

RESEARCH ARTICLE | AUGUST 03 2017

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AIP Conf. Proc. 1864, 020116 (2017)

<https://doi.org/10.1063/1.4992933>



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Effect of High-pressure on Pine Sawdust Pyrolysis: Products Distribution and Characteristics

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Abstract. In this work, the pressurized pyrolysis of pine sawdust was performed with a self-made pressurized pyrolysis reactor to investigate the influence of pyrolysis pressure in the range of 0-5 MPa on products distribution and characteristics. The combustion feature and microstructure of bio-char had analyzed by thermogravimetric (TG) and scanning electron microscopy (SEM), respectively. Elemental analyzer and Fourier transform infrared spectroscopy (FTIR) were used to confirm the identities of bio-oil. The results indicated the pressure had a notable impact on the biomass pyrolysis, which promoted the secondary cracking of bio-oil to produce more gaseous products and bio-char. The minimum bio-oil yield of 20.24% was obtained at the pressure of 5 MPa. Furthermore, the pressure improved the products characteristics. The increasing of pressure was favour to the deoxygenation and dehydrogenation reactions of bio-oil, which led to the increase of CH₄, H₂ and CO₂ in gas. At the same time, under the influence of pressure, the surface structure and compactedness of the bio-char were obviously improved.

Keywords: Pine sawdust, pressurized pyrolysis, bio-oil, bio-char.

INTRODUCTION

Biomass pyrolysis is a promising technology, which converts biomass into bio-oil with combustible gas and bio-char generation [1, 2]. However, normally the bio-oil was not exhibited preferable combustion characteristic, and frequently it brought about the blocking and fouling problems in the equipment. Therefore, the modification or transformation of bio-oil was crucial and attractive [3]. Pressurized pyrolysis was reported to enhance the bio-oil transformation and improve the characteristics of products [4-6], but most of the current research focused on the effect of lower pressures (0-2 MPa) on biomass pyrolysis, and these studies were mainly carried out by thermogravimetric (TG) analyzer [7, 8]. The systematic experimental studies are relatively insufficient.

In this study, the biomass pyrolysis was conducted at high-pressures (0-5 MPa) by the independently designed device. A series of experiments were carried out to determine the influence of pressure on product distribution with special focus on the bio-oil transformation. Meanwhile, the characteristics of products, including gas, bio-oil and bio-char, were analyzed to demonstrate the effect of high-pressures on bio-mass pyrolysis.

MATERIALS AND METHOD

Raw Material

The biomass used in this study was pine sawdust, which was dried at 60 °C and screened through 40 and 60 mesh sieves. The properties of pine sawdust are shown in Table 1.

TABLE 1.The properties of pine sawdust

	Proximate Analysis (wt%) ^{ad}				Ultimate Analysis (wt%)				HHV (MJ·kg ⁻¹)
	Moisture content	Volatile matter	Fixed carbon	Ash	C	H	O ^a	N	
Pine sawdust	1.62	83.43	13.52	1.16	47.86	6.66	44.22	0.12	19.40

^{Ad} Air dried; a By difference.

Experimental Device

The pressurized pyrolysis device was independently designed. As shown in Fig. 1, the main parts of the device are reactor body, feeding canister, counterbalance unit and heater. The reaction pressure is automatically controlled by the counterbalance unit at the designated pressure. When the inner temperature of the reactor reaches 600 °C, Pine sawdust pre-filled in feeding canister was blown into the reactor by nitrogen with slightly higher pressure than the inner. The reactor was filled with 11 g of samples and different pressures from 0 to 5 MPa were investigated. The temperature, heating rate and solid resistance time were held at 600 °C, 10 °C/s and 7min, respectively.

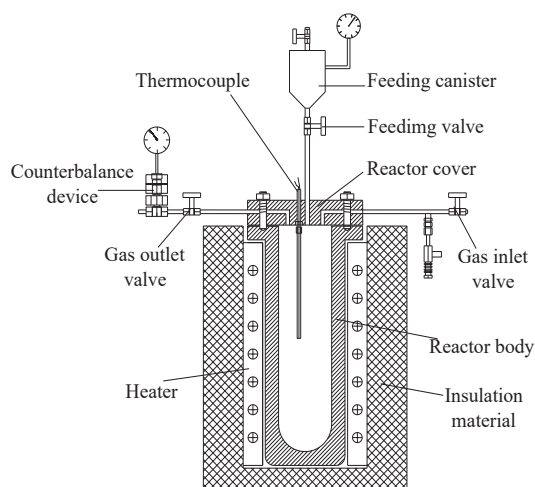


FIGURE 1. Structure diagram of the pressurized pyrolysis reactor

Analytical methods

The products, including gas, bio-oil and bio-char, were analyzed. The composition of gas was analyzed by gas chromatograph (MicroGC490, Agilent, USA). The moisture content, volatile matter and fixed carbon content were determined by automatic proximate analyzer (SDTGA5000, Sundry, China). The C, H and N content of the materials and bio-oil were analyzed using an element analyzer (Vario EL, Germany). Fourier transform infrared spectroscopy (FTIR) (EQUINOX55, Germany) was used to confirm the identities of bio-oil. The combustion feature of bio-char was analyzed by thermogravimetric (TG) with increasing temperature programming from 25 °C to 800 °C at rate of 10 °C /min. The Microstructure was observed by scanning electron microscopy (Hitachi S-4800, Japan).

RESULTS AND DISCUSSION

Products Distribution

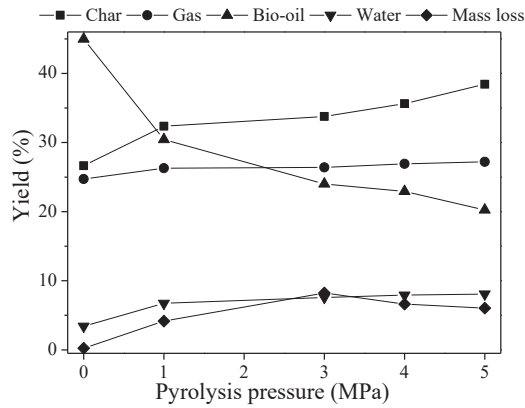


FIGURE 2. Effect of pyrolysis pressure on products distribution

Figure 2 presented the products distribution of pine sawdust pyrolysis under different pressures. Due to the adherence of reactor wall and condenser, less than 9% of the total mass was uncollected, which has negligible influence on the tendency of products distribution. It was noted that the yield of bio-oil decreased significantly from 44.97% to 20.24% along with the increase of pyrolysis pressure, and the yields of char and gas increased conversely, which indicated that the high pressure promoted the bio-oil decomposition, including polycondensation, dihydroxylation and cracking reaction, and enhanced the transformation into gas and solid phase with water generation, which was in agreement with the study of Newalla^[4]. Furthermore, it was noticed that higher pressures (above 3 MPa) did not promote the gas and bio-char formation effectively, and it might be attributed to the accomplishment of bio-oil decomposition in the lower pressures. It was confirmed that high pressure above 3 MPa was not essential for biomass pyrolysis.

Effect of Pyrolysis Pressure on Products Characteristics

Bio-Oil Characterization

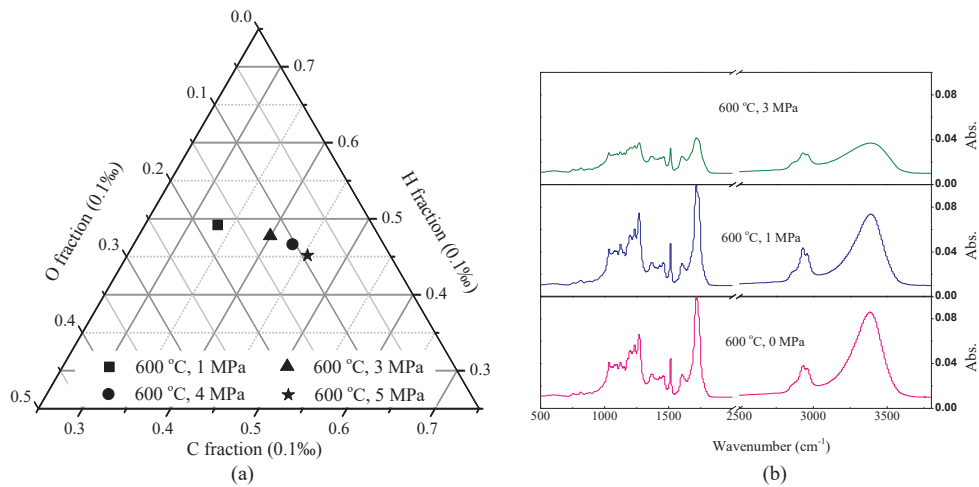


FIGURE 3. The compositions of major elements (a) and FTIR spectra (b) of bio-oil at different pyrolysis pressure

As mentioned above, the high pressure enhanced the bio-oil transformation. In order to further confirm the positive effect of pressure, characteristics of the bio-oil in pressurized pyrolysis was investigated. It is well known that high oxygen content is a major limit in the utilization of bio-oil as a fuel [9]. The results of ultimate analysis showed that the O content decreased from 17.54% to 9.36% along with the increase of pyrolysis pressure from 1 MPa to 5MPa, which indicated that the high pressure promoted the deoxygenation of bio-oil and the combustible performance of the bio-oil was improved. Furthermore, the H content decreased coincided with the O content decrease, which led to the increase of water generation in the products as shown in Figure 2. In addition, the FTIR analysis was conducted for further investigation of the functional groups change of the bio-oil. And it was proved that the high pressure promoted the secondary cracking of bio-oil with the less complex peaks observed. Meanwhile, the peak area of the same characteristic peak was reduced, e.g. the C-O stretching vibration peak at 1271 cm^{-1} and the aromatic skeleton (=C-H) stretching vibration at 3000-3020 cm^{-1} , which was coincided with decrease of O and H contents. The results indicated that high pressures contributed to the modification of bio-oil simultaneously.

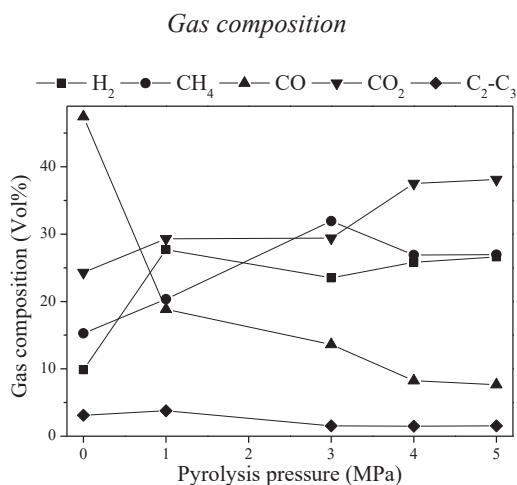


FIGURE 4. Effect of pyrolysis pressure on gas composition

The high pressure improved the gas generation, and the gas composition was analyzed to investigate the modification of pressure (Figure 4). It was indicated that CO was the main component of pyrolysis gas in the atmospheric pressure (0 MPa), which reached 47.45%. When the pressure increased, CO content decreased below 20%, and the decrease at the low pressure of 1 MPa was the most significant. On the other hand, the CH₄, H₂ and CO₂ contents increased conversely, which accounted for the decrease of H and O contents in bio-oil. It seemed that the high pressure promoted the CO₂ formation by enhancing the decarboxylic reaction with oxygen combination. In addition, the H₂ and CH₄ contents were enhance by high pressure, which contained high combustible potential. In summary, it was indicated that the high pressure modified the gas composition and improved its combustible potential.

Bio-char characterization

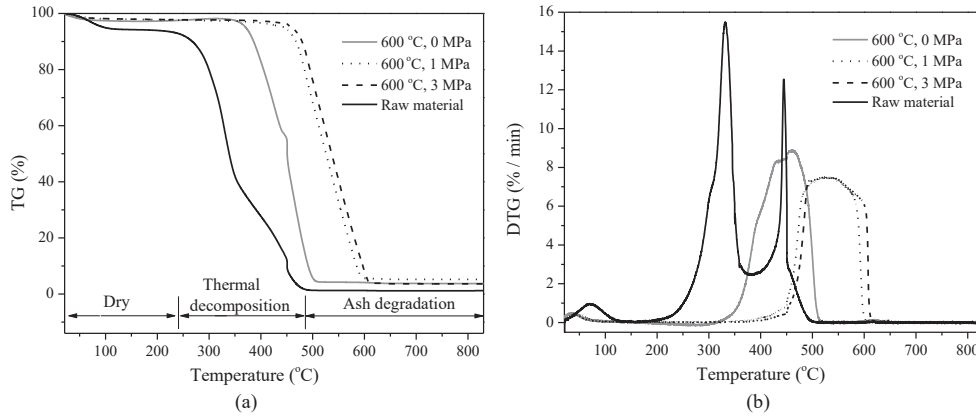


FIGURE 5. TG (a) and DTG (b) curves of pine sawdust and biochars obtained at different pyrolysis conditions

Due to the high pressure, yield of bio-char, which was an indispensable product, was also promoted. Normally, bio-char can be used as high quality fuel and good adsorbent [10]. To evaluate the combustion feature of bio-char as potential solid fuel, TG analysis of bio-char were conducted (Figure 5). The weight loss of all samples was between 91.53% and 96.64% at the thermal decomposition stage. After pyrolysis, the organic matter such as cellulose and lignin in the solid residue was greatly reduced, which should presented specific peak of weight loss at 250-350 °C as raw material [11]. Therefore, the thermal decomposition stage of the bio-char moves obviously to the high temperature region. In pressurized pyrolysis, the peaks of weight loss shifted to the range of 480-600 °C, which was higher than the non-pressurized pyrolysis. The result indicated that the high pressures improved the thermostability of the bio-char, which might not be suitable for utilization as a fuel. In addition, it was noted that the pressures of 1 MPa and 3MPa had no significant difference in weight of the bio-char, which further confirmed that the low pressurized pyrolysis was feasible without consumption of high pressure.

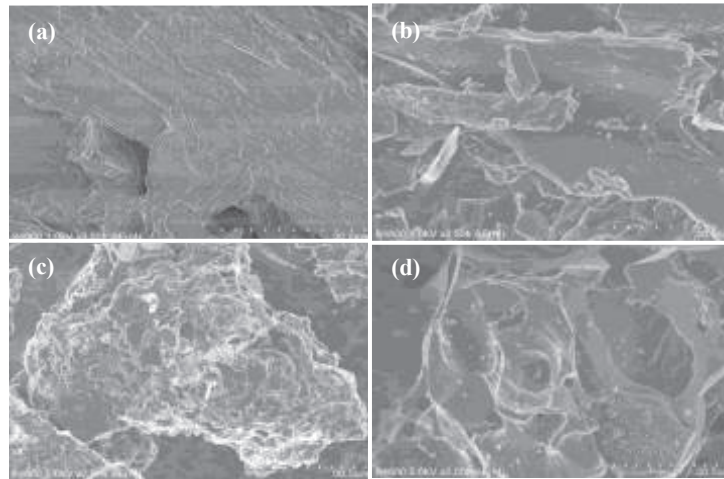


FIGURE 6. SEM picture of pine sawdust and biochar obtained at different pyrolysis pressure ((a): Pine sawdust; (b): 600 °C, 0 MPa; (c): 600 °C, 1 MPa; (d): 600 °C, 3 MPa)

In order to evaluate the feasibility of bio-char using as adsorbent, the surface structure was analyzed (Figure 6). It was observed that the expansion of bio-char was increased with more obvious protrusion along with the pressure increasing, and eventually it formed a rich irregular pore structure. The image of Figure 6(a) showed that the surface of the pine sawdust was relatively smooth with complete skeleton, and the internal structure was compact. In atmospheric pyrolysis, the solid product was difficult to maintain the original skeleton structure due to the

degradation of pine sawdust. Therefore, the bio-char broken into irregular, amorphous fragments as shown in Figure 6(b), and its surface is still relatively smooth. However, when the pyrolysis pressure increased to 1 MPa and 3 MPa, the bio-char was dilated severely and formed a lot of convex spherical bubbles without irregular fragments observed, which indicated that the pressure improve the bio-char compactedness and surface structure. In addition, the bio-char in higher pressure presented more expansion in the bio-char. The effect of the pressure on the inner structure of bio-char was still indefinite, which needed further investigation. However, the improvement of pressurized pyrolysis was obvious contrast with atmospheric pyrolysis. The high pressure promoted the surface expansion and compactedness of bio-char, which presented great potential for absorbent utilization.

CONCLUSION

The pressure had a notable impact on the biomass pyrolysis, which promoted the bio-oil transformation (from 44.97% to 20.24%) and gas and bio-char generation. Furthermore, the pressure improved the products characteristics. The pressures enhanced the deoxygenation and dehydrogenation reactions of bio-oil, which led to the increase of CH₄, H₂ and CO₂ in gas. In spite of the unimproved combustible performance of bio-char, the high pressure improved the bio-char surface structure and compactedness.

ACKNOWLEDGMENTS

The authors gratefully appreciate the financial support from the National Water Pollution Control and Management Technology Major Projects (No. 2012ZX07202003-004), Fundamental Research Funds for the Central Universities (DUT16LAB04) and Liaoning Natural Science Foundation (201602182).

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