PROPERTIES OF GAS AND CHAR FROM MICROWAVE PYROLYSIS OF PINE SAWDUST

Xian-Hua Wang, Han-Ping Chen,* Xue-Jun Ding, Hai-Ping Yang, Shi-Hong Zhang, and Ying-Qiang Shen

Pine sawdust pyrolysis was carried out respectively using microwave and conventional electrical heating at different temperatures in order to understand the properties of pyrolytic products from microwave pyrolysis of biomass. Less char material was obtained by microwave pyrolysis compared to conventional heating at the same temperature. While comparing the components of the pyrolytic gases, it was revealed that the microwave pyrolysis gas usually had higher H_2 and CO contents and lower CH_4 and CO_2 contents than those obtained by conventional pyrolysis at the same temperature. The texture analysis results of the microwave pyrolysis chars showed that the chars would melt and the pores would shrink at high temperatures, and hence, the specific surface areas of the chars decreased with increasing temperature. Similarly, the reactivity of the char was remarkably reduced when the microwave pyrolysis temperature exceeded 600°C.

Keywords: Pyrolysis; Microwave heating; Pine sawdust; Gaseous product; Char

*Contact information: State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074 China; *Corresponding author: hp.chen@163.com*

INTRODUCTION

Pyrolysis is an excellent method to realize the clean and efficient conversion of biomass resources, since its gas, liquid, and solid products are all of high value in use. This favorable combination of outcomes has attracted increasing attention (Yaman 2004). Besides the normal heating methods (e.g. electrical heating), plasma (Xiu et al. 2005), and microwave (Krieger-Brockett 1994), heating technologies have also been applied to biomass pyrolysis. Many researchers have already investigated the pyrolysis process and product characteristics of coal (Monsef-Mirzai et al. 1992, 1995), oil shales (Chanaa et al. 1994; El harfi et al. 2000), plastic wastes (Ludlow-Palafox and Chase 2001), and sewage sludge (Dominguez et al. 2008; Menendez et al. 2002) under microwave heating conditions. Among them, some researches focused on microwave pyrolysis of biomass. For example, Yu et al. (2007) investigated the physical and chemical properties of pyrolytic bio-oils produced from microwave pyrolysis of corn stover; Miura et al. (2004) studied the pyrolysis of a cylindrical piece of wood with a diameter of 100mm, finding the specific surface area of the char from microwave pyrolysis was larger than that from the normal method, and the tar contained more levoglucosans; Menendez et al. (2007) and Dominguez et al. (2007) compared the yields and characteristics of coffee hulls pyrolysis products using different heating methods, and the results showed that the gas yield increased and the tar yield decreased in microwave heating. Also the gas contained more H_2 and CO, which may be caused by the char self-gasification reaction during the microwave pyrolysis process. However, microwave pyrolysis, especially biomass microwave pyrolysis, is in the exploration stage.

The basic principle of microwave heating is that the polar molecules contained in the dielectric materials will move quickly and collide intensely with each other in a high-frequency microwave electromagnetic field. As a result, heat is created, and the temperature of the microwave absorbers will go up. Different materials have different microwave absorption abilities; however, biomass has a weak absorption ability. Therefore, the required pyrolysis temperature can’t be reached by merely placing biomass directly in a microwave field. In previous studies, charcoal or metallic oxides were usually added into biomass samples as microwave absorbents (Menendez et al. 2004). Thus, the absorbents were heated by microwave radiation first, and then the biomass samples were heated indirectly by conduction, causing them to decompose. However, when using this microwave heating method, namely premixing biomass with absorber and heating from a low temperature (e.g. room temperature), the heating rate isn’t fast enough. Moreover, the catalytic effects of the microwave field, biomass pyrolysis char, and microwave absorbent can’t be distinguished easily (Dominguez et al. 2005).

Consequently, this paper adopted a unique fast microwave heating method and took pine sawdust as the biomass material. By comparing the results to normal electric furnace heating, the microwave pyrolysis of pine sawdust was investigated, and in order to understand the microwave pyrolysis mechanism in depth, the components of pyrolytic gas and the characteristics of pyrolytic char were studied.

EXPERIMENTAL

Materials

The experimental pine sawdust came from a wood processing factory. The proximate and ultimate analysis results of pine sawdust are given in Table 1. The particle size of pine sawdust was between 0.45 and 0.9mm.

Table 1. Proximate and Ultimate Analysis of Pine Sawdust

Proximate Analysis [a] (%)				Ultimate Analysis [b] (%)					LHV [d] (MJ/kg)
Moisture	Ash	Volatile	Fixed Carbon	C	H	N	S	O [c]	
8.14	0.30	77.28	14.28	49.21	5.22	0.04	0.17	45.36	17.2

[a] Air dry basis [b] Dry ash-free basis [c] Calculated by difference [d] Low heating value

Microwave Pyrolysis

The laboratorial microwave oven was specially designed for biomass drying and pyrolysis, and the electricity parameters were ~380V, 50Hz, and 3900W, with three wave generators to supply the maximal output power of 2000W at a frequency of 2.45GHz. The heated object temperature was monitored by means of two infrared optical pyrometers: one works at 0~300°C, and the other works at 300~1300°C. The device is flexible to control the temperature curves during the microwave heating process. In this study, the temperature was increased from the room temperature to the pyrolysis temperature of 400°C, 500°C, 600°C, 700°C, and 800°C in ten minutes, and then was kept constant. The microwave output power, heating time, and temperature were displayed in real time.

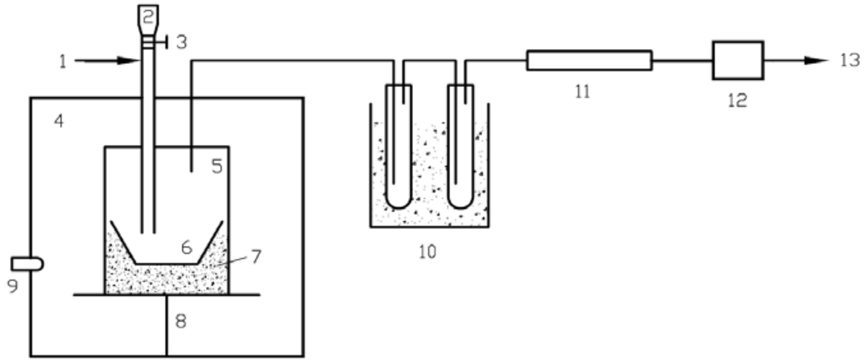


Fig. 1. Schematic diagram of the microwave pyrolysis system
1 carrier gas 2 silo 3 valve 4 microwave oven 5 reactor 6 crucible 7 microwave absorbent 8 bracket 9 infrared pyrometer 10 ice water tank 11 filter 12 infrared gas analyzer 13 gas bag

The microwave pyrolysis system shown in Fig. 1 was composed of three parts: biomass pyrolysis, tar separation, and gas collection. Before the experiment started, the microwave absorbent, the charcoal of 1~2mm particle diameter, was first added into the quartz glass reactor, and in turn the crucible was placed on the charcoal layer. During the experiment, the charcoal was heated by microwave. When the temperature was raised up to the set-point value, the temperature was kept constant for one hour. This procedure could make the temperature field of the reactor stable, and also empty the remnant air and steam released from charcoal, so as to ensure that the following biomass pyrolysis was carried out in an inert atmosphere. In this stage, the carrier gas was high-purity nitrogen, and the flow rate was 100ml•min^{-1}. Then the carrier gas flow rate was decreased to 30ml•min^{-1}, and the valve under the silo was opened to allow 4 grams sawdust fall into the crucible rapidly and begin to be heated and decomposed instantly. Thereby, in this study, pine sawdust pyrolysis occurred at the required temperature from beginning to end, which was much different from the microwave heating methods used by other researchers, i.e. with the biomass heated in step with absorbers from the room temperature to the pyrolysis temperature. In addition, the diameter of the tested pine sawdust was smaller than 1mm, instead of several centimeters or even larger, as in other experiments (Miura et al. 2004). In this way, the microwave-induced pyrolysis rate was very fast, and the pyrolysis process was finished in only about 1~3 minutes, while at least 20 minutes are required when using conventional microwave heating methods (Dominguez et al. 2007). It is worth notice that the char produced from biomass pyrolysis would absorb microwave energy, thus accelerating the pyrolysis process.

Pine sawdust pyrolysis gaseous products were taken out from the reactor by the carrier gas flow. Among them, the condensable components were first quenched and separated in an ice-water bath, and then were absorbed by the filter, which was full of cotton wool and silica gel. The residual non-condensable gas was collected by a gas bag after passing through an infrared gas analyzer (GASMET DX4000, Temet, Finland). The device can detect CO, CO_2, CH_4, etc. online, but can't detect N_2 and H_2. Therefore, it can only be used to judge whether or not the pyrolysis process is over. The gas component in the gas bag was determined by the gas chromatography method.

At the end of the experiment, the microwave oven was closed, and the carrier gas flow rate was increased to 100ml•min^{-1}. After the reactor was cooled to room temperature, the crucible was taken out and weighed to determine the char yield. The filter was washed by acetone, and the solution was analyzed by gas chromatography-mass spectroscopy (GC-MS).

Electric Furnace Pyrolysis

In order to study the influences of microwave heating on pyrolysis, the conventional electric heating pyrolysis of pine sawdust, using a thermobalance (WRT-2C, Beijing), was carried out for comparison. The thermobalance has a function of heating up to a certain temperature before loading the sample. In this way, pine sawdust was heated directly in a high-temperature environment, the same as the microwave pyrolysis method described earlier, and the heating rate could achieve several hundreds K per minute. The pyrolysis temperature was also 400°C, 500°C, 600°C, 700°C, and 800°C, the same as for the microwave pyrolysis.

In every experiment, 50mg of sample was placed in the thermobalance, the carrier gas was high-purity nitrogen, and the flow rate was 30ml/min. The gaseous product was first collected by gas bag and then analyzed by gas chromatography (GC). It could be easily judged whether or not the process was over, according to the weight loss curves of pine sawdust pyrolysis.

Analysis Method of Pyrolysis Products

Analysis method of gas product

The gas product from the pyrolysis of pine sawdust was analyzed using a quadchannels GC (Micro GC 3000, Agilent) with a thermal conductivity detector (TCD), with helium as the carrier gas. The four channels are MolSieve 5A PLOT, plot U, Al_2O_3, and OV-1, respectively. The applied columns were molecular sieve 5A (detecting H_2, CH_4, and CO) at 110°C, plot U (detecting CO_2, C_2H_4, C_2H_6, and C_2H_2) at 100°C, and plot Al_2O_3 (detecting C_3H_6 and C_3H_8) at 140°C. Each gas sample was measured 3 times to get the average.

Analysis method of solid char

The solid char from microwave pyrolysis was mixed with KBr powder to prepare the pellets for Fourier transform infrared spectroscopy (FTIR) analysis (EQUINOX 55, Bruker, Germany) (Yang et al. 2006). An accelerated surface area and porosimetry system (ASAP 2020, Micromeritics, Norcross, GA) was applied to measure the surface areas of the pyrolytic char, and scanning electron microscopic analysis (SEM, Quanta 200, FEI, Hillsboro, OR) was carried out for the char samples. The magnification was 1000×. Elemental analysis of solid char was preformed using a CNHS/O analyzer (EL-2, Vario, Germany).

Furthermore, the activities of the microwave pyrolysis char resulting from different pyrolysis temperatures were compared with each other, using the thermobalance to conduct char-CO_2 gasification experiments (Iniesta et al. 2001). The process in detail was as follows: First the temperature was heated to 1000°C with a heating rate of 15°C•min^{-1} and then kept constant, with 20mg sample and 100ml•min^{-1} N_2 flow rate; and then the carrier gas was switched from N_2 to CO_2 with the same flow rate. Meanwhile, in order to compare the pyrolysis char activity using different heating methods, pine sawdust pyrolysis was heated up from room temperature to 1000°C at the same heating rate using the thermobalance, and the pyrolysis char gasification with CO_2 was also carried out in the thermobalance.

Analysis method of liquid tar

The main components of pyrolytic tar dissolved in acetone were specified using GC-MS (FINNIGAN TRACE MS). The column used in GC-MS was a capillary column DB-1301 (30m×0.25mm i.d., 0.25μm film thickness). Helium was the carrier gas, with a constant flow of 0.5ml/min. The GC initial oven temperature was held at 50°C for 5 minutes and then programmed to increase to 250°C at 10°C/min. The oven temperature was held at 250°C for 20 minutes. The mass spectrometer ion source was at 200°C. The MS was operated in electron ionization mode with a 70eV ionization potential, and an m/z range from 30 to 500 was scanned. The identification of the peaks was based on computer matching of the mass spectra with the National Institute of Standards and Technology (NIST) library.

RESULTS AND DISCUSSION

Char Yield

The char yields of pine sawdust pyrolysis at different temperatures using microwave vs. electric heating methods are given in Fig. 2. It can be seen that with the increase of pyrolysis temperature, the char yields decreased continuously from 400 to 700°C and hardly changed after 700°C. This shows that a high temperature is favorable to the thermal decomposition of biomass under microwave heating, which is similar with normal heating (Demirbas 2004). Comparing the char yields from different heating methods at the same pyrolysis temperature, it can be found that the char yield of microwave pyrolysis was obviously lower than that of conventional pyrolysis. The first reason is that the heating rate of the microwave oven was higher than that of the electric furnace (the thermobalance) in the experimental condition of this study, since the pyrolysis char would absorb microwave energy and promote the pyrolysis process, which resulted in a lower char yield (Sensoz and Can 2002). The second reason is that there was a significant self-gasification reaction between char and CO_2 during microwave pyrolysis (Menendez et al. 2007), which would decrease the char yield.

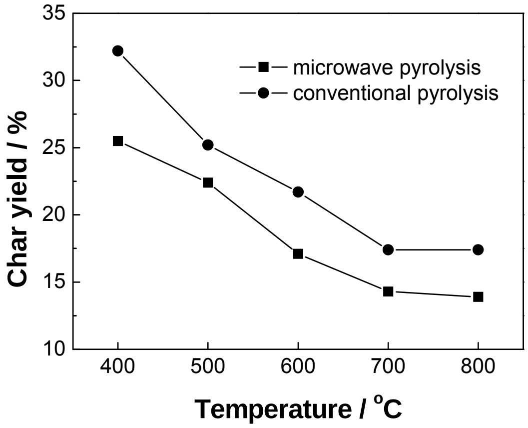


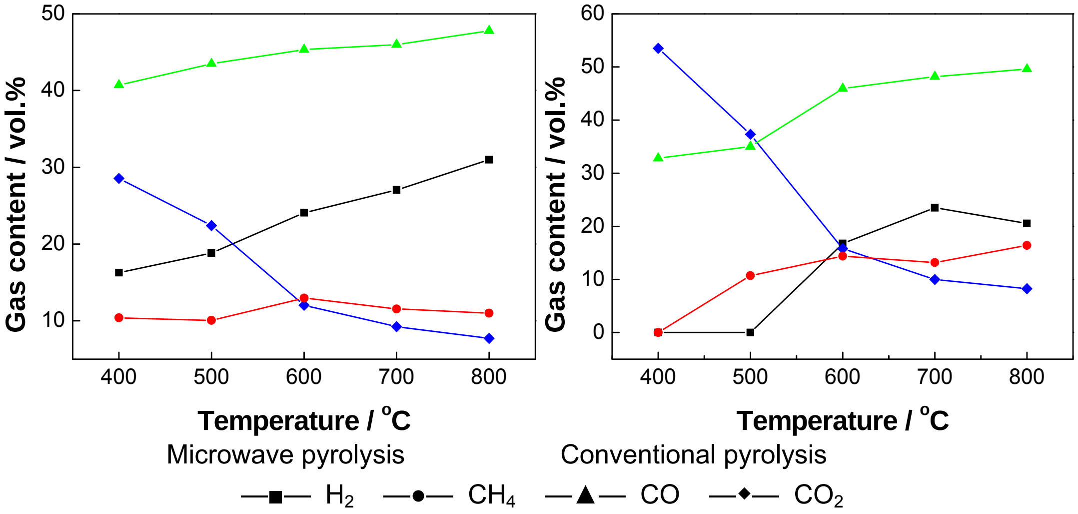
Fig. 2. Variation of the char yields from microwave and conventional pyrolysis with pyrolysis temperature

Gas Component

The non-condensable gas of pine sawdust pyrolysis was comprised of H_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, and so forth. In this study, only H_2, CH_4, CO, and CO_2 were taken into account, since they were the main gas components.

As seen in Fig. 3, with the increase of pyrolysis temperature, the CO_2 concentration decreased gradually, while the CO concentration increased gradually. Comparing the CO_2 concentration resulting from the two heating methods at the same pyrolysis temperature, it can be seen that CO_2 concentration of microwave pyrolysis was always lower than that of conventional pyrolysis, and the lower the temperature, the greater the difference. As we know, the char product from biomass pyrolysis may react with CO_2 and generate CO (reaction 1), and a high temperature will facilitate this reaction.

$$C(s) + CO_2 \leftrightarrow 2CO \quad \Delta H_{298K} = 173\ \text{kJ/mol} \tag{1}$$



Microwave pyrolysis Conventional pyrolysis

Fig. 3. Main gas components obtained by microwave and conventional pyrolysis at different temperatures

Char can absorb microwave energy, so the partial temperature of char particles during microwave pyrolysis should be higher than the surroundings'. As a result, under microwave heating condition, the char self-gasification reaction would occur remarkably, even if the pyrolysis temperature (surroundings temperature) was lower than 600°C, which is consistent with other researchers' conclusion (Dominguez et al. 2007).

In addition, as char's actual temperature was higher than the pyrolysis temperature using microwave heating, so the water-gas reaction (reaction 2) would also take place at lower temperatures. Therefore, as shown in Fig. 3, the H_2 volume concentration among non-condensable gas from microwave pyrolysis at 400°C was 16.3%. Moreover, the H_2 content rose with the increase of pyrolysis temperature, and reached 31% at 800°C. On the other hand, almost no H_2 was generated below 600°C under electric heating condition, and when the temperature was raised above 600°C, less H_2 was generated than microwave pyrolysis at the same temperature. H_2 was also produced from methane gasification (reaction 3) (Menendez et al. 2004). It is shown from Fig. 3 that no CH_4 was detected from conventional pyrolysis only at 400°C, while at other temperatures, CH_4 contents were all higher than in the case of microwave pyrolysis. This indicates gasification reaction of CH_4 becomes significant during microwave pyrolysis.

$$C(s) + H_2O \leftrightarrow CO + H_2 \quad \Delta H_{298K} = 132\ \text{kJ/mol} \tag{2}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_{298K} = 206.1\ \text{kJ/mol} \tag{3}$$

Attention should be paid to the fact that water-gas and CH_4 gasification reactions both produce CO, and the higher temperature will be beneficial to these two reactions, which can partially explain the higher CO content from microwave pyrolysis below 600°C.

As mentioned above, the gas product with higher content H_2 and CO, and lower content CH_4 and CO_2, could be obtained from biomass microwave pyrolysis even at relatively low temperatures, which will favor the generation of H_2 or high-grade liquid fuel production from biomass. At the same time, a lower process temperature is helpful for energy-saving.

Char Characteristics

The IR spectra of char from pine sawdust microwave pyrolysis at 400°C, 500°C, and 600°C are shown in Fig. 4. It can be observed that at 400°C the organic functional groups of char most likely consisted of O-H (3600~3000cm^{-1}), C-H_n (2970~2860cm^{-1}), C=O (1730~1700cm^{-1}, 1560~1510cm^{-1}), C=C (1632cm^{-1}), and C-H (900~700cm^{-1}) (Yang et al. 2007). As the pyrolysis temperature increased from 400 to 500°C, the content of hydroxyl groups in char was near to zero, while the other groups were reduced to different extent. Subsequently, with the temperature raised to 600°C, there was no obvious IR absorption in the spectra of char, which indicated that there was very little organic matter in the char. The IR spectra of char samples from microwave pyrolysis at 700°C and 800°C aren't shown in Fig. 4, because they are very similar with that at 600°C.

Therefore, in this study, the microwave pyrolysis process of pine sawdust mainly occurred below 600°C.

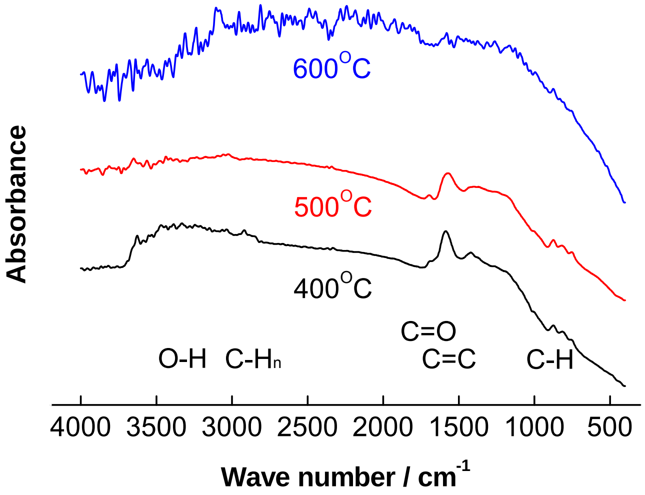


Fig. 4. IR spectra of char from microwave pyrolysis

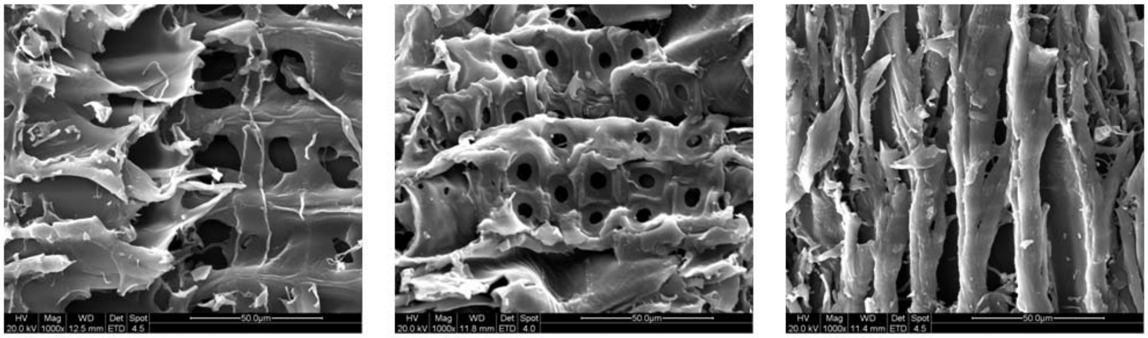
Table 2. Chemical and Textural Characteristics of Char from Microwave Pyrolysis of Pine Sawdust at Different Temperatures (wt%, dry ash free basis)

Temperature / °C	400	500	600	700	800
Volatile	36.45	19.74	16.10	11.23	8.72
Fixed Carbon	63.55	80.26	83.90	88.77	91.28
C	89.35	91.59	92.40	92.85	93.12
H	2.46	2.20	1.39	1.12	0.98
N	0.14	0.20	0.17	0.24	0.23
S	0.34	0.29	0.31	0.27	0.20
O *	7.71	5.72	5.74	5.53	5.47
BET specific surface area / $m^2 \cdot g^{-1}$	0.347	0.276	0.238	0.13	-
* Calculated by difference					

Table 2 gives the volatile and fixed carbon contents of the chars from microwave pyrolysis of pine sawdust at different temperatures, which were determined by the weight-loss of pyrolysis and gasification processes for the chars during the activity analysis tests using the thermobalance. It could be seen that the fixed carbon content increased and the volatile content decreased with increasing temperature. Moreover, the changes of volatile and fixed carbon contents were more obvious between 400 and 500°C, in comparison to higher temperatures', which showed that most volatiles were lost below 500°C. In addition, the ash contents of all chars were less than 2%.

The elemental analysis results of the chars from different temperatures are also shown in Table 2. The carbon content increased and the hydrogen content decreased gradually with the increase of pyrolysis temperature, while the nitrogen and sulfur contents were both very low. The oxygen content varied little when raising pyrolysis temperature above 500°C, which was consistent with the change trend of hydroxyl groups in Fig. 4.

As shown in Table 2, the BET specific surface areas of chars decreased with increasing temperature, and in comparison with the results from other studies, the microwave pyrolysis char had a much smaller specific surface area in this study (Menendez et al. 2007), which was attributed to different materials, smaller particle size, and greater microwave power.



400℃ 500℃ 600℃

Fig. 5. SEM of char from microwave pyrolysis

The SEM images of the chars from microwave pyrolysis at 400°C, 500°C, and 600°C are shown in Figure 5. It could be seen that with increasing pyrolysis temperature, the surface pore sizes of the chars decreased gradually, and they were difficult to distinguish at 600°C. This indicated that chars may melt and deform, while the pores would shrink and even close at a higher temperature. As a result, a smooth morphology of char could be obtained, which was consistent with the change of char BET surface areas in Table 2. The SEM images of the pyrolysis chars of 700 and 800°C were similar with that of 600°C, so weren't shown here.

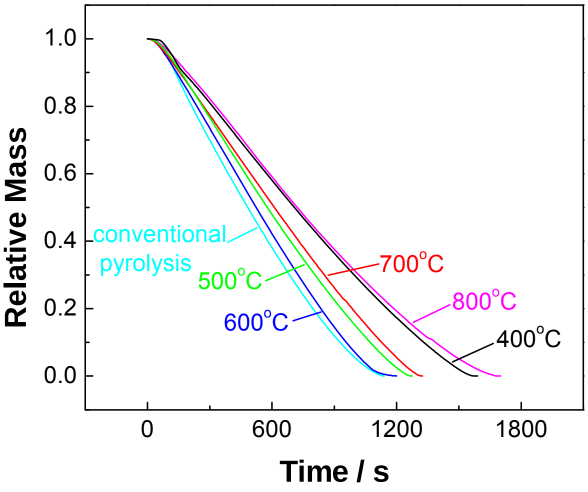


Fig. 6. TG curves for CO_2 gasification of chars under microwave and conventional heating (reactivity test gasification temperature = 1000°C)

The normalized weight-loss of char during CO_2-gasification process is shown in Fig. 6. It was obvious that if the required reaction time was shorter, namely the absolute value of TG curves slope was greater, the char reactivity was higher. As shown in Fig. 6, the reactivity of char increased with the temperature increase from 400 to 600°C, and then decreased when the temperature increased above 600°C. Compared with the electric pyrolysis char, the reactivity of char from microwave pyrolysis was lower.

It has been reported that the reactivity of char is affected by the heating rate (Kumar and Gupta 1994) and char surface area (Guerrero et al. 2005). However, the differences of the char surface area at different pyrolysis temperatures were not obvious (see Table 2), so the heating rate may be the main factor of char reactivity between 400 and 600°C. Because of the microwave heating method using in this study, the higher the pyrolysis temperature, the higher the heating rate; therefore the char reactivity increased with temperature increasing (Chen et al. 1997). On the other hand, at temperatures above 600°C, the surface morphology of char would play an important role in reactivity, thus the reactivity of char decreased due to the surface and pore structure gradually became unfavorable for gaseous diffusion.

In the test of char activity, the volatiles of microwave pyrolysis char would go on releasing at higher temperature (until 1000°C) and N_2 atmosphere before the gasification process, and secondary char was produced. In particular, the char from microwave pyrolysis at 400°C, with 36.45% volatile content (see Table 2), would give rise to the highest ratio of secondary char. The secondary char formed under electrical heating condition should have a similar characteristic with the char entirety produced using electrical heating. But as shown in Figure 6, the reactivity of the char from microwave pyrolysis at 400°C was far lower than that from the thermobalance pyrolysis. This seemed to indicate that the effect of the secondary char on the activity of microwave pyrolysis char could be negligible.

It is notable that the heating rates of conventional pyrolysis in Figs. 6 and 3 were different; the former was 15°C/min, and the latter could reach hundreds of degrees Celsius per minute. Thus the char from the latter should have a higher reactivity. That is, in comparison with microwave pyrolysis char, the electrical pyrolysis char reduced CO_2 to CO more easily once the char gasification reaction temperature was achieved. This can explain why the CO content of electrical heating was higher than that of microwave heating between 600~800°C in Fig. 3.

Tar Component

The total ion chromatogram of tar from pine sawdust microwave pyrolysis at 500°C is plotted in Fig. 7, and many peaks were displayed in the spectra. The results indicate that the compounds in liquid tar were very complex and the typical compounds were mainly alcohols, ketones, furfural, phenol, alkylated phenols, furan derivatives, and guaiacols, etc. (listed in Table 3).

In comparison to the components of liquid product from fluidized-bed pyrolysis of pine sawdust (Wang et al. 2008), most of the compounds were the same, but some volatile compounds, e.g. toluene, 3-penten-2-one, propanoic acid, cyclopentanone, etc., were detected in the microwave pyrolysis tar. This indicated that microwave heating may promote pine sawdust pyrolysis. As mentioned above, the pyrolysis process would go forward at a lower temperature because the pyrolytic chars could absorb microwave energy when using microwave heating method, and a lower temperature was helpful for the inhibition of second reaction of pyrolysis products; hence a high quality liquid product may be obtained by microwave pyrolysis.

Table 3. Tar Components

ID Number	Compound	Formula	Peak area (%)
1	acetic acid	$C_2H_4O_2$	47.36
2	acetol	$C_3H_6O_2$	9.21
3	toluene	C_7H_8	0.07
4	3-penten-2-one	C_5H_8O	0.26
5	propanoic acid	$C_3H_6O_2$	0.31
6	cyclopentanone	C_5H_8O	0.28
7	isobutylalcohol	$C_4H_{10}O$	0.80
8	propanal	C_3H_6O	0.18
9	1,2-dimethyl-benzene	C_8H_{10}	0.39
10	furfural	$C_5H_4O_2$	6.39
11	2-butanone	C_4H_8O	0.22
12	acetolacetate	$C_5H_8O_3$	1.78
13	2-methyl-2-cyclopentenone	C_6H_8O	0.91
14	2-furylmethylketone	$C_6H_6O_2$	0.39
15	2-hydroxy-2-cyclopentenone	$C_5H_6O_2$	0.08
16	butyrolactone	$C_4H_6O_2$	0.57
17	2(3H)-furanone	$C_4H_4O_2$	0.19
18	5-methyl-2-furfural	$C_6H_6O_2$	0.69
19	3-methyl-2-cyclopentenone	C_6H_8O	0.78
20	3-methyl-2(5H)-furanone	$C_5H_6O_2$	0.15
21	2,3-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	0.38
22	2-hydroxy-3-methyl-2-cyclopenten-1-one	$C_6H_8O_2$	1.50
23	phenol	C_6H_60	1.63
24	2-methoxy-phenol	$C_7H_8O_2$	3.20
25	2-methyl-phenol	C_7H_8O	1.15
26	3-ethyl-2-hydroxy-2-cyclopenten-1-one	$C_7H_{10}O_2$	0.39
27	dimethyl-phenol	$C_8H_{10}O$	2.75
28	4-methyl-phenol	C_7H_8O	3.68
29	2-methoxy-4-methyl-phenol	$C_8H_{10}O_2$	4.71
30	4-ethyl-phenol	$C_8H_{10}O$	0.12
31	4-ethyl-2-methoxy-phenol	$C_9H_{12}O_2$	2.21
32	2-methoxy-4-vinylphenol	$C_9H_{10}O_2$	0.91
33	eugenol	$C_{10}H_{12}O_2$	0.90
34	2-methoxy-4-propyl-phenol	$C_{10}H_{14}O_2$	0.50
35	isoeugenol (cis+trans)	$C_{10}H_{12}O_2$	3.25
36	vanillin	$C_8H_8O_3$	0.79
37	1-(4-hydroxy-3-methoxyphenyl)-ethanone	$C_9H_{10}O_3$	0.37
38	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	$C_{10}H_{12}O_3$	0.55

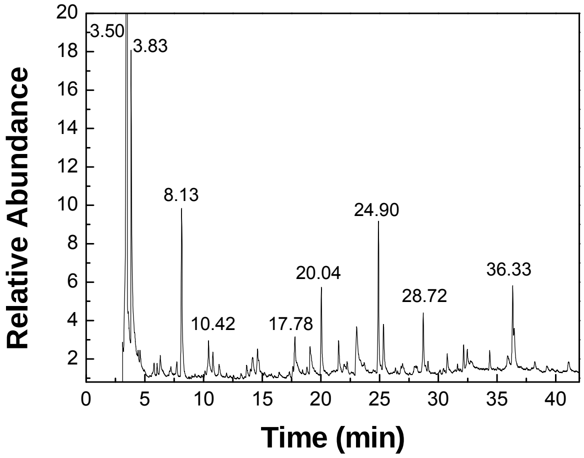


Fig. 7. Total ion chromatogram of tar from pine sawdust microwave pyrolysis at 500°C

CONCLUSIONS

1. The biomass pyrolysis and char gasification reactions occurred at relatively low temperatures under microwave conditions, as the pyrolytic chars could absorb microwave energy. Thereby the microwave pyrolysis gas had higher H_2 and CO contents than those obtained by conventional pyrolysis at lower temperatures (400~500°C).
2. The microwave pyrolysis of pine sawdust mainly happened below 600°C, while the volatiles were mostly released below 500°C.
3. With increasing temperatures, the activity of pyrolytic char increased in the temperature range of 400~600°C, and decreased in the temperature range of 600~800°C. However, the reactivity of the char from microwave pyrolysis was lower than that from conventional pyrolysis.

ACKNOWLEDGMENTS

The authors are grateful for the support of the National Basic Research Program of China (973 Program, Grant No. 2007CB210202) and the National Natural Science Foundation of China (Grant No. 50721005 and 50676037).

This article was presented at the First International Conference on Biomass Energy Technologies (ICBT 2008), which was held at the Baiyun International Convention Center, Guangzhou, China, and hosted by Chinese Renewable Energy Society and its affiliate Chinese Bioenergy Association during December 3-5, 2008. Sponsors were the National Development and Reform Commission (NDRC), the Ministry of Science and Technology of the People's Republic of China (MOST), and the Ministry of Agriculture of the People's Republic of China (MOA) and Chinese Academy of Sciences (CAS). Selected articles from the conference were submitted to *BioResources* and subjected to the standard peer-review process.

REFERENCES CITED

Chanaa, M. B., Lallemant, M., and Mokhlisse, A. (1994). "Pyrolysis of Timahdit, Morocco, oil shales under microwave field," *Fuel* 73(10), 1643-1649.

Chen, G. X., Yu, Q. Z., and Sjöström, K. (1997). "Reactivity of char from pyrolysis of birch wood," *Journal of Analytical and Applied Pyrolysis* 40-41, 491-499.

Demirbas, A. (2004). "Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues," *Journal of Analytical and Applied Pyrolysis* 72(2), 243-248.

Dominguez, A., Fernandez, Y., Fidalgo, B., Pis, J. J., and Menendez, J. A. (2008). "Bio-syngas production with low concentrations of CO_2 and CH_4 from microwave-induced pyrolysis of wet and dried sewage sludge," *Chemosphere* 70(3), 397-403.

Dominguez, A., Menendez, J. A., Fernandez, Y., Pis, J. J., Nabais, J. M. V., Carrott, P. J. M., and Carrott, M. M. L. R. (2007). "Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas," *Journal of Analytical and Applied Pyrolysis* 79(1-2), 128-135.

Dominguez, A., Menendez, J. A., Inguanzo, M., and Pis, J. J. (2005). "Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge," *Fuel Processing Technology* 86(9), 1007-1020.

El harfi, K., Mokhlisse, A., Chanaa, M. B., and Outzourhit, A. (2000). "Pyrolysis of the Moroccan (Tarfaya) oil shales under microwave irradiation," *Fuel* 79(7), 733-742.

Guerrero, A., Ruiz, M. P., Alzueta, M. U., Bilbao, R., and Millera, A. (2005). "Pyrolysis of eucalyptus at different heating rates: Studies of char characterization and oxidative reactivity," *Journal of Analytical and Applied Pyrolysis* 74(1-2), 307-314.

Iniesta, E., Sanchez, F., Garcia, A. N., and Marcilla, A. (2001). "Yields and CO_2 reactivity of chars from almond shells obtained by a two heating step carbonisation process. Effect of different chemical pre-treatments and ash content," *Journal of Analytical and Applied Pyrolysis* 58-59, 983-994.

Krieger-Brockett, B. (1994). "Microwave pyrolysis of biomass," *Research on Chemical Intermediates* 20(1), 39-49.

Kumar, M., and Gupta, R. C. (1994). "Influence of carbonization conditions and wood species on carbon dioxide reactivity of resultant wood char powder," *Fuel Processing Technology* 38(3), 223-233.

Ludlow-Palafox, C., and Chase, H. A. (2001). "Microwave-induced pyrolysis of plastic wastes," *Industrial and Engineering Chemistry Research* 40(22), 4749-4756.

Menendez, J. A., Dominguez, A., Fernandez, Y., and Pis, J. J. (2007). "Evidence of self-gasification during the microwave-induced pyrolysis of coffee hulls," *Energy & Fuels* 21(1), 373-378.

Menendez, J. A., Dominguez, A., Inguanzo, M., and Pis, J. J. (2004). "Microwave pyrolysis of sewage sludge: Analysis of the gas fraction," *Journal of Analytical and Applied Pyrolysis* 71(2), 657-667.

Menendez, J. A., Inguanzo, M., and Pis, J. J. (2002). "Microwave-induced pyrolysis of sewage sludge," *Water Research* 36(13), 3261-3264.

Miura, M., Kaga, H., Sakurai, A., Kakuchi, T., and Takahashi, K. (2004). "Rapid pyrolysis of wood block by microwave heating," *Journal of Analytical and Applied Pyrolysis* 71(1), 187-199.

Monsef-Mirzai, P., Ravindran, M., McWhinnie, W. R., and Burchill, P. (1992). "The use of microwave heating for the pyrolysis of coal via inorganic receptors of microwave energy," *Fuel* 71(6), 716-717.

Monsef-Mirzai, P., Ravindran, M., McWhinnie, W. R., and Burchill, P. (1995). "Rapid microwave pyrolysis of coal - Methodology and examination of the residual and volatile phases," *Fuel* 74(1), 20-27.

Sensoz, S., and Can, M. (2002). "Pyrolysis of pine (Pinus Brutia Ten.) chips: 1. Effect of pyrolysis temperature and heating rate on the product yields," *Energy Sources* 24(4), 347-355.

Wang, X. H., Chen, H. P., Luo, K., Shao, J., and Yang, H. P. (2008). "The influence of microwave drying on biomass pyrolysis," *Energy & Fuels* 22(1), 67-74.

Xiu, S. N., Yi, W. M., and Li, B. M. (2005). "Flash pyrolysis of agricultural residues using a plasma heated laminar entrained flow reactor," *Biomass & Bioenergy* 29(2), 135-141.

Yaman, S. (2004). "Pyrolysis of biomass to produce fuels and chemical feedstocks," *Energy Conversion and Management* 45(5), 651-671.

Yang, H. P., Yan, R., Chen, H. P., Lee, D. H., Liang, D. T., and Zheng, C. G. (2006). "Mechanism of palm oil waste pyrolysis in a packed bed," *Energy & Fuels* 20(3), 1321-1328.

Yang, H. P., Yan, R., Chen, H. P., Lee, D. H., and Zheng, C. G. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86(12-13), 1781-1788.

Yu, F., Deng, S. B., Chen, P., Liu, Y. H., Wan, Y. Q., Olson, A., Kittelson, D., and Ruan, R. (2007). "Physical and chemical properties of bio-oils from microwave pyrolysis of corn stover," *Applied Biochemistry and Biotechnology* 137-140(1-12), 957-970.

Article submitted: Feb. 12, 2009; Peer review completed: May 9, 2009; Revised version received and accepted: May 25, 2009; Published: May 26, 2009.