INVESTIGATING GASEOUS CARBON, NITROGEN, AND SULFUR COMPOUNDS OF BAMBOO, WOOD, AND COAL DURING PYROLYSIS PROCESS

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Abstract. Bamboo, wood, and coal were pyrolyzed by a thermogravimetric analyzer coupled with Fourier transform infrared spectrometry to investigate gaseous carbon, nitrogen, and sulfur compounds from fuels. It was found that the main gas compounds of fuels included carbon dioxide, carbon monoxide, methane, sulfur dioxide, hydrogen sulfide, ammonia gas, and hydrogen cyanide. Compared with masson pine, bamboo had a higher gas release and more mass loss due to its lower pyrolysis temperatures when temperature was lower than 350°C. Coal had the lowest gas release and the least mass loss due to the higher pyrolysis temperature during the whole pyrolysis process. The char-C, N, and S contents of all fuels increased with increase in pyrolysis temperature. The results from this research will be helpful to utilize the wastes of masson pine and bamboo for energy products.

Keywords: Bamboo, masson pine, coal, gas compounds, pyrolysis.

INTRODUCTION

Biomass is one of the most important sustainable energy sources with a great potential to keep the carbon neutral and replace the use of fossil fuel (Sharan et al 2011). Many policies, regulations, and support of bioenergy have been promulgated around the world. The United States plans to use bio-oil to replace 10% of its fuel oil and to replace 25% of fossil materials. Sweden plans to use biomass to replace 30% of its energy consumption by 2020. So far,

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bioenergy use is about 16.5% of the total energy requirement in Sweden, is 20.4% in Finland, and is 23.4% in Brazil (Li 2006).

The pyrolysis of biofuels plays an important role as the first chemical step in the combustion process, because a large part of the original biomass is converted to volatile products. The conversion of carbon, nitrogen, and sulfur compounds during the pyrolysis process is very complex and important to investigate the release of greenhouse gas or other pollutants. Research on carbon, nitrogen, and sulfur conversion from fuels is also an effective way to promote biomass utilization and environmental protection (Kawser et al 2004; Wang et al 2016). Naoto (2014) investigated effects of residence time and metal cations on nitrogen conversion in six types of coals. They found when the residence time was 0, 20-30% of coal-N was released as volatile-N species. When the residence time was increased to 120 s, the yields of tar-N, HCN, and NH_3 were almost unchanged, although N_2 yield increased and the char-N decreased with increase in residence time. Stubenberger et al (2008) investigated nitrogen releases from sawdust, bark, food waste, and medium density fiberboard (MDF) board. They found that the most important NO_x precursor under fuel-rich conditions was NH_3. HCN was almost insignificant with the exception of sawdust and NO was detected mainly under air-rich conditions. Knudsen et al (2004) found that 35-50% of S compounds were released when pyrolysis temperature was up to 500°C, suggesting that the initial release of S compounds was related to the organically associated sulfur. Ndibe et al (2015) investigated cofiring characteristics of torrefied biomass fuels. It was found that blending woody biomass with coal decreased the emissions of SO_2 mainly as a result of dilution. NO_X emissions had a more complex dependency on the nitrogen contents.

Bamboo and masson pine are two types of fast-growing forestry plants, which have been widely cultivated in China. The total area of planted bamboo was more than 6 million hectares (Liu et al 2014) and that of masson pine was about 2 million km^2 in 2012, which was 13.2% of the total fast-growing forestry in China. Bamboo and masson pine have been used to make industrial products, which leads to huge amounts of waste. This abundant waste has a great potential to be used as a bioenergy resource of the future. Coal is one of the most abundant resources of fossil fuels in the world and is also the primary energy source in China (Pu et al 2015). Despite previous researches are very helpful to understand the gas release of fuels, bamboo and masson pine are two types of biomass materials. To the best of our knowledge, there is a lack of sufficient information concerning carbon, nitrogen, and sulfur conversions of bamboo and masson pine. In this research, the carbon, nitrogen, and sulfur conversion of bamboo, masson pine, and coal during the pyrolysis process was investigated using thermogravimetry (TA Instrument) coupled with Fourier transform infrared spectroscopy (Bruker IFS 66/S, Bruker Optics, Billerrica, MA) (TG-FTIR). The results from this research will be very helpful to utilize the wastes of masson pine and bamboo for energy products.

MATERIALS AND METHODS

Materials

Phyllostachys praecox (CV. Ventricousinternode) and masson pine (*Pinus massoniana* Lamb.) were used in this study. The following samples were taken from Zejiang province, Anhui province, and Hebei province in China: 4-yr-old bamboo, 20-yr-old masson pine, and coal (anthracite), respectively. The samples were broken down to particles using a Wiley Mill (Thomas-Wiley). Samples were screened to get 250-425 μm particles. Then, they were dried at temperature 105°C in drying oven until the weight loss stabilized.

Determination of carbon, nitrogen, and sulfur conversion. Thermal decomposition of bamboo, masson pine, and coal was observed in terms of global mass loss through TG-FTIR. A helium sweep gas flow of 500 mL/min was used to bring the evolved pyrolysis gases from

the TGA directly to the gas cell, which was heated to 150°C. The system collected FTIR spectra every 30 s and the sample temperature and mass were logged every 3 s. The sample pan was placed close to the end of the furnace, where a steeply decreasing temperature profile existed. This, combined with the high gas flow, minimized the residence time of the evolved gases in the hot zone. In the experiment, sample mass was about 20 mg and was heated from 50°C to 1000°C at 20°C/min of heating rate. The flow rate of the entering gases, the emission rates of the products, and the weight of the fuels were continuously monitored by computer system. The IR spectrum had identifiable bands for each product attributed to the functional groups. Thus, the combustion characteristics and pollutant emissions were recorded (Wang et al 2011). Three replicates were carried out for each TG-FTIR experiment and the results showed good reproducibility. But the average of three experimental data was used in the tests.

Ultimate analysis. Ultimate analyses of samples were determined according to standard methods. The determination of C, H, and N was performed according to GB/T 476-2008. The determination of S was performed according to GB/T 217-2007.

<div style="text-align:center">RESULTS AND DISCUSSION</div>

Pyrolysis Characteristics

Figure 1 shows the pyrolysis process of bamboo, masson pine, and coal with a heating rate of 10°C/min from 50°C to 1000°C. The pyrolysis process of bamboo and masson pine included three steps. In the first step, the thermal degradation occurred in the low-temperature zone due to removal of absorbed water from the samples. Mass loss was 0.63% for bamboo and 1.19% for masson pine. In the second step, the degradation temperature of bamboo was from 155°C to 395°C and mass loss was about 68.86%. The thermal degradation of masson pine occurred between 213°C and 400°C and mass loss was about 72.77%. The thermal degradation of extractives, cellulose, and hemicelluloses contributed to
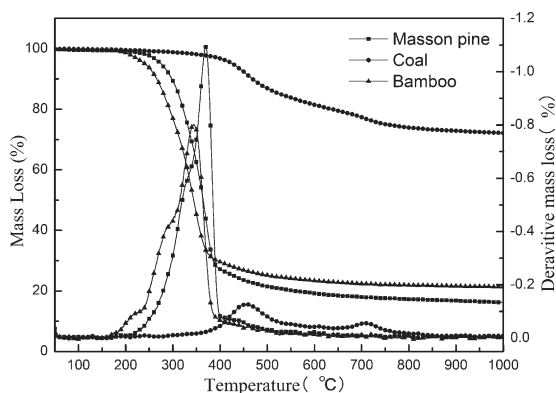

Figure 1. Pyrolysis process of samples with a heating rate of 10°C/min.

the mass loss of samples. In this step, the main occurrence is the rupture of glucocidic bounds between cellulose molecules cellulose, which are converted to levoglucosans and with cellulose molecules being decomposed to glycolaldehyde (Richards 1987; Richards and Zheng 1991). At the same time, hemicelluloses are converted to liquids, such as moisture, formic acid, acetic acid, methyl alcohol, acetone, acrolein, furfural, and to gases, such as carbon monoxide, carbon dioxide, and formaldehyde (Beaumont 1985; Ivan et al 1988). The peak temperatures corresponding to maximum of mass loss were 345°C for bamboo and 370°C for masson pine. In the third step, where the degradation occurs at the high-temperature zone, mass loss was about 9.17% for bamboo and 9.81% for masson pine. Mass loss was due to thermal degradation of lignin and formed the tar and char of the samples. The variation of chemical compositions of bamboo and masson pine led

Table 1. Chemical composition of bamboo and masson pine.

Chemical composition	Masson pine	Bamboo
Solvent of cold water (%)	1.55	7.18
Solvent of hot water (%)	3.09	9.09
Solvent of benzene-alcohol (%)	2.54	5.64
Solvent of 1% NaOH (%)	13.87	23.26
Lignin (%)	28.43	25.65
Pentose (%)	12.02	22.39
Holocellulose (%)	75.87	65.77
α-cellulose (%)	45.08	40.81

Table 2. The typical absorbance peaks and pyrolysis products of samples.

Pyrolysis products	Absorbance peaks (cm^{-1})
Carbon dioxide (CO$_2$)	2345 and 650
Carbon monoxide (CO)	2175 and 2117
Methane (CH$_4$)	2913, 1533, 3018 and 1305
Sulfur dioxide (SO$_2$)	2512, 1360, and 1149
Hydrogen sulfide (H$_2$S)	1298
Ammonia gas (NH$_3$)	860
Hydrogen cyanide (HCN)	737

to the difference of pyrolysis characteristics. Jiang (2007) and Tan et al (2012) determined the chemical compositions of *Phyllostachys praecox* and masson pine, respectively, as shown in Table 1. They found that bamboo had higher contents of extractives and pentose, and lower contents of lignin and cellulose. It is well known that extractives and hemicelluloses (pentose) are more sensitive to thermal decomposition than cellulose and lignin. Therefore, bamboo has lower pyrolysis temperatures and higher mass losses. The thermal decomposition of coal was different from that of masson pine and bamboo and demonstrated two stages. In the first stage, the peak temperature corresponding to maximum of mass loss was located at about 456°C, representing the evolution of light hydrocarbons (Montiano et al 2016). A second stage of pyrolysis with 710°C of T_{max} represented the dissociation of strongly bonded carbonate salts (Li et al 2015). It was very obvious that coal had higher pyrolysis temperatures, indicating that the coal was more difficult to pyrolyze than biomass. This conclusion was consistent with previous results (Skodras et al 2007; Chen et al 2012).

In this research, the main gas compounds of fuels were determined by TG-FTIR. Table 2 shows that the main pyrolysis products included

1) carbon dioxide (CO$_2$) (corresponding to absorbance peak of 2345 cm^{-1} and 650 cm^{-1}); 2) carbon monoxide (CO) (corresponding to absorbance peak of 2175 cm^{-1} and 2117 cm^{-1}); 3) methane (CH$_4$) (corresponding to absorbance peak of 2913 cm^{-1}, 1533 cm^{-1}, 3018 cm^{-1}, and 1305 cm^{-1}); 4) sulfur compounds, including sulfur dioxide (SO$_2$), (corresponding to the absorbance peak of 1369 cm^{-1}) and hydrogen sulfide (H$_2$S) (corresponding to absorbance peak of 1298 cm^{-1}); 5) nitrogen compounds were composed of ammonia gas (NH$_3$) (corresponding to absorbance peak of 860 cm^{-1} and hydrogen cyanide [HCN] corresponding to absorbance peak of 737 cm^{-1}) (Zhang et al 2014).

The Release of Carbon Compounds

Carbon is a main compound for biomass and coal. Table 3 shows that the carbon content of bamboo, masson pine, and coal was 49.59%, 50.95%, and 73.90%, respectively. Conversion of carbon compounds is the most significant chemical event. In this research, the CO, CO$_2$, and CH$_4$ releases of masson pine, bamboo, and coal were determined in Fig 2. The CO$_2$ release of masson pine had a good linear correlation with temperature during the pyrolysis process. It was found that the CO$_2$ release of bamboo was similar to masson pine at the low-temperature zone (before 300°C). After 300°C, CO$_2$ release of bamboo was less than that of masson pine. When the temperature was up to 600°C, the variation of CO$_2$ released from bamboo materials was not significant. During the whole pyrolysis process, CO$_2$ release of coal was less than that of bamboo and masson pine. The CO release of masson pine also increased with increase in temperature before 750°C. After

Table 3. Char-C contents of samples in pyrolysis process.

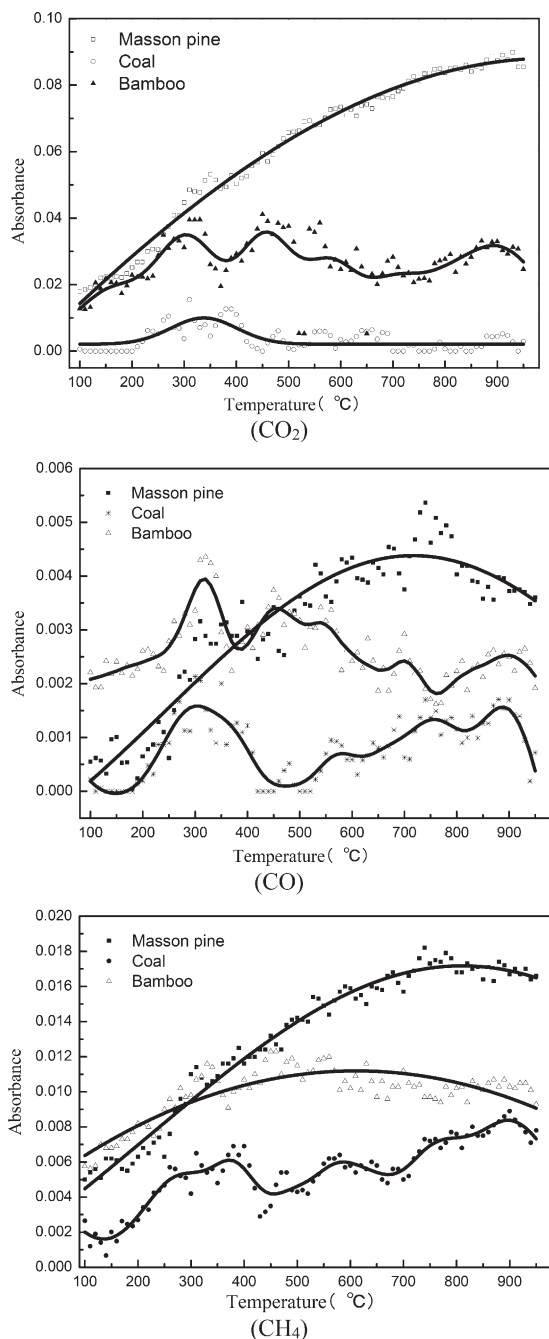| Samples	Char-C contents corresponding to different pyrolysis temperature (%)									
	Control	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C	1000°C
Coal	73.90	69.90	69.97	70.73	72.36	74.77	76.07	77.78	78.36	78.84
Masson pine	50.95	51.74	61.28	79.70	86.37	91.80	94.16	95.46	96.87	96.55
Bamboo	49.59	50.28	67.73	75.94	81.31	85.48	86.25	87.37	87.58	88.23

Figure 2. The releases of carbon compounds during pyrolysis process.

750°C, CO release of masson pine started to decrease up to 950°C. Bamboo had higher CO release compared with masson pine before 450°C. Coal had the lowest CO release. The variation of CO gas from coal was not significant during the pyrolysis process. CH_4 is an important type of greenhouse gas, which is 21 times more potent than CO_2 in terms of global warming impact (Sahu et al 2014). CH_4 release of masson pine increased with increase in temperature. Bamboo had a higher CH_4 release at the low-temperature zone (before 300°C). Similar with CO_2 and CO gases, coal had the lowest CH_4 release. This phenomenon was mainly due to different pyrolysis characteristics of bamboo, masson pine, and coal. The release of CO_2, CO, CH_4 mainly came from thermal decomposition of cellulose, hemicelluloses, and lignin in bamboo and wood. Previous researches (Yang et al 2005; Qu et al 2011; Wang et al 2011) showed that the CO_2 and CO mainly came from the cellulose and hemicelluloses, whereas the CH_4 came from the lignin. However, thermal decomposition of coal came from the oxygen-containing functional groups. According to the chemical composition of bamboo and masson pine, the CH_4 release of masson pine was more than that of bamboo when pyrolysis temperature was between 300°C and 900°C. Before 300°C, bamboo had more mass losses compared with masson pine. This resulted in higher CO_2, CO, and CH_4 release of bamboo at the low-temperature zone. During the whole pyrolysis process, the mass losses of coal were the lowest, resulting in the least release of carbon compounds. Table 3 shows the char-C contents of fuels corresponding to different pyrolysis temperatures. It was found that the char-C contents of all fuels increased with increase in pyrolysis temperatures, especially for masson pine and bamboo. The char-C contents of masson pine gradually increased from 50.95% to 96.55%. Similarly, char-C content of bamboo also increased from 49.59% to 88.23%. It was found that mass losses of bamboo and masson pine were, respectively, about 79% and 83% during pyrolysis process, whereas that of coal was only 18%. This resulted in different char-C
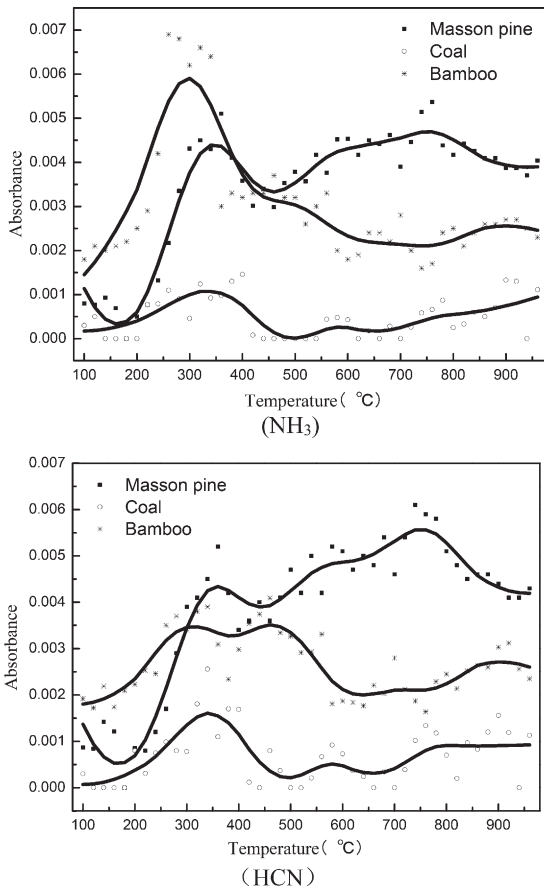
Figure 3. The releases of nitrogen compounds during pyrolysis process.

contents of bamboo, masson pine, and coal at different pyrolysis temperatures.

The Release of Nitrogen Compounds

The release of nitrogen compounds during fuel pyrolysis, combustion, or gasification process can result in a series of problems. The nitrogen-derived pollutants from fuel pyrolysis

or gasification were mainly NH_3 and HCN (Zhang et al 2013). HCN and NH_3 are also the main NO_X precursors, resulting in acid rain and photochemical smog. The NH_3 and HCN releases of masson pine, bamboo, and coal during pyrolysis process were shown in Fig 3. The effect of pyrolysis temperatures on the yields of NH_3 and HCN was investigated. It was found that bamboo had the highest NH_3 release at the low-temperature zone (before 350°C). The NH_3 from this stage mainly originated from the thermal decomposition of ammonium adsorbed or protein-type nitrogen in the fuels. NH_3 yields increased from about 100°C to 300°C and then decreased from 300°C to 450°C for bamboo. The main possibility for decrease in the NH_3 yields was attributed to the catalytic effect of minerals in the fuels, which converted NH_3 to N_2 at the high-temperature zone (Guan et al 2004). After 450°C, the change of NH_3 release of bamboo was not significant. When temperature was higher than 350°C, the NH_3 release of masson pine was more than that of bamboo. The trend of HCN release was similar to that of NH_3. Bamboo had the highest HCN releases at the low-temperature zone (before 300°C). When the temperature was higher than 300°C, masson pine had higher HCN releases. During the whole pyrolysis process, coal had the lowest NH_3 and HCN releases. Table 4 shows the char-N contents of fuels at different pyrolysis temperatures. It was found that masson pine had the lowest nitrogen content in its char. The char-N contents of masson pine increased from 200°C to 900°C, but decreased from 0.50% of 900°C to 0.46% of 1000°C. Bamboo had higher char-N contents than masson pine at each pyrolysis temperature. Coal had the highest char-N contents. But its char-N contents decreased when it was pyrolyzed.

Table 4. Char-N contents of samples in pyrolysis process.

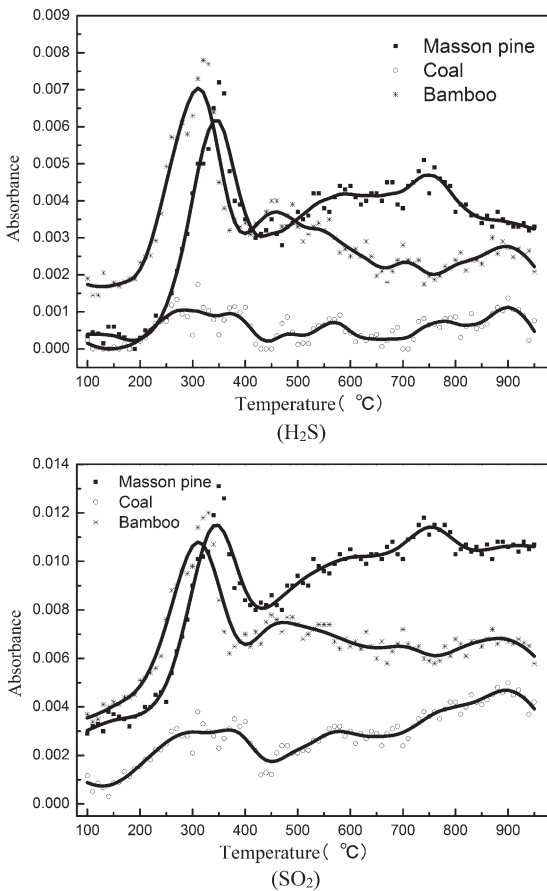| Samples	Char-N contents corresponding to different pyrolysis temperature (%)									
	Control	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C	1000°C
Coal	1.34	0.90	0.93	0.97	1.02	1.08	0.94	0.87	0.83	0.78
Masson pine	0.02	0.16	0.17	0.32	0.36	0.44	0.44	0.47	0.50	0.46
Bamboo	0.14	0.22	0.50	0.54	0.64	0.57	0.63	0.63	0.54	0.64

Figure 4. The releases of sulfur compounds during pyrolysis process.

The Releases of Sulfur Compounds

Sulfur emissions into the atmosphere have brought many problems, such as acid rain, corrosion of equipment, and serious environmental pollution. Pyrolysis, as a method of precombustion desulfurization of fuel, is an effective approach to control sulfur emission in fuel utilization (Zhao et al 2012). The H_2S and SO_2 releases of masson pine, bamboo, and coal during pyrolysis process were shown in Fig 4. It was found that bamboo had higher sulfur releases than masson pine at the low-temperature zone. The peak temperature corresponding to maximum H_2S release was 320°C for bamboo and 350°C for masson pine. Similarly, the peak temperature of maximum SO_2 release was 300°C for bamboo and 330°C for masson pine. Because the sulfur compounds in biomass were distributed between organic and inorganic compounds, a two-step mechanism of sulfur release could be observed. First, the sulfur would be in a gaseous phase when pyrolysis of fuels occurred at the low-temperature zone. Then, it could become a stabilized solid phase after compounding with K and Ca at the high-temperature zone. The coal was anthracite, which contains more fixed carbon and less S, and that is why coal had the lowest H_2S release during the pyrolysis process. Table 5 shows the char-S contents of fuels. It was found that char-S contents of bamboo and coal increased with increase in pyrolysis temperatures.

CONCLUSION

The main pyrolysis products of fuels included carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), ammonia gas (NH_3), and hydrogen cyanide (HCN). Compared with masson pine, bamboo had a higher amount of gas release and more mass loss at lower temperatures, especially lower than 350°C of temperature. This is due to the higher amount of hemicellulose and extractives found in bamboo than in masson pine. Overall, coal had the lowest gas release due to its higher pyrolysis temperature, and

Table 5.　Char-S contents of samples in pyrolysis process.

Samples	Char-S contents corresponding to different pyrolysis temperature (%)									
	Control	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C	1000°C
Coal	0.53	0.85	0.85	0.82	0.94	0.90	0.92	0.98	0.99	1.02
Masson pine	—	—	—	—	—	—	—	—	—	—
Bamboo	0.02	0.16	0.24	0.28	0.31	0.30	0.32	0.32	0.36	0.34

therefore the lowest mass loss. The char-C, N, and S contents of all fuels increased with increase in pyrolysis temperature.

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