrolysis.

The objective of this study is to gain a comprehensive understanding of hemicellulose pyrolysis with focus mainly on the distribution and properties of products (gas, char, and tar) under varied temperatures, thus facilitating the establishment of a model to simulate hemicellulose pyrolysis and contribute to a better understanding of the processes and mechanism of biomass pyrolysis. For this purpose, pyrolysis of actual hemicellulose isolated from corn stalk was investigated in a tubular reactor at different temperatures, and the releasing profile and characteristics of the obtained products were thoroughly identified using various approaches.

EXPERIMENTAL

Materials

Corn stalk (with leaves removed) obtained from Changzhi City, Shanxi Province, China, was ground in a Wiley mill and screened with 40 to 60 mesh sizes (0.28–0.45mm) for the experiments. The composition (w/w) of corn stalk used was as follows: cellulose, 42.4%; hemicellulose, 29.6%; lignin, 21.7%; and ash, 5.1%, obtained on a dry weight basis. The hemicellulose was isolated using a modified method as previously described (Lv et al. 2010). Elemental analysis of corn stalk and hemicellulose were determined using an elemental analyzer (Vario EL, ELEMENTAR, Germany), and the results are shown in Table 1.

Table 1. Elemental Analysis of Materials (%)

Materials	Elements					
	C	H	O*	N	S	Cl
Corn stalk	41.87	5.42	52.34	0.11	0.07	0.19
Hemicellulose	39.05	5.73	55.22	-	0.003	-
* calculated by difference						

Experimental Set-up and Procedures

Pyrolysis was performed with a horizontal tubular reactor as shown in Fig. 1. The apparatus mainly consists of a stainless steel block furnace of 35mm in inner diameter, an inner quartz tube of 30mm in inner diameter, a temperature controller, and a power control system. A thermocouple is placed at the center of the quartz tube in order to monitor and control the actual pyrolysis temperature. A porcelain boat of 10mm in width and 50mm in length is suspended on the thermocouple for placing the samples.
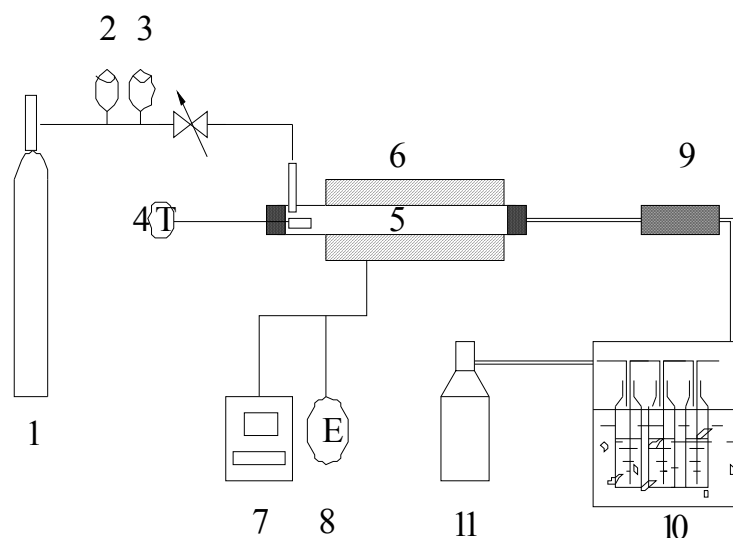
1. Nitrogen cylinder 2,3.Flowmeter 4.Thermocouple and porcelain boat 5.Quartz tube 6.Tubular furnace 7.Temperature controller 8.Electric power 9.Filter 10.Cooling system 11.Gas collecting unit

Fig. 1. Schematic diagram of pyrolysis experimental set-up

For each set of the experiments, about 350 mg of hemicellulose sample was put into the porcelain boat. The porcelain boat containing hemicellulose was placed in the left of the quartz tube, and kept 25 cm from the furnace in order to avoid the previous heating of the sample before reaching the desired temperature. High purity nitrogen (99.9995%) was first fed into the tubular reactor with a flow rate of 200ml/min, and oxygen in the quartz tube was purged until its concentration declined below 0.01%. Subsequently, the reactor was preheated to the desired pyrolysis temperature (temperatures at 400, 450, 500, 550, 600, 700, 800, and 900°C, respectively). After the desired temperature was reached and maintained stable, fast pyrolysis was conducted by inserting the sample into the center of the furnace. The decomposed volatiles were purged out by nitrogen and passed through a metallic sieve to remove solid particles, then were further cooled in three sequential ice-salt baths, in which the isopropanol was set to absorb the condensed liquid products (tar). The gaseous product that had passed through the condenser was collected in a gasbag and analyzed offline. After 1 min of pyrolysis, the solid products (char) were pulled out and continuously cooled with a nitrogen flow for 5 min until they had reached room temperature so that they could be recovered. The amounts of the gases and char fractions were directly calculated, and the tar was determined from the weight difference. All experiments were carried out at atmospheric pressure. For each pyrolysis condition, at least three sets of experiments were performed, and all results were found to be reproducible.

Product Analysis

The gas, char, and tar products obtained from hemicellulose pyrolysis were characterized with different methods.

The gas products collected in the gasbag were analyzed using a gas chromatograph with a thermal conductivity detector (GC-TCD 20B, Shimadzu, Japan). GC-TCD analysis was carried out with mixed standard gas (H_2 9.08%, CH_4 2.12%, CO 10.3%, CO_2 3.31%, C_2H_4 1.01%, C_2H_6 1.02%, C_2H_2 1.12%, O_2 1.10%, N_2 70.94%, mol/%) as external standard under the following conditions: carrier gas: Ar (99.9995%), with a flow rate of 25ml/min; column: GDX104 and 5A molecular sieve packed column (TECHCOMP, Shanghai, China); injector temperature: 50^oC; column temperature: 50^oC; TCD temperature: 100^oC, with TCD current of 70mA.

Char surface morphology was examined with a scanning electron microscope (S-3700N, Hitachi, Japan). A coating Au film was applied to the sample using a sputter coater. The coated samples were then examined and imaged using SEM. Signals were transformed by secondary electron at a working distance of 19.8 mm and an accelerating voltage of 10kV.

The compositions of tar were detected by a gas chromatography-mass spectroscopy (GC-MS) system (7890A-5975C GC-MS with 7683B ALS, Agilent Technology, USA). It should be noted that the liquid sample must be first dehydrated with anhydrous sodium sulfate and filtered with a 0.22μm microporous membrane. High purity helium (99.9995%) was used as the carrier gas. Other parameters about GC and MS were as follows: The capillary column (HP-INNO Wax, 30m×0.25mm×0.25μm) temperature was 2min isothermal at 40°C, then 10°C/min to 100°C, then 4°C/min to 120°C, and then 10°C/min to 230°C for 5min; the injector temperature was 250°C with a

split ratio of 5:1; EI ionization energy was 70eV, and the scan range was 33-500amu with a scan speed of 1.0s/decade. Identification of the pyrolysis compounds was achieved by comparison of their mass fragments with the Perkin Elmer NIST 08 mass spectral library.

RESULTS AND DISCUSSION

Gas, Char, and Tar-Forming Behaviors

The pyrolysis products derived from corn stalk hemicellulose can be divided into gas, tar, and char. The term tar refers to liquid products condensed during the pyrolysis process (Mohan et al. 2006), and char is the solid residue after pyrolysis. The yields of gas, tar, and char products from hemicellulose pyrolysis at different temperatures from 400 to 900°C are presented in Fig. 2.

As can be seen from Fig. 2, the pyrolysis temperatures had a major impact on the distribution of hemicellulose pyrolysis products. The char content was reduced greatly from 44.5 to 25.9% as the temperature was increased from 400 to 500°C. After that, with temperature increasing further, the char yield decreased slightly, and only 2.3% more of hemicellulose mass was lost when the final temperature increased from 500 to 900°C. This indicates that the devolatilization of hemicellulose occurs mainly at lower temperatures (<500°C), which is in accordance with previous thermal analysis results using model compounds (Di Blasi and Lanceta 1997; Órfão et al. 1999). The pyrolysis temperature had a positive impact on the formation of gas products; that is, the gas yield tended to increase as the final pyrolysis temperature increased from 400 to 900°C and reached its maximum value (40.2%) at 900°C. Clearly, the increase in the rate of gas yield in the temperature range of 550-900°C was not as fast as that in the range of 400-550°C (i.e., 33.1-40.2% vs. 11.9-33.1%). As for liquid products, the tar yield also increased with increasing temperature at first, reached a maximum value of 48.2% at 450°C, then decreased gradually with further increase of temperature. This may be because the release of tar was accompanied by secondary reactions before condensation, thus affecting the pyrolysis products distribution at high temperature. As the temperature increases, the relatively poor stability components of tar further broke up and generated small molecule gaseous components, resulting in an increase of the gas yields and a decrease of the tar production. According to the views of Wei and his colleagues (2006), the extent of secondary reactions is affected by reactor temperature and vapor residence time in the reactor.

Gas

The gas components from hemicellulose pyrolysis analyzed by gas chromatography mainly consisted of CO_2, CO, H_2, and CH_4, together with trace C_2H_4 and C_2H_6. By further approximate calculation, the molar percentage results from GC analysis were converted into volumes of gas per gram of sample at ambient temperature and atmospheric pressure (the volume of 1mol gas equals 24.45L at 1atm and 25°C). A typical profile of gas yields with temperature increasing is plotted in Fig. 3.
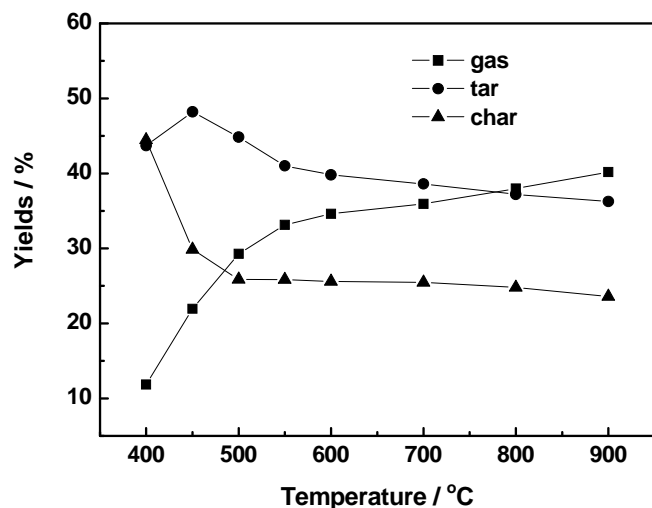
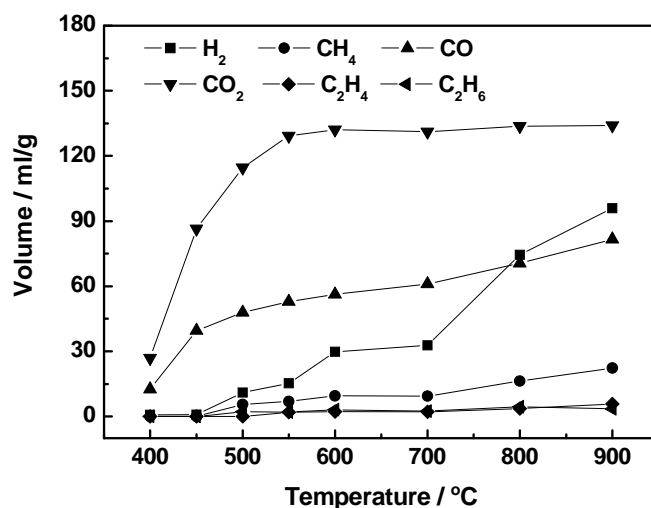**Fig. 2.** Yields of hemicellulose pyrolysis products with temperature

Fig. 3. Gas releasing profile of hemicellulose pyrolysis

It can be observed that the CO_2 production was significantly higher than that of other gases throughout the temperature region. This is because there are a large number of acetyl groups originating from uronic acid in the structure of hemicellulose, which undergo a decarboxylation reaction during pyrolysis, and thus release large amounts of CO_2 (Ponder and Richards 1991). As can be seen from Fig. 3, the CO_2 yield increased significantly from 26.9 to 129.2ml/g as temperature increased from 400 to 550°C, then, as the temperature further increased, CO_2 yield basically remained unchanged. This indicates that CO_2 can easily evolve out from the cracking of acetyl and carboxyl groups in hemicellulose at a relatively low temperature, and this process does not change significantly with temperature after it reaches a certain level. Over the whole temperature range studied, CO content increased slightly with increasing temperature and reached a maximum yield of 81.6ml/g at 900°C. This trend is consistent with the previous

experimental results by Wang et al. (2006), who studied the rapid pyrolysis characteristics of xylan on a heat radiation reactor. They proposed that CO_2 is mainly released due to the cracking of unstable carbonyl and carboxyl groups, and the formation of CO is largely due to secondary cracking of tars. The releasing profile of H_2 showed a similar pattern with that of CO. However, its increasing rate was much higher after 700°C, and the maximum yield of 95.9ml/g at 900°C was higher than that of CO. It can be concluded that H_2 production from hemicellulose pyrolysis is mainly dependent on the secondary reactions of volatiles, especially in the high temperature range. The CH_4 started to evolve at temperature >400°C because of the cracking of methoxyl functions, then it increased as temperature increase until it reached a maximum yield at 900°C. With regards to other hydrocarbon gases, such as C_2H_4 and C_2H_6, these generally were produced only at high temperatures with low yield. They are generally caused by secondary cracking of volatiles. With increasing temperature, volatile secondary cracking increased, resulting in their yield slightly increasing.

Char

To describe the morphological characteristics of hemicellulose chars at different temperature, a selection of char particles obtained in the tubular reactor were observed under a scanning electron microscope at magnifications up to 2000 times. Figure 4 (a)-(c) shows the SEM images of char particles of hemicellulose pyrolyzed at 400, 550, and 900°C, respectively.

(a)

(b)

(c)
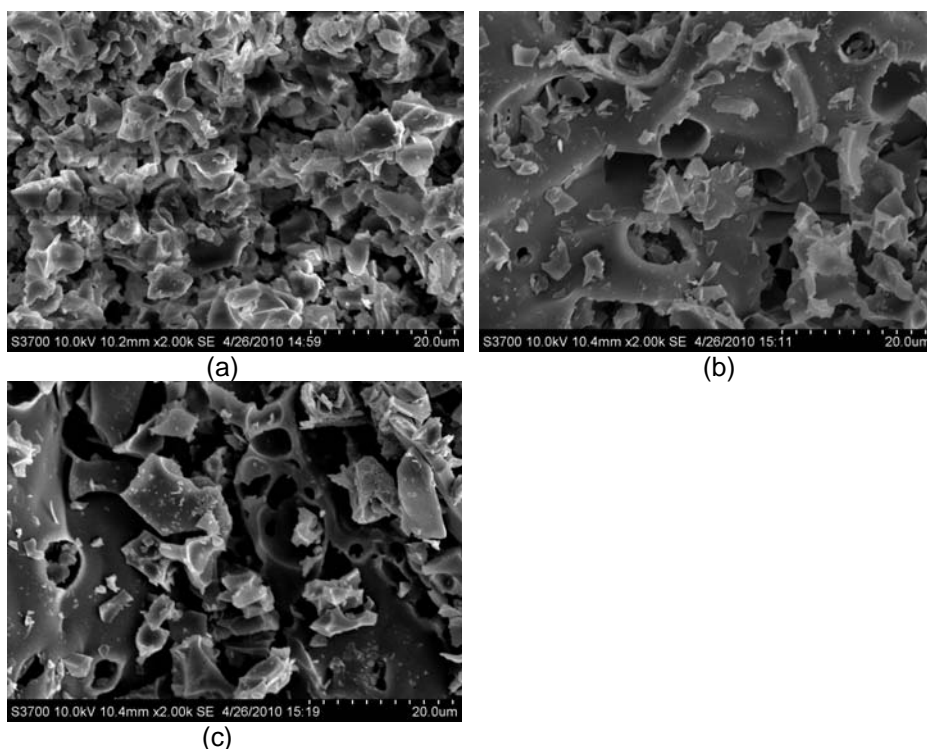
Fig. 4. SEM photographs of char from hemicellulose pyrolysis at different temperatures: (a) 400°C, (b) 550°C, (c) 900°C

As can be seen, the final pyrolysis temperature had a greater impact on surface morphology of hemicellulose char. At low temperature of 400°C, the char showed severe irregular agglomeration. With final temperature increasing to 550°C, the char surface became smooth and began to form small pores. With temperature increasing further to 900°C, there were more fine pores emerging, in addition to large pores, and cavities were still evident. Aguado et al. (2000) have studied the char-formation kinetics of sawdust pyrolysis in a conical spouted bed reactor, and concluded that the char formation is controlled by internal diffusion of gaseous products and volatile liquids. In addition, according to Yang et al.'s (2006) viewpoints, the morphological changes of the char might be attributed to the quick volatile decomposition and release of gas at high temperatures. However, compared with that of other biomass (Cetin et al. 2004) or components like lignin (Chihiro et al. 2003), hemicellulose pyrolysis char showed a higher density and smaller porosity, which can be ascribed to the specific polysaccharide structure of hemicellulose.

Tar

GC-MS is a rapid and reliable procedure for qualitative screening and semi-quantitative analysis of various tar components. To learn more information about the composition of tar, isopropanol soluble fractions at different pyrolysis temperatures were characterized by GC-MS. As the space is limited, only the total ion chromatogram of isopropanol soluble tar fractions obtained at 550°C is shown in Fig. 5. Identification of the products was conducted with the retention times and mass fragmentation patterns compared with those of the NIST 08 mass spectral library. Table 2 summarizes the identification results and relative area percent of the compounds.

In view of the results presented in Table 2, it could be seen that the hemicellulose pyrolysis tars were a very complex mixture of organic compounds that can be further categorized into ketones, furans, carboxylic acids, and alcohols. Among all of the identified compounds, ketones possessed the largest share both in product variety and in content. Ketones, especially cyclopentanone and cyclopentenone, mainly originated from the decomposition of sugar units and recombination of opened bonds. Furans are known to be produced from mono-, di- and poly-saccharides in reasonable yields. Sanders and Goldsmith (2003) have proposed that significant yields of furan derivatives are obtained only from substrates containing furanose units. For hemicellulose pyrolysis, the furans mainly originated from the dehydration of xylose units. Furfural was a typical product of such compounds, and accounted for a large proportion of the identified products. As one of the main products, acetic acid mainly came from the ring-scission of uronic acid residues, as well as the elimination of acetyl groups originally linked to the xylose unit. Although it has been already reported that all three components of biomass may produce acetic acid during the pyrolysis process, hemicellulose definitely makes the greatest contribution to the formation of acetic acid due to its structural characteristics (Shen et al. 2010).

It can be seen from Table 2 that the compositions of tar obtained at different temperatures were similar; however, the relative contents of various types of compounds were different. This illustrates that the final pyrolysis temperature is indeed a critical parameter in terms of not only the tar yields but also the component distribution of tar.
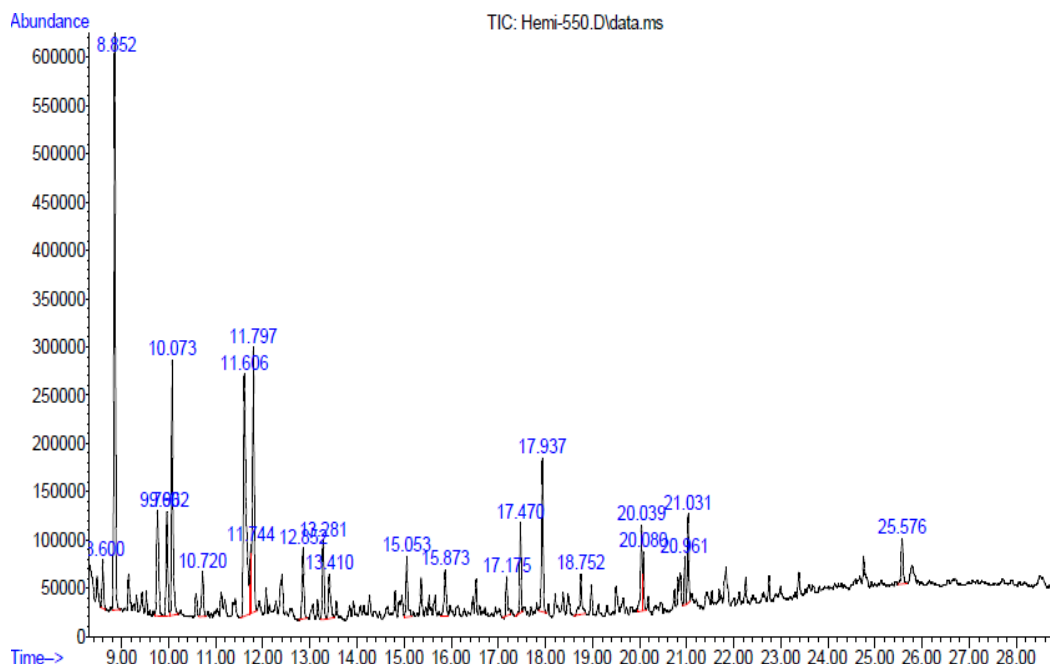
Fig. 5. Total ion chromatogram of tar from hemicellulose pyrolysis at 550°C

Table 2. Identification of the Main Components of the Tar

Groups	Compound	Formula	Area percent (%)			
			450°C	550°C	700°C	900°C
Ketones			60.47	63.09	63.54	71.05
	3-hydroxy-2-butanone	$C_4H_8O_2$	2.04	1.77	1.87	2.15
	1-hydroxy-2-propanone	$C_3H_6O_2$	19.49	20.40	20.72	26.31
	2-cyclopenten-1-one	C_5H_6O	5.04	5.17	5.06	7.04
	2-methyl-2-cyclopenten-1-one	C_6H_8O	4.39	4.14	4.25	5.75
	1-hydroxy-2-butanone	$C_4H_8O_2$	12.02	9.96	10.64	11.25
	4-hydroxy-3-hexanone	$C_6H_{12}O_2$	3.17	1.99	1.93	-
	3-methyl-2-cyclopenten-1-one	C_6H_8O	2.36	3.28	3.24	4.49
	2,3-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	2.85	3.38	3.39	4.56
	3-ethyl-2-hydroxy-2-cyclopenten-1-one	$C_7H_{10}O_2$	2.49	4.37	4.12	-
	2-hydroxy-3,4-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O_2$	2.60	2.90	2.74	2.86
	3-methyl-1,2-cyclopentanedione	$C_6H_8O_2$	4.02	5.73	5.58	6.64
Furans			19.02	16.16	16.78	17.89
	furfural	$C_5H_4O_2$	14.65	13.35	12.91	14.58
	dihydro-2(3H)-furanone	$C_4H_6O_2$	2.71	2.81	2.22	3.31
	2,5-dihydro-3,5-dimethyl-2-furanone	$C_6H_{10}O_2$	1.66	-	1.65	-
Acids			18.28	17.83	17.46	11.07
	acetic acid	$C_2H_4O_2$	15.57	15.38	15.01	11.07
	propanoic acid	$C_3H_6O_2$	2.71	2.45	2.45	-
Alcohols			2.25	2.92	2.21	-
	cyclobutanol	C_4H_8O	2.25	2.92	2.21	-

Ketones content accounted for 60.47% of the total identified peak areas at 450°C. But as the temperature rose to 900°C, the content increased to 71.05%. Meanwhile, the carboxylic acids content decreased linearly from 18.28% to 11.07% with temperature increasing from 450 to 900°C. There was also an obvious variation trend with temperature for a particular compound, such as 1-hydroxy-2-propanone, acetic acid, etc. These can be interpreted as originating from the successive decomposition or secondary cracking reactions that the volatiles may undergo before condensation. It should be stressed that the present work mainly concern volatile organic compounds that can be detected in chromatographic analysis. To elucidate the heavier constituents and trace components of pyrolysis liquids, Sholze et al. (2001) and Bayerbach et al. (2007) have described various physico-chemical characterization methods and done a lot of valuable work.

CONCLUSIONS

1. The experimental results show that temperature is indeed a critical parameter affecting the yield and quality of different products (gas, char, and tar) from hemicellulose pyrolysis. The devolatilization of hemicellulose mainly occurred at lower temperatures (<500°C). When temperature was increased further to 900°C, the char yield remained at about 25.9%, while gas yield continued to increase and tar yield decreased, respectively.
2. The main gases produced were CO_2, CO, H_2, and CH_4, with small amounts of C_2H_4 and C_2H_6. The CO_2 evolved out easily because of the breakage of acetyl and carboxyl groups in hemicellulose at relatively low temperature. A higher reactor temperature favored the cracking and reforming of the volatiles, and thus increased CO and H_2 formation.
3. The surface structures of char varied with different pyrolysis temperature, i.e., the char from the aggregation at low temperature became more smooth and porous as the temperature increased.
4. The maximum yield of tar (48.2%) was achieved at 450°C. The tars were mainly composed of a range of oxygenated compounds, including ketones, furans, carboxylic acids, and alcohols, and their contents were influenced by the final pyrolysis temperature.

ACKNOWLEDGMENTS

REFERENCES CITED

Adjaye, J. D., and Bakhshi, N. N. (1994). "Upgrading of a wood-derived oil over various catalysts," *Biomass and Bioenergy* 7(1), 201-211.

Aguado, R., Olazar, M., and Barona, A. (2000). "Char-formation kinetics in the pyrolysis of sawdust in a conical spouted bed reactor," *J. Chem. Technol. Biotechnol.* 75, 583-588.

Badal, C. S. (2003). "Hemicellulose bioconversion," *J. Ind. Microbiol Biotechnol.* 30, 279-291.

Bayerbach, R., Nguyen, V. D., Schurr, U., and Meier, D. J. (2006). "Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin) Part III Molar mass characteristics by SEC, MALDI-TOF-MS, LDI-TOF-MS, and Py-FIMS," *J. Anal. Appl. Pyrol.* 77, 95-101.

Cetin, E., Moghtaderi, B., Gupta, R., and Wall, T. F. (2004). "Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars," *Fuel* 83, 2139-2150.

Chihiro, F., Kenichi, A., and Yohsuke, Y. (2003). "Effect of heating rate on steam gasification of biomass: 1. Reactivity of char," *Ind. Eng. Chem. Res.* 42, 3922-3928.

Di Blasi, C., and Lanceta, M. (1997). "Intrinsic kinetics of isothermal xylan degradation in inert atmosphere," *J. Anal. Appl. Pyrol.* 40(41), 287-303.

Hu, S., Andreas, J., and Xu, M. H. (2007). "Kinetic study of Chinese biomass slow pyrolysis: Comparison of different kinetic models," *Fuel* 86, 2778-2788.

Li, S., Hart, J. L., Banyasz, J., and Shafer, K. (2001). "Real-time evolved gas analysis by FTIR method: An experimental study of cellulose pyrolysis," *Fuel* 80, 1809-1817.

Lv, G. J., Wu, S. B., and Lou, R. (2010). "Kinetic study of the thermal decomposition of hemicellulose isolated from corn stalk," BioResources 5(2), 1281-1291.

Mangut, V., Sabio, E., and Gãnán, J. (2006). "Thermogravimetric study of the pyrolysis of biomass residues from tomato processing industry," *Fuel Processing Technology* 87, 109-115.

Mohan, D., Pittman, C. U. Jr., and Steele, P. H. (2006). "Pyrolysis of wood/biomass for bio-oil: A critical review," *Energy & Fuels*, 20, 848-889.

Morten, G. G., Gábor, V., and Colomba, D. B. (2002). "Thermogravimetric analysis and devolatilization kinetics of wood," *Ind. Eng. Chem. Res.* 41, 4201-4208.

Órfão, J. J. M., Antunes, F. J. A., and Figueiredo, J. L. (1999). "Pyrolysis kinetics of lignocellulosic materials-three independent reactions model," *Fuel* 78, 349-358.

Perez, M. G., Chaala, A., Pakdel, H., Kretschmer, D., Roy, C. (2007). "Characterization of bio-oils in chemical families," *Biomass and Bioenergy* 31, 222-242.

Ponder, G. R., and Richards, G. N. (1991). "Thermal synthesis and pyrolysis of a xylan," *Carbohydrate Research* 218(30), 143-155.

Sanders, E. B., Goldsmith, A. I., Seeman, J. I. (2003). "A model that distinguishes the pyrolysis of D-glucose, D-fructose, and sucrose from that of cellulose: Application to the understanding of cigarette smoke formation," *J. Anal. Appl. Pyrol.* 66, 29-50.

Serdar, Y. (2004). "Pyrolysis of biomass to produce fuels and chemical feedstocks," *Energy Conversion and Management* 45, 651-671.

Shen, D. K., and Gu, S. (2009). "The mechanism for thermal decomposition of cellulose and its main products," *Bioresource Technology* 100, 6496-6504.

Shen, D. K., Gu, S., and Bridgwater, A. V. (2010). "Study on the pyrolytic behaviour of xylan-based hemicellulose using TG-FTIR and Py-GC-FTIR," *J. Anal. Appl. Pyroly.* 87, 199-206.

Shen, D. K., Gu, S., and Bridgwater, A. V. (2010). "The thermal performance of the polysaccharides extracted from hardwood: Cellulose and hemicellulose," *Carbohydrate Polymers* 82, 39-45.

Sholze, B., and Meier, D. (2001). "Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY–GC/MS, FTIR, and functional groups," *J. Anal. Appl. Pyrol.* 60, 41-54.

Scholze, B., Hanser, C., and Meier, D. (2001), "Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin) Part II. GPC, carbonyl goups, and 13C-NMR," *J. Anal. Appl. Pyroly.* 58-59, 387-400.

Sun, X. F., Sun, R. C., and Fowler, P. (2005). "Extraction and characterization of original lignin and hemicelluloses from wheat straw," *J. Agric. Food Chem.* 53, 860-870.

Thomas, F. M., Michael, L. B., William S. B. (2009). *Biomass and Alternate Fuel Systems: An Engineering and Economic Guide,* John Wiley & Sons, Hoboken, N.J.

Várhegyi, G., Antal, M. J. J., and Jakab, E. (1997) "Kinetic modeling of biomass pyrolysis," *J. Anal. Appl. Pyrol.* 42, 73-87.

Wang, S. R, Tan, H., and Luo. Z. Y. (2006). "Experimental research on rapid pyrolysis of xylan," *Journal of Zhejiang University* 40(3), 419-423.

Wei, L. G., Xu, S. P., and Zhang, L. (2006). "Characteristics of fast pyrolysis of biomass in a free fall reactor," *Fuel Processing Technology* 87, 863-871.

Xu, F., Liu, C. F., Geng, Z. C. (2006). "Characterisation of degraded organosolv hemicelluloses from wheat straw," *Polymer Degradation and Stability* 91, 1880-1886.

Yang, H. P., Yan, R, and Chen, H. P. (2006). "Mechanism of palm oil waste pyrolysis in a packed bed," *Energy & Fuels* 20, 1321-1328.