

## Pyrolysis Characteristics of Corn Stalk with Solid Heat Carrier

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Pyrolysis of corn stalk with a solid heat carrier was studied under temperatures ranging from 430 to 620 °C. The solid heat carrier used was high-temperature ash from a CFB boiler. The yields of three products and their characteristics were investigated. Moreover, the distributions of sulfur and nitrogen in the products were determined. The results indicate that with increasing temperature, the char yield decreased, gas yield increased, and calorific value of the gas increased from 10.13 to 16.65 MJ/m<sup>3</sup>. The yield of bio-oil reached a maximum, 14.24 wt.%, at 510 °C. Light-oil in the bio-oil accounted for more than 69.12 wt.%. The elemental composition of the char and char ash were analyzed. The distribution of sulfur and nitrogen in the char decreased to 60.44 and 46.52 wt.%, respectively, depending on the raw materials used. These results provide basic data for the possible industrial application of corn stalk.

*Keywords:* Corn stalk; Pyrolysis; Solid heat carrier; Sulfur and nitrogen

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### INTRODUCTION

Currently, increased energy consumption and environmental pollution caused by fossil fuel usage has forced people to seek renewable clean energy sources such as solar, wind, and hydroelectric power, as well as biomass energy. In contrast to other renewables used to provide heat or power, biomass is the only resource that can be converted to solid, liquid, and gaseous fuels. Moreover, biomass is CO<sub>2</sub> emission-neutral and contains low amounts of sulfur and nitrogen, making it relatively environmentally friendly. Various mechanical (biomass solid forming fuel), biological (anaerobic digestion and fermentation), and thermochemical (direct combustion, gasification, pyrolysis, and liquefaction) conversion technologies have been developed for the use of biomass and applied in industry to produce various types of fuels, chemicals, and derived bioproducts.

Pyrolysis technology (Balat *et al.* 2009) for biomass use has been studied recently because it has several advantages. It can be used to convert biomass resources to three products: solid char, liquid oil, and gas. These products can be used in many different ways. The gas can be combusted, generating heat, or used in an engine or turbine for electricity generation. The liquid oil can serve as a substitute for fuel oil in boilers or be used as a chemical raw material. The charcoal can be used as a gasification material, adsorbent, or fuel. Reaction conditions for pyrolysis are more moderate and simpler than in other thermochemical conversion technologies such as gasification and liquefaction. Gasification is often carried out under high temperature, high pressure, and in the presence of various agents. Liquefaction is usually carried out under high pressure and

solvent. But pyrolysis, especially in this paper, was carried out at low temperature, under atmospheric pressure and without any agent or solvent. It can improve the utilization efficiency of biomass. During pyrolysis, the volatiles in biomass evolve to form liquid oil and gas, which can be used as chemicals with added value rather than being burned directly. In recent years, research on biomass pyrolysis has developed considerably. Numerous researchers using various types of biomass raw materials (Aclkgoz *et al.* 2004; Tsai *et al.* 2007; Duman *et al.* 2011) and reactors (Zanzi *et al.* 1996; Şen and Kar 2011) under various reaction conditions (Pütün *et al.* 2007; Demiral and Ayan 2011) have investigated the behaviors of biomass pyrolysis, analyzing the mechanism (Shafizadeh 1982; Bridgwater and Peacocke 2000), kinetics (Lv and Wu 2012), pyrolysis parameters (Zanzi *et al.* 1996; Demiral and Ayan 2011), and product properties (Aclkgoz *et al.* 2004; Tsai *et al.* 2007).

Pyrolysis first requires a heat source. Most laboratory studies use electrically heated reactors for pyrolysis. Some research has explored the use of heat carriers such as sand or steel shot (Zheng 2008; Brown and Brown 2012). However, previous studies of biomass pyrolysis with high-temperature ash from a circulating fluidized bed (CFB) boiler as the solid heat carrier, which can rapidly pyrolyze biomass, are limited. This technology was inspired by coal pyrolysis with a solid heat carrier and poly-generation system, as studied previously in our laboratory (Liang *et al.* 2007; Qu *et al.* 2011). In a poly-generation system, a pyrolyzer is installed beside the CFB boiler. High-temperature circulating ash from the CFB boiler is transported into the pyrolyzer to provide heat for coal pyrolysis, yielding tar and gas. The char produced in the pyrolyzer is returned to the boiler for combustion to provide heat for steam production, and hence for electricity generation. Poly-generation of tar, gas, heat, and power can be realized in a power plant using a CFB boiler connected to a pyrolyzer, improving the coal utilization efficiency. In recent years, boilers burning biomass (Saidur *et al.* 2011; Ray *et al.* 2014) and biomass-based power-generation projects (Zhang *et al.* 2009) have been developed, making it possible for biomass to be used in poly-generation similarly to coal. If biomass is used in a poly-generation system, pyrolysis with high-temperature circulating ash in the pyrolyzer is the first problem needing resolution. This study focused on this problem. The solid heat carrier used in this study was high-temperature circulating ash fetched from a 75 t/h CFB boiler in a power plant. A furnace heated the ash to high temperatures.

Corn is one of the main crops grown in China. Large quantities of corn stalk agricultural residues are generated annually (Liao *et al.* 2004). However, only a small portion of them are used as fuel for household cooking or as forage in rural areas. Most of them are discarded or burnt by farmers, resulting not only in the poor use of resources, but also in pollution. Efficient and clean utilization of corn stalk residues is very significant, especially in China. In addition, if corn stalks are properly utilized, farmers and enterprises will enjoy economic benefits because corn stalk is so cheap. Corn stalk was selected as the raw material for the present pyrolysis research.

Temperature is the most critical parameter influencing the performance of biomass fast pyrolysis (Williams and Besler 1996; Uçar and Karagöz 2009; Angin 2013). In this study, the pyrolysis characteristics of corn stalk at various temperatures were evaluated. Moreover, the distribution of biomass sulfur and nitrogen into gaseous, liquid, and solid products was studied. Although biomass contains little sulfur and nitrogen, this research also provides reference for the clean use of biomass, especially in terms of sulfur and nitrogen removal prior to use in a boiler.

## EXPERIMENTAL

### Materials

The corn stalk used was obtained from Taiyuan in the Shanxi province of China. To conveniently feed the pyrolyzer, the air-dried corn stalk was first crushed into a powder, then granulated to cylinders 2.0 mm in diameter and 6.0 mm in length. The proximate and ultimate analyses of the granulous corn stalk samples are listed in Table 1. To eliminate the effect of moisture content, prior to each test, sufficient amounts of samples were dried at 105 °C for several hours and stored in a desiccator to prevent absorption of moisture from the atmosphere. The ash (from a circulating fluidized bed boiler) used as the solid heat carrier was first sieved to obtain samples of particle size 0.12 to 4 mm. Its density was  $1.06 \times 10^3 \text{ kg/m}^3$ . The ash was also dried before experiments.

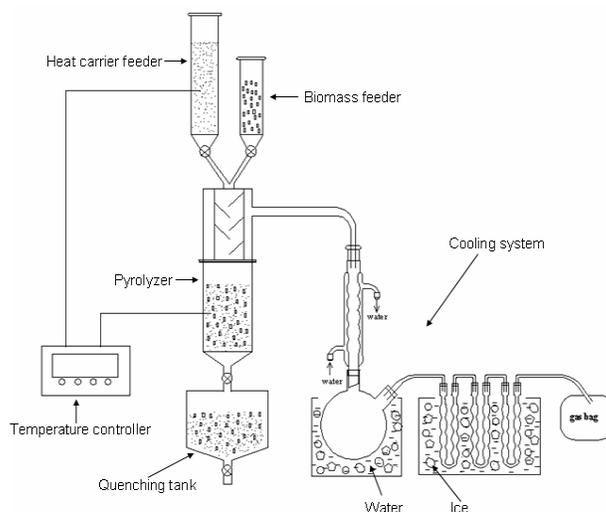
**Table 1.** Proximate and Ultimate Analyses of the Raw Materials

Materials	Proximate Analysis (wt. %, ad)				CV (MJ/kg)	Ultimate Analysis (wt. %, dry)					H/C
	M	V	A	FC <sup>a</sup>		C	H	N	S	O <sup>a</sup>	
Corn stalk	3.54	73.94	5.50	17.02	15.75	45.97	5.59	0.70	0.23	42.01	1.46

<sup>a</sup> by difference; M:Moisture; V:Volatile matter; A:Ash; FC:Fixed Carbon; CV:Calorific value.

### Apparatus and Procedure

A schematic diagram of the experimental setup is shown in Fig. 1. It consists of six principal components. These components are the heat carrier feeder (diameter of 60 mm, length of 500 mm), biomass feeder (diameter of 50 mm, length of 200 mm), pyrolyzer (diameter of 100 mm, length of 400 mm), quenching tank (diameter of 140 mm, length of 120 mm), cooling system, and a temperature controller.



**Fig. 1.** Schematic diagram of the experimental setup

In the upper part of the pyrolyzer, a mixer fully mixed the solid heat carrier and the biomass samples to ensure adequate heat transfer between them. The heating rate can reach more than 600 °C/min. To fully condense the condensable gas, the cooling system

consisted of three condensers in series. The first was cooled with cool water. The second and third were further cooled by mixtures of cool water and ice placed in a stainless steel container. The temperature controller was connected with K-type thermocouples to the heat carrier feeder and pyrolyzer. The entire system was well sealed.

For every run, 1500 g of ash was loaded into the heat carrier feeder and was heated to a set temperature, such as 800 °C. At the same time, 50 g of biomass was loaded into the biomass feeder. The pyrolyzer was heated to about 400 °C to make up for heat losses. Pure nitrogen was introduced into the entire apparatus to ensure complete air removal. After the heat carrier feeder was heated to the desired temperature, the ash and corn stalk samples were simultaneously dropped into the pyrolyzer by opening the valves under the two feeders. To prevent loss of pyrolysis gases, the valves were immediately closed once the ash and samples fell into the pyrolyzer. The ash and corn stalk sample particles were mixed evenly with the mixer, and the corn stalk samples were rapidly pyrolyzed because of the high heat transfer rates from the high-temperature ash. Volatiles flowed into the cooling system, in which condensable volatiles were collected in liquid form. The vapor residence time in the pyrolyzer was less than 2 seconds. The gases not condensable at ambient temperature flowed into a gas bag and were collected for subsequent analysis. Experiments lasted for at least 20 min, until no further significant release of gas was observed. After the completion of pyrolysis, the residual solid blends of ash and char were discharged into the quenching tank to cool to ambient temperature and were then discharged to be weighed. After the blends of ash and char were discharged, some chars were picked out by hand from the blends for analysis. The solid char yield, determined by subtracting the content of the carrier ash from the discharged blends, was recorded. The yield of gaseous products was calculated after the analysis with analyzers combining with the volume of it, seen in the analysis section. The yield of liquid products was determined as the weight difference of the cooling system before and after the experiment. The estimated mass balance for the different experiments, described as the total yield of char, liquid, and gases divided by the mass of the feedstock, was above 99%, which is considered reasonable. In this study, each experiment was carried out at least twice, until good repeatability was achieved. The analysis of the products obtained in each trial was carried out according to the following methods.

## Analysis

Three types of gas analyzers were used to determine the chemical composition of the non-condensable gas products. The non-condensable gases (H<sub>2</sub>, CH<sub>4</sub>, and CO) were analyzed with a gas chromatograph with a thermal conductivity detector (Model SP-2305, 5A molecular sieve column, pure Ar as the carrier gas). The light hydrocarbon gases (C<sub>2</sub> to C<sub>4</sub>) were analyzed by a gas chromatograph with a flame ionization detector (Model GC-1790, C18 column, pure nitrogen as the carrier gas). CO<sub>2</sub> was analyzed by an Orsat gas analyzer. The volume of gas was obtained by drainage. After the gas product was analyzed by gas analyzers, the average molecular weight of the gas can be calculated. The number of moles of the gas can be calculated by the volume of the gas. Then the mass of the gas product can be calculated by the average molecular weight and the number of moles.

The liquid products were present in both the aqueous phase and oil phase. First, the liquid products were poured from the condensers into a separating funnel, where the aqueous phase was separated from the oil phase after settling for at least 10 min. The bio-oil remaining in the condensers was recovered with tetrahydrofuran (THF) washing. The

THF was removed by a rotavapour. The two parts of the bio-oil were blended together and extracted with *n*-hexane in an ultrasonic extractor. After extraction, the bio-oil was separated into light-oil (*n*-hexane-soluble fraction) and asphaltene (*n*-hexane-insoluble fraction).

The characteristics of the solid char were analyzed. The testing included ultimate analysis, ash melting point, and composition of the char-ash. Ultimate analysis of the char for its carbon, hydrogen, nitrogen, and sulfur contents was carried out with a CHNS/O elementary analyzer (Vario Micro cube, Germany). The ash melting point was determined by an ash melting point analyzer (5E-AF-3, China). The composition of the ash was analyzed with an XRF (X-ray fluorescence) analyzer (S4 PIONEER Supplement, Bruker AXS, USA).

Chars and bio-oils were analyzed with the elementary analyzer mentioned above for their sulfur and nitrogen contents (Middleton *et al.* 1997). Gases were analyzed with a Microcoulomb Analyzer (LC-4, China) for their sulfur content. The nitrogen in the gases was obtained by the difference method.

The calorific values of raw material, bio-oil, and char were calculated by the formula (1) after the elemental analysis,

$$\text{Calorific value: CV(MJ/kg)}=0.3383C+1.443(H-O/8) \quad (1)$$

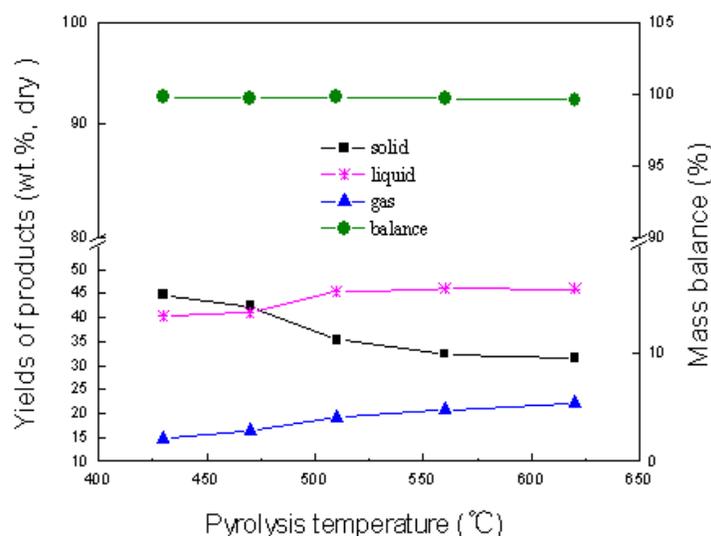
where C, H, O are, respectively, the mass fractions of carbon, hydrogen, and oxygen (Şen and Kar 2011).

## RESULTS AND DISCUSSION

### Yield Distribution of Products

The yield distribution of solid, liquid, and gaseous products from the pyrolysis of corn stalk as related to the final pyrolysis temperature (430, 470, 510, 560, or 620 °C) is shown in Fig. 2. The mass balance during the experimental processes exceeded 99%, which is considered acceptable. The yields of char decreased from 44.72 to 31.58 wt.% as the pyrolysis temperature increased from 430 to 620 °C. The decrease in char yield with increasing temperature could be due either to the greater primary decomposition of the corn stalk at higher temperatures or to secondary decomposition of the char (Horne and Williams 1996; Demiral *et al.* 2012). Increases in the pyrolysis temperature increased the gas yields from 14.78 to 22.20 wt.%. The increase in gaseous product generation is thought to be due to secondary decomposition of the char at higher temperatures, forming some non-condensable gaseous products. Secondary cracking of the pyrolysis vapors at higher temperature also contributed to increased gas yield (Demiral *et al.* 2012). The liquid product yield reached 45.40 wt.% at 510 °C and remained stable with further increases in the temperature from 510 to 620 °C. According to Chen's report (cotton stalks were electrically heated to pyrolyze rapidly), during the same pyrolysis temperature range of 430 to 620 °C, the yield of char decreased from 32.12 to 26.93 wt.%, while the yield of gas increased from 26.21 to 31.86 wt.% approximately (Chen *et al.* 2012). It can be seen there is some difference between this paper and Chen's report. This may be due to the different particle size and nature of the materials considered in the two papers. As for the liquid yield, Chen reported the liquid yield comprised 40 wt.% of the mass of the biomass sample and showed a slight increase with temperatures greater than 350 °C. A similar trend was found in this work, as stated above. From the comparison

above, it can be concluded that when biomass is pyrolyzed with heat carrier ash, the yields of char, gas, and liquid products are similar with that of biomass being electrically heated to pyrolyze. But the yields of volatile substances are lower than from the fluidized bed with sand as heat carrier, where the heating rates are very high (about 1000 °C/s) (Zheng 2008). In the poly-generation system, when the biomass was first pyrolyzed, the high added gas and bio-oil can be received. These products can improve the economy of the system. In addition, the cheapness of the biomass can also reduce the overall cost. The experiments above demonstrate that biomass can be pyrolyzed by the high-temperature ash from the CFB boiler. But if the whole poly-generation system can operate successful, the pyrolysis stage should be operated combined with the boiler, just as the reference stated with coal (Liang *et al.* 2007; Qu *et al.* 2011). Such work can be regarded as a priority for future studies.



**Fig. 2.** Yields distribution of corn stalk pyrolysis products obtained at various temperatures

### Properties of Gaseous Products

The properties of the gaseous pyrolysis products are shown in Fig. 3. The contents of CO and CO<sub>2</sub> were much higher than those of H<sub>2</sub>, CH<sub>4</sub>, or C<sub>2+</sub>, accounting for more than 75 vol.%. Even at the lowest temperature, 430 °C, the contents of CO and CO<sub>2</sub> accounted for about 90 vol.%. This is because the oxygen content in the biomass was relatively high, and at the onset temperature, CO<sub>2</sub> and CO were released more rapidly than the other gases (Chen *et al.* 2012). With increasing temperature, the CO<sub>2</sub> content decreased markedly, from 53.01 to 35.18 vol.%. Previous researchers have confirmed that CO<sub>2</sub> is generated during the low-temperature decarboxylation of the hemicelluloses and cellulose found in biomass (Yang *et al.* 2006; Mahinpey *et al.* 2009; Shen and Gu 2009). The CO content changed little throughout the entire temperature range examined. CO may be generated during the decarbonylation process during the aromatic condensation of lignin (Fu *et al.* 2009). In addition, the contents of H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2+</sub> increased from 9.18 to 24.20 vol.% with increasing temperature. The releases of H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2+</sub> exhibited similar trends. Aromatic condensation and thermal cracking of heavy hydrocarbons contributed to the release of H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2+</sub> (Yang *et al.* 2006; Chen *et al.* 2012). The calorific value of the gas increased from 10.13 to 16.65 MJ/m<sup>3</sup> with increasing temperature because of the increase in the amount of combustible H<sub>2</sub>, CH<sub>4</sub>,

and C<sub>2+</sub> generated and released. The trend exhibited by the gas release is similar to that found in several previous studies (Fu *et al.* 2009; Mahinpey *et al.* 2009; Duman *et al.* 2011; Chen *et al.* 2012).

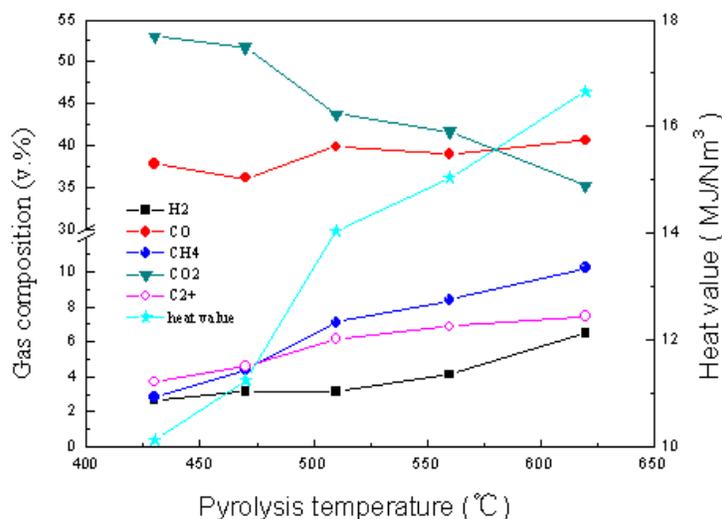


Fig. 3. Properties of gaseous products obtained at various temperatures

### Properties of Liquid Products

The liquid products were separated into two fractions: an aqueous phase, referred to as water, and an oil phase, referred to as bio-oil. Then, the bio-oil fraction was further separated into two parts: light-oil (*n*-hexane-soluble) and asphaltene (*n*-hexane-insoluble). The yields of water, bio-oil, and light-oil as functions of pyrolysis temperature are shown in Fig. 4. The yield of water increased from 27.00 to 32.28 wt.% with increases of pyrolysis temperature from 430 to 620 °C. Above 510 °C, the extent of this increase was smaller, from 31.16 to 32.28 wt.%. The law of the water yield in this work is similar with the finding of Williams and Besler (1996), who came to the conclusion that the aqueous yield of wood samples pyrolysis at 420 °C and above remained virtually constant at about 37 wt.%. The yields of bio-oil first increased and then decreased with increasing temperature, and the maximum value, 14.24 wt.%, was obtained at 510 °C. This is in agreement with another report in which the maximum yields of pyrolysis oil were obtained at temperatures within the range of 450 to 550 °C during the rapid pyrolysis of maize stalk (Zheng 2008). Higher treatment temperature leads to more bio-oil cracking, resulting in higher gas yield and lower bio-oil yield. In this work, due to the method of separation which made some of the water-soluble organic matter get into the water, the yield of bio-oil was lower than that reported in some literature. Table 2 presents the analysis results of the bio-oil obtained at 510 °C. The average chemical composition of the bio-oil was CH<sub>1.29</sub>O<sub>0.29</sub>N<sub>0.03</sub>S<sub>0.01</sub>. The oxygen content of the bio-oil was noticeably lower than that of the original feedstock, which is favorable because high oxygen content can inhibit the production of transportation fuels. Both the H/C molar ratio, 1.29, and the calorific value, 27.68 MJ/kg, were lower than those of traditional light or heavy petroleum products. If the bio-oil obtained in this study were to be used as a transportation fuel, it would need extensive refining.

Figure 4 also shows that the yield of light-oil decreased from 11.70 to 9.35 wt.% with increasing pyrolysis temperature. The light-oil content in the bio-oil was more than

69.12 wt.% across the range of pyrolysis temperatures tested, as shown in Table 3. Table 3 also indicates that the light-oil content in the bio-oil gradually decreased from 87.81 to 69.12 wt.% with increasing pyrolysis temperature. Pyrolysis at increased temperatures provided enough energy to pyrolyze macromolecules from the biomass. The heavy-oil (asphaltene) content in the oil gradually increased with increasing pyrolysis temperature. Light-oil, as analyzed by GC-MS, was found to be a complicated organic oxygen mixture consisting primarily of aldehydes, ketones, esters, furans, and other substances usable as sources of chemical commodities.

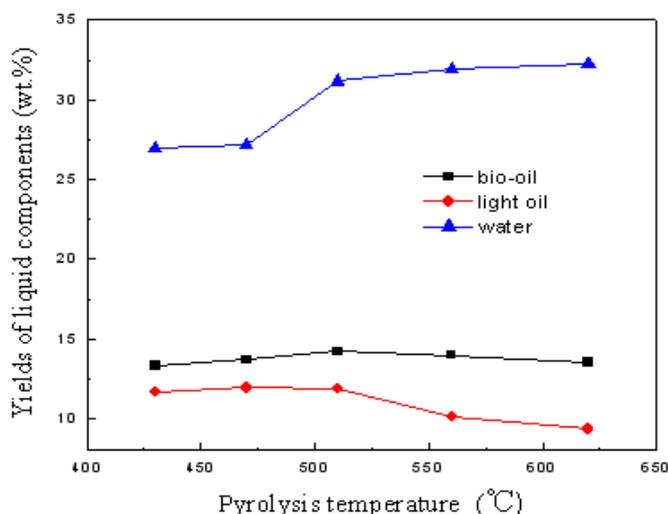


Fig. 4. Yields of liquid components at various pyrolysis temperatures

Table 2. Properties of Bio-Oil

Bio-oil <sup>a</sup>	Ultimate Analysis (wt. %)					H/C	O/C	CV (MJ/kg)	Empirical Formula
	C	H	N	S	O <sup>b</sup>				
	65.30	7.01	2.10	0.51	25.08	1.29	0.29	27.68	CH <sub>1.29</sub> O <sub>0.29</sub> N <sub>0.03</sub> S <sub>0.01</sub>

<sup>a</sup> Obtained at 510 °C; <sup>b</sup> By difference; CV: Calorific value.

Table 3. The Content of Light-Oil in Bio-Oil at Different Temperatures

Temperature	430 °C	470 °C	510 °C	560 °C	620 °C
Light-Oil (wt. %)	87.81	86.88	83.29	72.46	69.12

### Properties of Solid Products

The characteristics of the chars are summarized in Table 4. For comparison with the properties of the raw corn stalk, these data are also listed in the table. In the ultimate analysis, with an increase in the pyrolysis temperature from 430 to 620 °C, the carbon content of the chars increased from 63.61 to 64.37 wt.%. However, the hydrogen content of the chars decreased from 3.35 to 2.23 wt.%, and the oxygen content exhibited a similar trend, decreasing from 16.89 to 12.65 wt.%. Comparing with the raw corn stalk, the carbon content of the chars increased, while the hydrogen and oxygen content of the chars decreased. This indicates that after pyrolysis, more hydrogen and oxygen of corn stalk were released into volatiles (much of them forming water), while more carbon was accumulated in char. The contents of sulfur and nitrogen were both higher than in the raw

material. Ash contents in the chars were far higher than in the raw corn stalk. In addition, the calorific value of the chars exceeded 21.48 MJ/kg, much larger than that of the raw materials (15.75 MJ/kg), which means that it is possible for char to be used as a fuel. These results are similar to those of previous studies (Fu *et al.* 2009, 2011).

Because of the high ash content of the chars, ash may have important effects on the boiler when char is used as a fuel. The melting point and composition of the ash were determined. Table 4 shows that the melting point of char ash was higher than raw material ash. This is because the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents (which can increase the ash melting point) in the char ash were higher than in the raw material ash, while the K<sub>2</sub>O (which can decrease the ash melting point) content in the char ash was lower than in the raw material ash. With increasing pyrolysis temperature, the ash melting point of the char ash increased from 1118 to 1148 °C. This is because the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents increased, while that of K<sub>2</sub>O decreased. However, the extent of increase was not large.

**Table 4.** Properties of Char Obtained at Different Temperatures

	Char (430 °C)	Char (470 °C)	Char (510 °C)	Char (560 °C)	Char (620 °C)	Raw Corn Stalk
<b>Ultimate Analysis (wt. %)</b>						
Carbon	63.61	63.95	63.26	64.01	64.37	45.97
Hydrogen	3.35	3.33	2.58	2.28	2.23	5.59
Nitrogen	1.17	1.17	1.08	1.08	1.04	0.70
Sulfur	0.33	0.34	0.40	0.42	0.43	0.23
Oxygen	16.89	15.46	14.26	13.48	12.65	42.01
Ash	14.64	15.75	18.40	18.71	19.28	5.50
Calorific value (MJ/kg)	23.30	24.17	22.56	21.48	22.71	15.75
<b>Ash Melting Point (°C)</b>						
Deformation Temperature	1053	1050	1060	1074	1070	1047
Softening Temperature	1118	1121	1132	1141	1148	1083
Hemispheric Temperature	1141	1149	1150	1152	1163	1098
Flow Temperature	1174	1176	1181	1185	1190	1140
<b>Ash Composition (wt. %)</b>						
Al <sub>2</sub> O <sub>3</sub>	4.01	4.11	4.23	4.26	4.59	3.70
CaO	10.13	9.66	9.68	10.27	9.80	9.05
Fe <sub>2</sub> O <sub>3</sub>	4.26	4.39	4.38	4.44	3.85	4.13
K <sub>2</sub> O	22.33	22.17	22.59	20.43	19.14	23.07
MgO	7.28	7.34	7.33	7.32	7.03	7.24
Na <sub>2</sub> O	2.07	2.25	1.79	2.23	1.60	1.48
P <sub>2</sub> O <sub>5</sub>	2.16	2.30	2.32	2.33	2.02	2.20
SO <sub>3</sub>	6.52	6.35	6.44	6.62	6.13	6.46
TiO <sub>2</sub>	0.14	0.16	0.15	0.10	0.15	0.15
SiO <sub>2</sub>	34.46	35.89	36.21	36.49	36.91	34.05

### Distribution of Sulfur and Nitrogen in Products

During corn stalk pyrolysis, sulfur and nitrogen in the raw material were distributed among the three products. The distribution of sulfur and nitrogen in the gaseous, liquid (bio-oil), and solid products is shown in Fig. 5. The sulfur and nitrogen distributions exhibited similar tendencies in the three phases. With increasing temperature, the sulfur and nitrogen distributed in the chars decreased, and those distributed in the bio-oil and gas increased. The sulfur distributed in the chars accounted for around 60 wt.%. The nitrogen distributed in the chars decreased from 74.18 to 46.52 wt.% with increasing pyrolysis temperature. If char is used as fuel in a boiler, it can

reduce the desulfurization and denitrification load for the boiler comparing with the directly getting into the boiler burning of the raw materials. The sulfur and nitrogen distributed in the liquid phase were much greater than those in the gaseous phase.

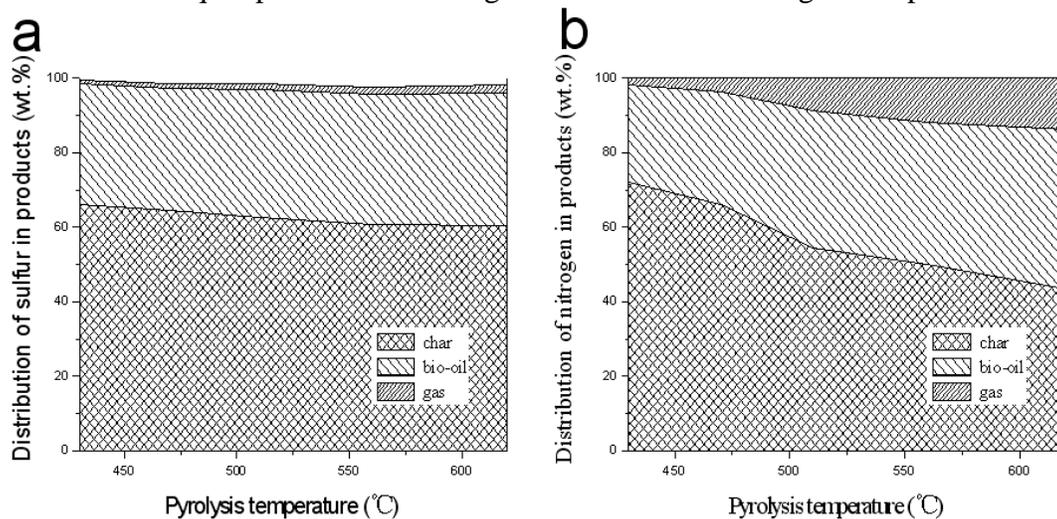


Fig. 5. Distribution of sulfur (a) and nitrogen (b) in pyrolysis products

### Properties of Heat Carrier

The characteristics of the heat carrier were also analyzed, as shown in Table 5. Little change in the heat carrier occurred before and after the experiments. The heat carrier simply provided heat for pyrolysis. Neither the pyrolysis process nor the biomass influenced the heat carrier. Thus, heat carrier ash can continue to enter into the CFB boiler and will not affect boiler operation.

Table 5. Properties of Heat Carriers Before and After the Experiments

	Ash (430 °C)	Ash (470 °C)	Ash (510 °C)	Ash (560 °C)	Ash (620 °C)	Original Ash
<b>Ash Melting Point (°C)</b>						
Deformation Temperature	1428	1419	1446	1437	1423	1435
Softening Temperature	1521	1528	1520	1486	1486	1494
Hemispheric Temperature	1541	1542	1550	1549	1550	1534
Flow Temperature	1550	1550	1550	1550	1550	1541
<b>Ash Composition (wt. %)</b>						
Al <sub>2</sub> O <sub>3</sub>	25.08	25.46	24.93	25.49	25.43	24.98
CaO	0.73	0.77	0.70	0.68	0.72	0.79
Fe <sub>2</sub> O <sub>3</sub>	3.25	4.06	3.70	3.12	3.06	4.73
K <sub>2</sub> O	3.00	2.80	2.80	2.90	2.88	2.74
MgO	0.77	0.75	0.75	0.77	0.77	0.73
Na <sub>2</sub> O	0.07	0.08	0.06	0.12	0.10	0.09
P <sub>2</sub> O <sub>5</sub>	0.16	0.20	0.18	0.16	0.17	0.24
SO <sub>3</sub>	0.27	0.24	0.36	0.26	0.29	0.39
TiO <sub>2</sub>	1.02	1.06	1.01	1.04	1.02	1.00
SiO <sub>2</sub>	65.26	64.50	65.58	65.14	65.26	64.25

## CONCLUSIONS

1. With increases in pyrolysis temperature from 430 to 620 °C, the char yield decreased from 44.72 to 31.58 wt.%, the gas yield increased from 14.78 to 22.20 wt.%, and the liquid yield reached a maximum of 45.40 wt.% at 510 °C.
2. The gas product components included CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2+</sub>. The molecules CO and CO<sub>2</sub> accounted for more than 75 vol.% of the gas product. Increasing the pyrolysis temperature greatly decreased the CO<sub>2</sub> content, did not greatly affect the CO content, and increased the H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2+</sub> contents.
3. The yield of bio-oil reached a maximum value of 14.24 wt.% at 510 °C. The light-oil in the bio-oil accounted for over 69.12 wt.% of the bio-oil across the entire range of pyrolysis temperatures examined.
4. The calorific value of the chars exceeded 21.48 MJ/kg, much greater than that of the raw material.
5. Ash contents in the chars were far greater than those in the raw corn stalk. The ash melting point of the char ash was higher than that of the raw material ash.
6. After pyrolysis, the sulfur content in the chars accounted for roughly 60 wt.% of the total sulfur and the nitrogen content in the chars decreased from 74.18 to 46.52 wt.% with increasing pyrolysis temperature.
7. The characteristics of the heat carrier changed little before and after the experiments. It simply provided heat for pyrolysis.

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Article submitted: February 13, 2015; Peer review completed: April 12, 2015; Revisions received and accepted: May 1, 2015; Published: May 6, 2015.  
DOI: 10.15376/biores.10.3.3839-3851