Energy & Fuels **2008,** *22,* 67–74

The Influence of Microwave Drying on Biomass Pyrolysis[†]

Xianhua Wang, Hanping Chen,* Kai Luo, Jingai Shao, and Haiping Yang

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology,
Wuhan 430074, People's Republic of China

Received May 28, 2007. Revised Manuscript Received August 14, 2007

Microwave drying is a rapid, high-effect, and economical method to decrease the moisture content of biomass materials to produce higher quantity and better quality bio-oil during the fast pyrolysis process. In this paper, the influence of microwave drying on the behavior of biomass pyrolysis was investigated in a bench-scale fluidized-bed reactor in comparison to drying in an electrical oven at 105 °C. Three types of biomass were studied, comprising pine wood sawdust, peanut shell, and maize stalk. First, biomass samples were dried using a microwave oven at four different power levels, i.e., 200, 400, 600, and 800 W. It was found that the power capacity of the microwave showed great influence on the moisture removing property. The dehydration was very fast, and it was finished in 6 min at 600 W; however, it was quite slow with electrical oven drying (about 40 min). The specific surface area of biomass was found, being increased greatly after microwave drying. Then, the pyrolysis of biomass samples dried by two different methods was carried out in the bench-scale reactor at 500 °C. Samples dried at 600 W in 6 min were selected as representative for microwave drying. The yields and properties of pyrolysis products, including liquid oil, solid char, and uncondensable gas, were determined and analyzed. It was observed that the yields of solid char and liquid oil increased, while the yield of the gas product decreased by microwave oven drying compared to conventional electrical oven drying. A higher CO_2 concentration in gas but a lower organic compound content in char was achieved using microwave drying. At the same time, the viscosity and heating value increased because the water content decreased and the average molecular weight increased in the bio-oil from the samples dried by the microwave. These results were all caused by the fact that microwave drying suppressed the second reaction of volatiles during biomass pyrolysis. A higher heating value and lower water content are beneficial to bio-oil use as a fuel, and more primary pyrolysis products make bio-oil produce high add-value chemical materials. Thus, microwave drying is a technically and economically feasible pretreatment method for biomass fast pyrolysis.

1. Introduction

Biomass pyrolysis technology offers a method to produce gas, liquid, and char synchronously. A maximum liquid production can be obtained from the pyrolysis at a medium temperature, high heating rate, and short gas residence time.[1] Pyrolysis liquid, also named bio-oil, can be used both as an energy source and a feedstock for chemical production.[2] Bio-oil is convenient to store and transport, with the potential to be used as a fossil oil substitute. In comparison to conventional fossil oil, bio-oil has a distinct advantage of being carbon dioxide neutral. Consequently, in the past 30 years, a great amount of research on the fast pyrolysis of various types of biomass has been carried out and different pyrolysis technologies have been developed and applied.[3]

At present, forestry and agricultural wastes are the main raw materials to produce bio-oil in commercial demonstration plants, which are usually with high water content. It is obvious that the moisture of the biomass will be transferred into bio-oil during the pyrolysis process. In addition, when the water content of bio-oil is over 30%, phase separation will occur with great probability, which is a definite handicap for fuel applications.[4] Therefore, it is necessary to dry biomass materials to reduce the water content to less than 10% before pyrolysis.

Microwave drying is capable of a much higher drying rate and energy efficiency than conventional heated air drying and is widely applied to treat various kinds of raw materials and products, including food, vegetables, fruits, wood, etc.[5–10] However, it has not been reported for using this technique for raw material drying of biomass pyrolysis. In addition, the physicochemical characteristics of biomass, which are the most critical parameters determining the behavior of biomass pyrolysis, varied to a certain extent after microwave treatment.[9,11] It means that, taking into account the microwave drying technique, the pyrolysis products, especially bio-oil, may be

---

[†] Presented at the International Conference on Bioenergy Outlook 2007, Singapore, April 26–27, 2007.

* To whom correspondence should be addressed. Telephone: 86-27-87542417-8305. Fax: 86-27-87545526. E-mail: hp.chen@163.com.

(1) Bridgwater, A. V.; Meier, D.; Radlein, D. *Org. Geochem.* **1999**, *30*, 1479.

(2) Bridgwater, A. V. *Chem. Eng. J.* **2003**, *91*, 87.

(3) Bridgwater, A. V.; Peacocke, G. V. C. *Renewable Sustainable Energy Rev.* **2000**, *4*, 1.

(4) Oasmaa, A.; Czernik, S. *Energy Fuels* **1999**, *13*, 914.

(5) Wang, J.; Wang, J. S.; Yu, Y. *Int. J. Food Sci. Technol.* **2007**, *42*, 148.

(6) Ozkan, I. A.; Akbudak, B.; Akbudak, N. *J. Food Eng.* **2007**, *78*, 577.

(7) Clary, C. D.; Mejia-Meza, E.; Wang, S.; Petrucci, V. E. *J. Food Sci.* **2007**, *72*, E23.

(8) Zhang, M.; Tang, J.; Mujumdar, A. S.; Wang, S. *Trends Food Sci. Technol.* **2006**, *17*, 524.

(9) Kaasova, J.; Kadlec, P.; Bubnik, Z.; Hubackova, B.; Prihoda, J. *Chem. Zvesti* **2002**, *56*, 32.

(10) Antti, A. L. *Holz Roh- Werkst.* **1995**, *53*, 333.

(11) Walde, S. G.; Balaswamy, K.; Velu, V.; Rao, D. G. *J. Food Eng.* **2002**, *55*, 271.

10.1021/ef700300m CCC: $40.75

Table 1. Properties of Biomass Samples

	pine wood sawdust	peanut shell	maize stalk
	Ultimate Analysis (daf, wt %)		
C	49.21	46.15	42.47
H	5.22	3.07	3.27
N	0.04	1.27	1.18
S	0.17	0.08	0.26
O[a]	45.36	49.43	52.82
	Proximate Analysis (ad, wt %)		
moisture	8.14	8.84	8.52
volatile matter	77.28	68.48	68.09
ash	0.30	4.69	7.09
fixed carbon	14.28	17.99	16.30
LHV (MJ/kg)	17.2	16.1	15.5
	Ash Components (wt %)		
K_2O	10.45	16.84	18.98
Na_2O	1.5	1.71	0.8
Al_2O_3	4.97	6.78	0.44
Fe_2O_3	1.21	4.66	0.29
CaO	17.54	10.78	7.54
MgO	4.91	6.32	6.93
TiO_2	0.77	1.35	0.17
SiO_2	52.66	49.61	36.18

[a] Calculated by difference.

different from that obtained through the conventional drying method and pyrolysis process.

In this paper, three kinds of biomass wastes, pine wood sawdust, peanut shell, and maize stalk, were selected. The drying effect of a laboratorial microwave oven (MO) and an electrical oven (EO) on biomass samples was studied. Especially, the influence of microwave drying on the pyrolysis process and pyrolysis products, including gas, char, and bio-oil, was investigated.

2. Sample and Experimental Method

2.1. Sample Materials. As the representative forestry wastes and agricultural wastes in China, pine wood sawdust, peanut shell, and maize stalk, were involved in this study. The ultimate and proximate analyses are listed in Table 1. It can be observed that pine wood sawdust contained higher volatile content, while peanut shell and maize stalk contained more ash. The inorganic matters were measured using X-ray fluorescence spectroscopy (XRF, EAGLE III, Mahwah, NJ), and the results are shown in Table 1 in oxides. It can be found that K, Ca, and Si compounds accounted for the main part of the ash matter. The particle sizes of all samples studied were in the range of 0.5–1.0 mm.

2.2. Experimental Setup and Method. *2.2.1. Drying Equipment and Method.* The laboratorial microwave oven is specially designed for biomass drying and pyrolysis, and the electricity parameter is ~380 V, 50 Hz, and 3900 W, with three wave generators to supply the maximal output power of 2000 W at a frequency of 2.45 GHz. It is flexible to adjust the power supply and heating time. The heating area is 450 × 400 × 450 mm and consisted of a rotating plastic plate to carry the sample at the base of the oven. The heated object temperature is monitored by means of two infrared optical pyrometers: one works at 0–300 °C, and the other works at 300–1300 °C.

The drying experiments were carried out at four different power levels, 200, 400, 600, and 800 W, and other conditions were kept constant. To test the repeatability, each trial was tested 3 times, the average value was obtained, and the drying parameters were determined. During the drying process, the crucible was removed from the oven periodically, and the moisture loss was determined by weighing the crucible using a digital balance with a sensitivity of ±0.01 g. The weighing process was completed in 10 s. In addition, the drying trial was carried out in an EO at 105 °C as the reference.

2.2.2. Bench-Scale Pyrolysis Plant. The pyrolysis of dried biomass samples was performed in a bench-scale fluidized-bed reactor shown in Figure 1. The system consists essentially of a stainless steel tube (inner diameter of 35 mm and height of 1700 mm, with an air freeboard of 200 mm) with a continuous feeding system, a gas cleaning section containing a cyclone solid collector and a quartz wool filter, and a cooling system for the separation of water and condensable organic vapors (bio-oil), as well as various gas measurement devices.

The reactor is heated indirectly by two independently controlled electric furnaces. The temperature and pressure of the pyrolysis zone were measured using three thermocouples and three pressure sensors. The pyrolysis temperature of the fluidized bed could be fixed in a certain range, which was 500 ± 20 °C in the trials. The apparent pyrolysis vapor residence time in the free volume of the reactor was less than 1 s. Biomass was fed into a feed hopper and conveyed by a screw feeder into a feeder tube, where high-velocity nitrogen gas entrained the biomass feed and carried it into the fluidized-bed reactor. The feeding rate is ~2 kg/h, with a screw feeder combined with pneumatic conveying. The fluidizing medium was silica sand, with the particle size of 0.3–0.45 mm, and the carrier gas was pure nitrogen. The fluxes of carrying and fluidizing gases were both controlled by gas mass flowmeters. The pyrolysis vapors releasing from the reactor passed through a cyclone separator to separate the char, and an added hot filter coated with aluminum silicate fiber was used to capture the fine char particles escaping from the cyclone. The clean pyrolysis gas condensed in an ice-water condenser operating at about 0 °C. The uncondensable gas components were collected for further analysis.

After each experiment, the residues collected from the reactor and the separators were combined and recorded as solid char yield after subtracting the weight of the bed material. The weight of the liquid oil exhausted from the condenser and the increased weight of connection tubes and cotton filter were recorded as the liquid yield. The total gas yield (wt %) could thus be calculated by

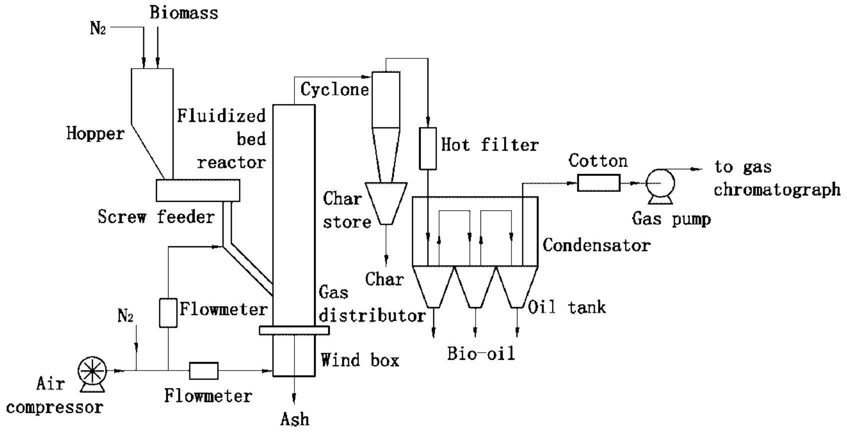
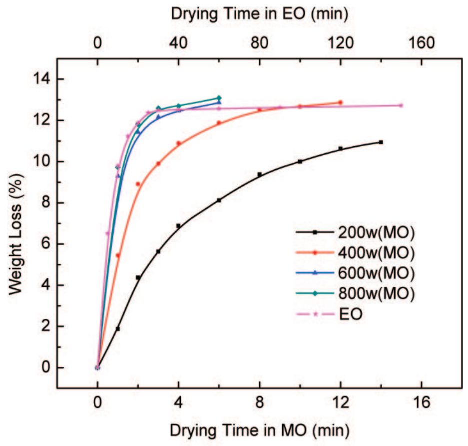
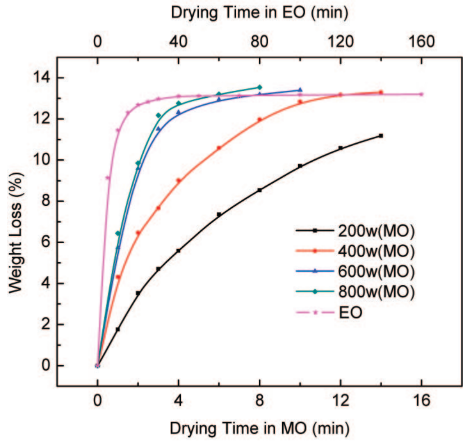


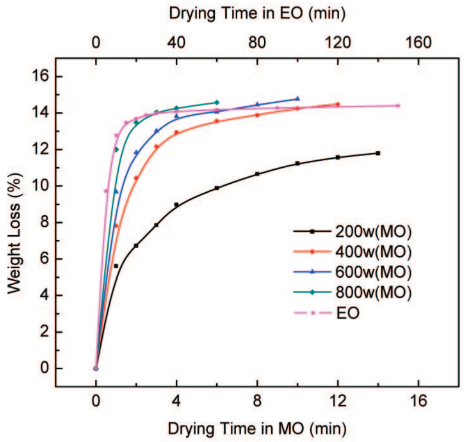
Figure 1. Schematic diagram of a bench-scale plant.



Pine Wood Sawdust



Peanut Shell



Maize Stalk

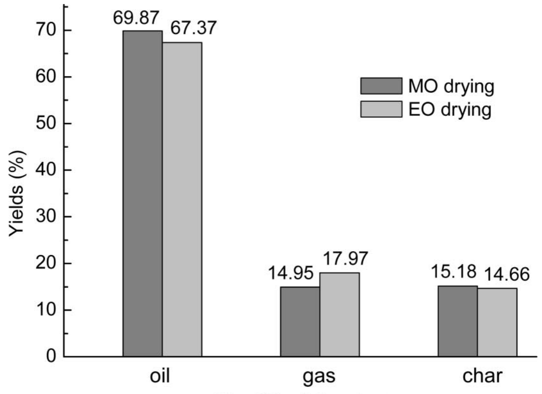
Figure 2. Drying curves of biomass samples in a MO and an EO.

Table 2. BET Surface Areas of Samples (m^2/g)

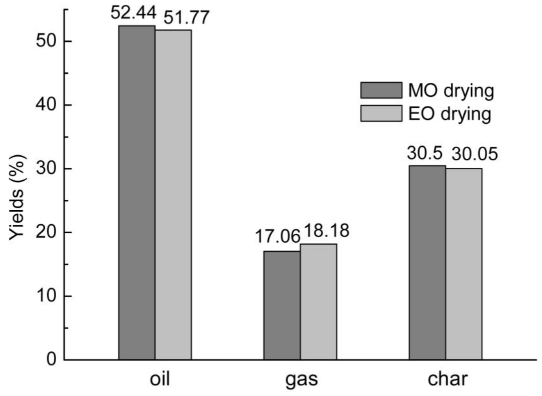
	MO drying	EO drying
pine wood sawdust	0.8123	0.0883
peanut shell	0.9454	0.1623
maize stalk	1.8435	0.5188

difference based on the mass balance of the fed biomass in a specific time period at a constant feeding rate.

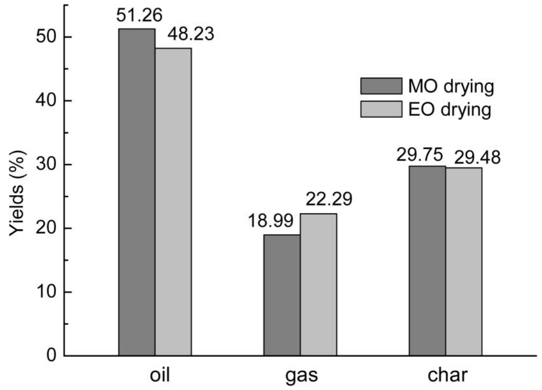
The stable operation time of every trial was not under 1 h to ensure the representative products. At the same time, the pyrolysis experiment of pine wood sawdust dried by the electrical oven had been carried out twice and repetitive results were obtained. This indicated the repeatability of experiments was good in this study.



Pine Wood Sawdust



Peanut Shell



Maize Stalk

Figure 3. Yields of pyrolysis products from biomass dried in a MO and an EO.

2.2.3. Analysis Method of Pyrolysis Products.

Analysis Method of the Gas Product. The gas product from the fast pyrolysis of biomass materials was analyzed using a quad-channels 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. During the stable operation period, the uncondensable gas was sampled every 10 min and each gas sample was measured 3 times to get the average.

Analysis Method of Solid Char. An accelerated surface area and porosimetry system (ASAP 2020, Micromeritics, Norcross, GA) was applied to measure the surface areas of the dried raw samples and the pyrolysis char. Liquid N_2 was applied for isothermal adsorption at the temperature of 77 K.

The solid char from pyrolysis was mixed with KBr powder to prepare the pellets for Fourier transform infrared spectroscopy (FTIR) analysis (EQUINOX 55, Bruker, Germany). The total weight

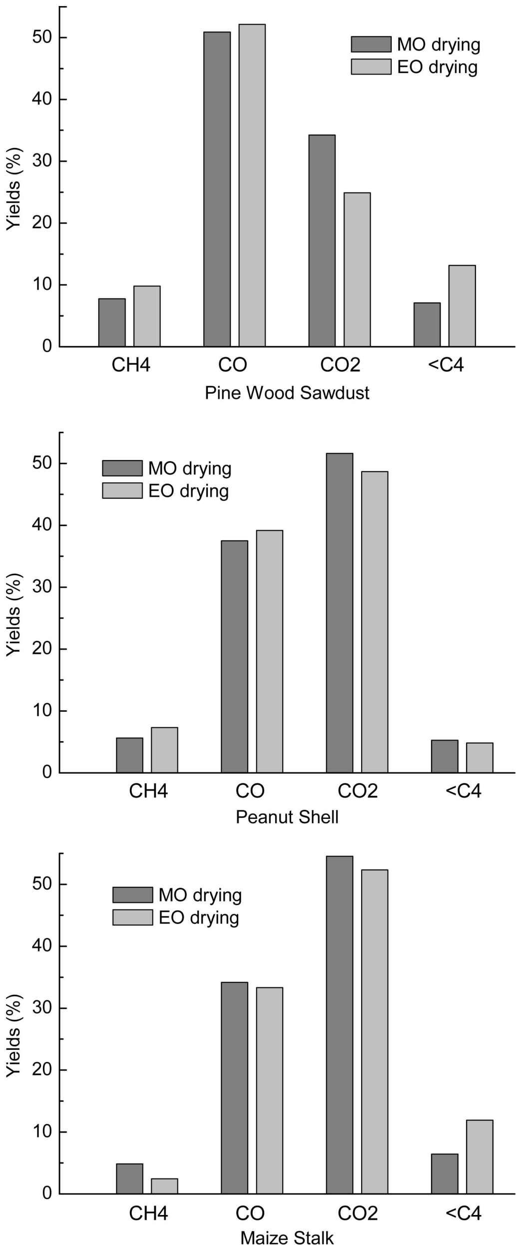


Figure 4. Gas components.

of the pellet was 100 mg, and the ratio of the sample to KBr powder was kept at about 1:99. The mixture of char and KBr powder was dried in the electrical oven at 105 °C for overnight. The pellet was made under the same conditions, including the sample weight, size of the pellet, pelleting time, and pressure.[12] Prior to each measurement, the instrument was run to establish the background, for which KBr was taken as the reference. The background was then automatically subtracted from the sample spectrum.

Scanning electron microscopic analysis (SEM, Quanta 200, FEI, Hillsboro, OR) was carried out for the char samples from the pyrolysis of biomass dried with different methods. The magnification is 1000×.

Analysis of Liquid Oil. Water content, pH value, viscosity, and heat value are the main properties affecting the oil quality. To catch the physical characteristics in detail, water content was measured with Karl-Fischer titration (TitroLine KF-10, SCHOTT, Germany), and the pH value was detected by a pH meter (Delta 320, Mettler-Toledo, Columbus, OH). Viscosity was analyzed with a rotary viscosimeter (NDJ-5S, Shanghai, China) at 40 °C, and a low heating value (LHV) was detected using a bomb calorimeter (6300, Parr, Moline, IL). Element analysis of liquid oil was preformed using a CNHS/O analyzer (EL-2, Vario).

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

Before all tests, bio-oil was sufficiently stirred and then sampled. Double tests were carried out, and the average values were provided at last.

3. Results and Discussion

3.1. Property of Microwave Drying. Weight loss–time diagram of biomass samples along the drying period is given in Figure 2. When the microwave heating mechanism is taken into account, the water molecule is very polar and absorbs microwave energy more readily than other components. Therefore, during the microwave drying process, the weight loss of the sample was nearly equal to the water loss until all moisture was removed. As shown in Figure 2, a reduction in the drying time occurred with the increase of the microwave power level. When dried with an EO, the sample weight would be stable at the end of evaporation. However, when dried in a MO, the weight loss process of the sample did not stop as soon as drying finished because the sample temperature would increase to cause pyrolysis or the combustion reaction to occur without endothermic evaporation of water. Although the end point of the microwave drying process was not usually distinguishable, it was showed in Figure 2 that the horizontal asymptote of the drying curve was very close to that of an EO when the microwave power was 400 W. This means that the water content of the sample can be determined using a MO at an appropriate power level (e.g., 400 W). It is a fast and simple method compared to the traditional method.

The drying time achieving the same water loss rate using a MO with the power levels more than 600 W was almost 10 times shorter than that in an EO at 105 °C. However, when the microwave power was lower than 400 W (e.g., 200 W, shown in Figure 2), the time was too long to achieve the fast drying aim. On the other hand, when the microwave power reached 800 W, the samples were easy to be over heated, and thus, some chemical reactions were likely to take place. To dry biomass samples using a MO as fast as possible and without any destroying, the samples dried at 600 W for 6 min were chosen for the following study.

As mentioned above, the drying rate of the sample in a MO with 600 W was almost 10 times faster than that in an EO. In other words, a large amount of moisture was released from the inside of the sample in a very short time, which would create more inner paths, and as a result, the sample dried using MO should have more surface areas than those using the conventional method. To prove this, the surface areas of dried samples using different methods (MO drying at 600 W for 6 min and EO drying at 105 °C for 2 h) were measured using ASAP 2020, and the results are listed in Table 2. It can be observed that the surface areas of biomass dried with a MO were much larger than

---

[12] Yang, H. P.; Yan, R.; Chen, H. P.; Lee, D. H.; Liang, D. T.; Zheng, C. G. *Energy Fuels* **2006**, *20*, 1321.

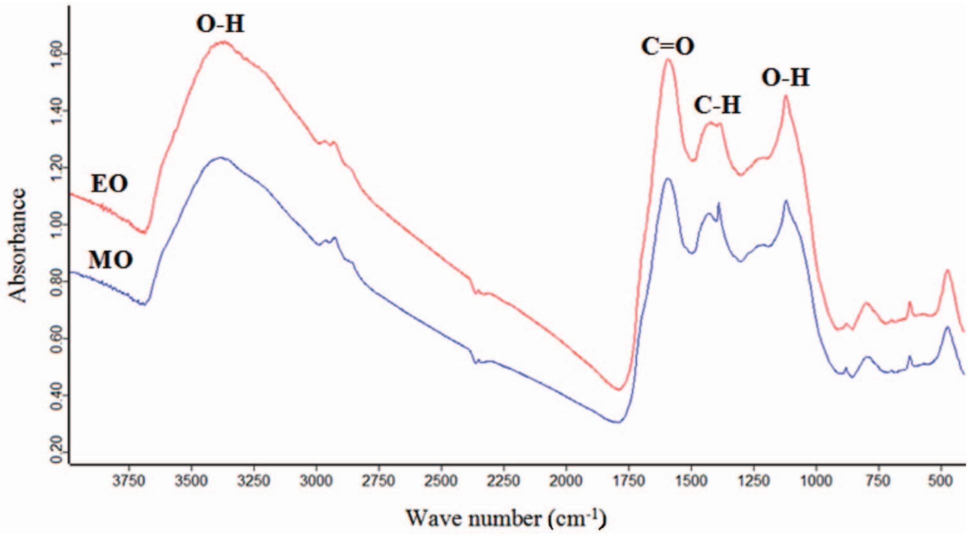


Figure 5. FTIR spectra of the char from maize stalk pyrolysis.

Table 3. Surface Area and Pore Properties of Pyrolysis Char

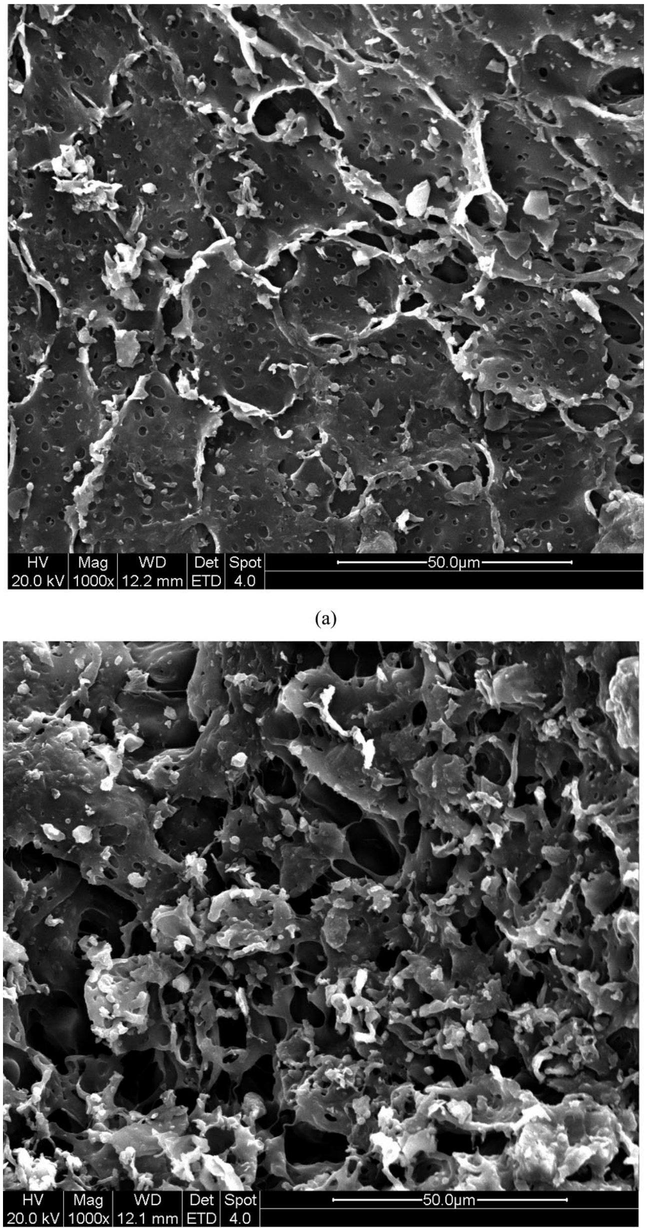
	BET surface area (m^2/g)		pore volume (single-point method) (cm^3/g)		average pore width ($\times 10^{-10}$ m)	
	MO	EO	MO	EO	MO	EO
pine char	1.1190	0.7084	0.001 716	0.001 248	61.3436	70.4465
peanut char	1.4804	1.6391	0.001 493	0.001 832	40.3389	44.7041
maize char	2.2245	2.1613	0.003 786	0.005 177	68.0763	95.8106

those of an EO drying for all of the samples. It indicated that the moisture was vaporized with a violent behavior during the microwave drying process; thus, more new paths from inside to outside were broken, which would be helpful for the quick release of volatiles in biomass during the pyrolysis process.

3.2. Effect of Microwave Drying on Biomass Pyrolysis. The pyrolysis products of dried biomass are presented in Figure 3. The yields of bio-oil, gas, and solid char of dried samples in a MO and an EO respectively are compared for three kinds of biomass. It was found that the yield of bio-oil and char increased, while the yield of gas decreased accordingly with microwave drying. It might be attributed to the decrease of the secondary reaction of volatiles. As pointed out, the metal components, which contained in the biomass concentrate into char largely during the pyrolysis process, have a great role on secondary cracking,[13] which would decrease the bio-oil yield, whereas the gas yield was increased. The biomass dried by a MO has a larger surface area and more inner paths. Therefore, the volatiles can quick leave the char layer; hence, the secondary reaction was partially prohibited. Similarly, the gas–solid reactions between char and vapors would reduce char output, and the char yield decreased when the biomass was dried in an EO. However, the extent was slight because char was also the product of the secondary reaction.

In comparison to three different materials, it can be observed that the yield of bio-oil was lower for agricultural wastes than for the pyrolysis of wood, largely because the organic content is lower but the ash content is higher in agricultural wastes than in wood. It is consistent with previous literature.[14]

3.3. Effect of Microwave Drying on Gas Components. The product gas from the pyrolysis of biomass was mainly comprised



(a)

(b)

Figure 6. SEM images of pine pyrolysis char.

---

[13] Gray, M. R.; Corcoran, W. H.; Gavalas, G. R. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 646.

[14] Lee, K. H.; Kang, B. S.; Park, Y. K.; Kim, J. S. *Energy Fuels* **2005**, *19*, 2179.

Table 4. Properties of Bio-oil

sample drying method	pine wood sawdust		peanut shell		maize stalk	
	MO	EO	MO	EO	MO	EO
ultimate analysis (%)[a]						
C	48.756	49.669	46.198	50.599	39.799	50.588
H	6.842	7.365	7.432	7.005	7.730	7.367
O[b]	43.479	42.262	44.955	40.468	50.985	40.438
N	0.923	0.561	1.415	1.751	1.284	1.599
S	0	0.143	0	0.177	0.202	0.008
H/C[c]	1.684	1.779	1.931	1.661	2.331	1.748
water (%)	26.2	26.8	34.0	36.3	34.5	44.2
density (kg/m^3)	1145	1165	1101	1111	1088	1066
pH	2.5	2.5	2.6	2.9	2.7	2.9
viscosity (mPa s, 40 °C)	15.2	15.1	12.6	11.3	9.8	<9
LHV (MJ/kg)	14.97	14.72	13.88	13.01	11.45	10.14

[a] Dehydrate base. [b] Calculated by difference. [c] Mole ratio.

of CH_4, CO, CO_2, and some other hydrocarbons (<C4), such as C_2H_4, C_2H_6, C_2H_2, C_3H_6, and C_3H_8. The hydrogen content was <1% in each experiment and not shown here, because the pyrolysis temperature was low (~500 °C) and the residence time was short (~1 s). It was difficult for H_2 evolving.[12] The gas product distribution is shown in Figure 4. It can be observed that EO drying lead to a low yield of CO_2, which results mainly from the secondary cracking of volatiles, followed by the increase of CO or hydrocarbons.[14] The metal elements contained in char might enhance the secondary reaction; hence, the shifting of solid char might be increased and form more gas products. Nevertheless, the gas products of the secondary cracking of volatiles were not consistent for different biomass. In detail, the concentrations of all gases, except CO_2, were decreased for pine wood sawdust by MO drying, and for peanut shell, CO and CH_4 would be the main gas products in the secondary pyrolysis, while C_2H_4, C_2H_6, etc. might result from the secondary cracking of volatiles for the pyrolysis of maize stalk. It might also be caused by the different ash components in biomass (refer to Table 1). The mechanism of metal materials catalyzing the secondary pyrolysis reaction is very complex and still unclear. An in-depth study about the microwave drying effect on biomass pyrolysis would help us to better understand the mechanism.

3.4. Effect of Microwave Drying on Char Properties. The typical IR spectra of the solid char observed from maize stalk pyrolysis with previous drying in a MO and an EO respectively is shown in Figure 5. From the spectra, it can be observed that there are many organic functional groups in the solid char particles, which might be due to the very short residence time (<1 s) of the solid materials. The char from the pyrolysis of maize stalk using different drying methods contained almost the same functional groups, e.g., O–H stretching vibration (~3400 cm^{-1}), C=O stretching vibration (~1600 cm^{-1}), C–H deformation (~1400 cm^{-1}), and O–H association (~1100 cm^{-1}), etc. From Figure 5, it can be found that the IR absorbance of char with a MO predried is lower than that with EO drying, which indicated that the residue of the volatile in pyrolysis char of maize stalk dried by a MO is lower than that of char pretreated with an EO, which is consistent with the higher liquid yield (see Figure 3). Similar results were obtained for pine wood sawdust and peanut shell.

The surface area and pore properties of solid char are summarized in Table 3. In comparison to Brunauer–Emmett–Teller (BET) surface areas of biomass samples (see Table 2), it can be observed that the solid char from fast pyrolysis had greater surface areas than the dried biomass materials, which was possibly attributed to the devolatilization process, and a large amount of pores were open. The smaller increase of surface areas of the char after pyrolysis when dried by a microwave indicates that the releasing of the volatiles is very smooth and rapid with small resistance during the pyrolysis process. Although the surface areas of pyrolysis char of the samples dried by different methods had no significant difference, the biomass dried in an EO produced the char with a bigger average pore diameter. As analyzed above, the inner paths of the pyrolysis char were formed mainly during moisture evaporation for the MO drying, while the inner paths of the pyrolysis char were formed mainly during devolatilization

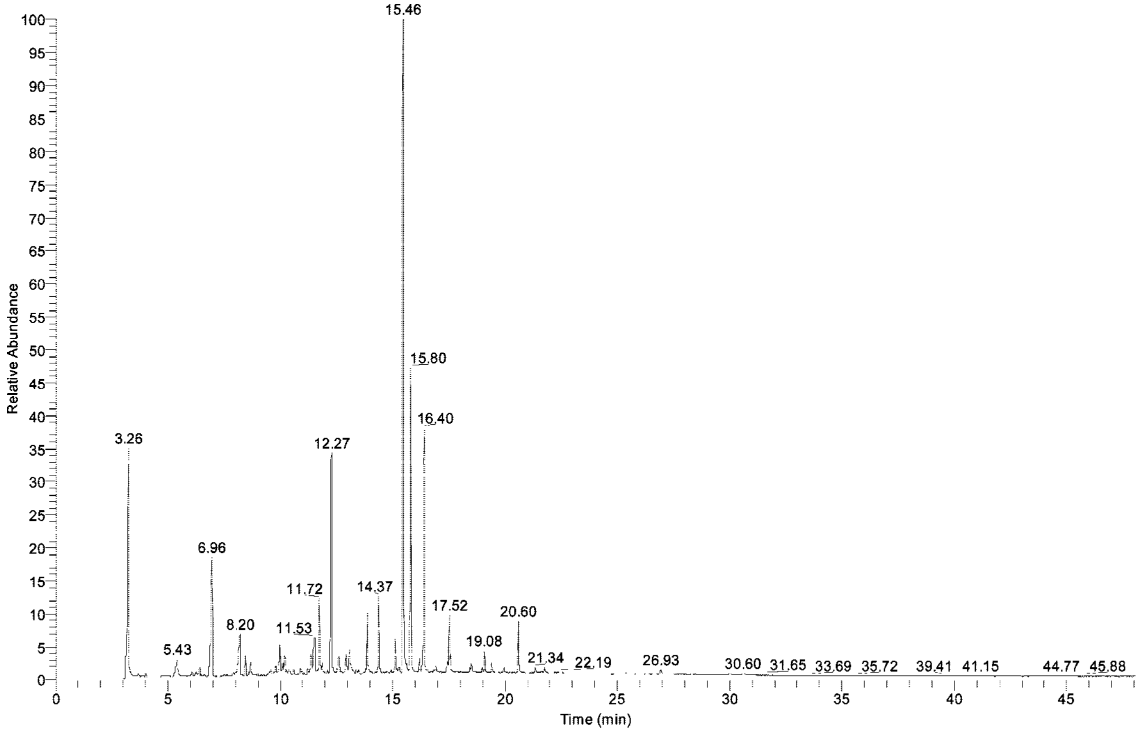


Figure 7. Total ion chromatogram of bio-oil from pine wood sawdust dried in a MO.

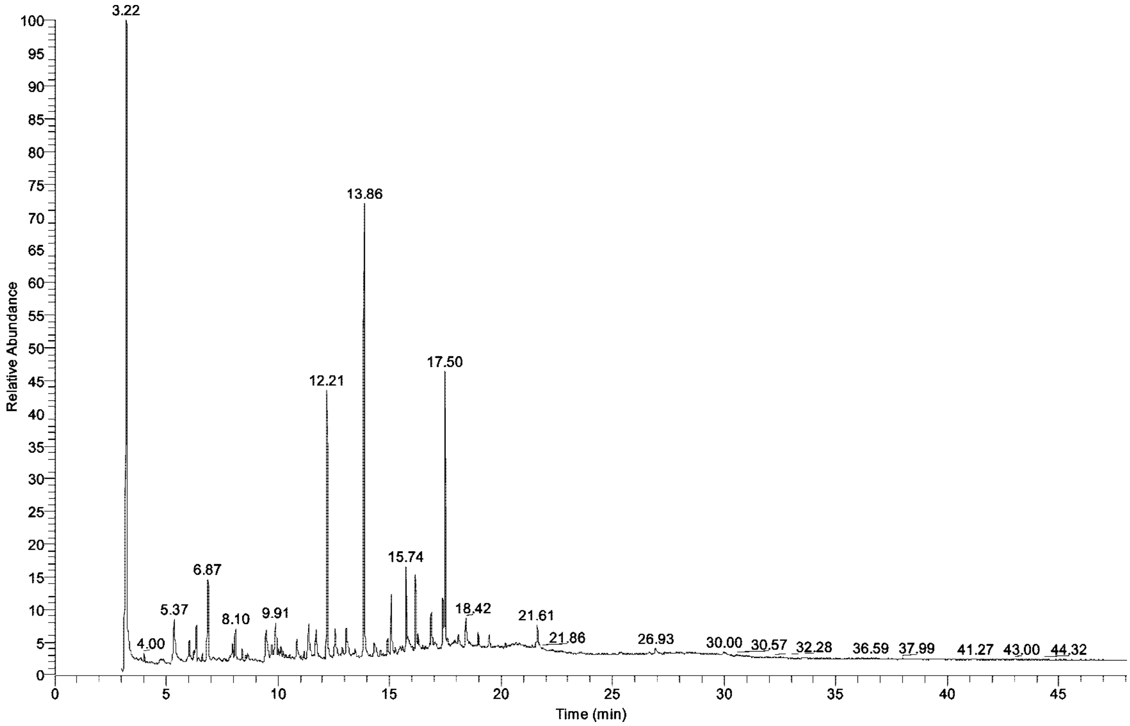


Figure 8. Total ion chromatogram of bio-oil from pine wood sawdust dried in an EO.

Table 5. Bio-oil Components

ID number	compound	formula	molecular weight	peak area (%) MO	peak area (%) EO
1	acetol	$C_3H_6O_2$	74	11.78	31.54
2	isobutyl alcohol	$C_4H_{10}O$	74	1.91	4.13
3	propanal	C_3H_6O	58	0.18	1.49
4	methyl pyruvate	$C_4H_6O_3$	102	0.26	1.45
5	furfural	$C_5H_4O_2$	96	9.30	4.11
6	2-butanone	C_4H_8O	72	0	0.53
7	acetol acetate	$C_5H_8O_3$	116	2.73	1.02
8	2-methyl-2-cyclopentenone	C_6H_8O	96	0.88	0.44
9	2-furyl methyl ketone	$C_6H_6O_2$	110	0.54	0.22
10	2-hydroxy-2-cyclopentenone	$C_5H_6O_2$	98	0.15	2.21
11	butyrolactone	$C_4H_6O_2$	86	0.32	0.66
12	2(3*H*)-furanone	$C_4H_4O_2$	84	1.20	1.96
13	3-methyl-2-cyclopentenone	C_6H_8O	96	0.46	0.32
14	3-methyl-2(5*H*)-furanone	$C_5H_6O_2$	98	0.39	1.07
15	vinyl cyclopentane carboxylate	$C_8H_{12}O_2$	140	0.44	0
16	2,3-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.60	0.34
17	2-hydroxy-3-methyl-2-cyclopenten-1-one	$C_6H_8O_2$	112	2.39	2.73
18	phenol	C_6H_60	94	2.73	1.21
19	2-methoxy-phenol	$C_7H_8O_2$	124	8.13	8.15
20	2-methyl-phenol	C_7H_8O	108	0.89	2.19
21	2,3-dimethyl-phenol	$C_8H_{10}O$	122	0	0.29
22	3-ethyl-2-hydroxy-2-cyclopenten-1-one	$C_7H_{10}O_2$	126	0.70	0
23	4-methyl-phenol	C_7H_8O	108	0.76	0.98
24	2-methoxy-4-methyl-phenol	$C_8H_{10}O_2$	138	1.63	12.04
25	4-ethyl-phenol	$C_8H_{10}O$	122	2.38	0.21
26	4-ethyl-2-methoxy-phenol	$C_9H_{12}O_2$	152	1.02	1.98
27	benzofuran	C_8H_8O	120	26.14	0
28	2-methoxy-4-vinylphenol	$C_9H_{10}O_2$	150	8.96	2.66
29	eugenol	$C_{10}H_{12}O_2$	164	0.36	2.12
30	2,6-dimethoxy-phenol	$C_8H_{10}O_3$	154	8.33	0
31	isoeugenol (cis and trans)	$C_{10}H_{12}O_2$	164	1.37	8.30
32	vanillin	$C_8H_8O_3$	152	0.42	1.84
33	1-(4-hydroxy-3-methoxyphenyl)-ethanone	$C_9H_{10}O_3$	166	0.13	1.68
34	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	$C_{10}H_{12}O_3$	180	0.19	0.51
35	4-(3-hydroxy-1-propenyl)-2-methoxy-phenol	$C_{10}H_{12}O_3$	180	0.60	0.55
36	2,6-dimethoxy-4-(2-propenyl)-phenol	$C_{11}H_{14}O_3$	194	1.73	0
37	4-hydroxy-2-methoxycinnamaldehyde	$C_{10}H_{10}O_3$	178	0	1.08

for the EO drying biomass. In addition, volatile molecules are usually bigger than water molecule; therefore, bigger pores were created in the EO drying sample.

SEM images of pine pyrolysis char are shown in Figure 6. Two obvious different surface structures were displayed. A large amount of fine pores with regular shape were observed for MO char, while the majority of pores in EO char were large and irregular, which might be formed during the devolatilization process. As mentioned above, a different pore-forming mechanism was validated again.

3.5. Effect of Microwave Drying on Bio-oil Properties. The physico-chemical properties of liquid oil were analyzed, and the results are given in Table 4. In comparison to the two predried methods (EO and MO), it can be observed that the carbon content decreased, while O content increased in the liquid oil from biomass pyrolysis pretreated with MO drying. The water content decreased; hence, the viscosity increased but the density decreased. With the water content decreasing, the heat value of liquid oil increased. As mentioned above, EO drying promoted the secondary cracking during biomass pyrolysis, the hydroxyl bond was liable broken during secondary cracking, and more water was evolved. Furthermore, the average molecular weight of bio-oil would decrease when the secondary reaction occurred. These changes are more obvious for peanut shell and maize stalk because of their high ash content.

The total ion chromatograms of bio-oil from pine wood sawdust pyrolysis are plotted in Figures 7 and 8, and many peaks were displayed in the spectra. It indicated that the compounds in liquid oil were very complex and the typical compounds were mainly alcohols, ketones, furfural, phenol, alkylated phenols, furan derivatives, and guaiacols, etc. (listed in Table 5). The percentage values of the peak area were calculated by dividing the area of individual peaks by the total area. These values just give rough estimates of the major compounds. Standard curves should be obtained to determine the actual quantity of those compounds.[15] However, it still provided sufficient information to compare the same species of liquid oil observed from different conditions, with other measure parameters consistent. It was noticed that the percentage value of acetol (partly results of the reverse aldol condensation, i.e., the less specific splitting of pyranose rings[16]) is largest for the EO-dried pine oil, while benzofuran (as a consequence of primary degradation and then a slight decrease, possibly because of secondary, vapor-phase reactions[15]) has the largest peak area for the MO-dried pine oil. The results reveal the influence of the microwave drying treatment on secondary cracking of volatiles and bio-oil compounds to a certain extent. More primary pyrolysis products, which usually contain some valuable compounds, would be obtained in bio-oil when using microwave drying.

4. Conclusion

The drying characteristics of biomass wastes using a MO were investigated and compared with conventional EO drying. The drying rate for a MO at 600 W was almost 10 times higher than that for an EO, and meanwhile, the BET surface area increased more than 5 times. The modified surface and pore structure caused by the quick evaporation of moisture would be helpful for the quick releasing of volatiles in biomass during the pyrolysis process when using microwave drying. Thus, the probability of secondary cracking of volatiles was decreased, and as a result, more liquid oil and solid char were obtained with microwave drying. In comparison to the gas product, bio-oil and char have a greater application value.

Because of secondary pyrolysis being weakened, the viscosity and heating value of bio-oil from MO-drying biomass was increased with less water content and a higher average molecular weight and more primary pyrolysis products were reserved in bio-oil. A higher heating value and lower water content are beneficial properties of bio-oil to be used as fuel, and more primary pyrolysis products make bio-oil to be used as a high add-value chemical material.

Microwave drying equipment have been successfully applied in other fields on a large scale; thus, there would be no technical risk in drying biomass materials with microwave energy in the aim of pyrolysis, which has been proven more energy saving than heated air drying. Considering the use of waste heat during the pyrolysis process, microwave drying combined with heated air drying should be a technically and economically feasible pretreatment method for biomass fast pyrolysis. In this way, a higher efficient dehydration of biomass materials can be achieved and a higher quantity and better quality bio-oil from fast pyrolysis can be obtained.

Acknowledgment. This research is supported by the National Natural Science Foundation of China (Grant 50676037). The authors express their appreciation to the Analytical and Testing Center, Huazhong University of Science and Technology, People's Republic of China.

EF700300M

---

[15] Branca, C.; Giudicianni, P.; di Blasi, C. *Ind. Eng. Chem. Res.* **2003**, *42*, 3190.

[16] Ucar, G.; Meier, D.; Faix, O.; Wegener, G. *Holz Roh- Werkst.* **2005**, *63*, 57.