BIOMASS PYROLYSIS WITH BIO-OIL RECYCLE TO INCREASE ENERGY RECOVERY IN BIOCHAR

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ABSTRACT: This study aims at increasing char yield by recycling bio-oil without negative impact on char qualities, i.e. carbon content and heating value. Pyrolysis experiments on spruce and birch chips were carried in a macro-thermogravimetric analyzer. To examine the effect of bio-oil recycle, dried raw woodchips, pure bio-oil, and woodchips impregnated with bio-oil (10, 20 and 25% on mass basis) were compared. The experiments were carried out by introducing sample into the reaction zone with the flow of N_2 and at the temperature range of 300 to 600 ˚C. Pyrolysis of the bio-oil impregnated woodchip gave higher char yield than the pyrolysis of raw woodchip. By the 20% (m/m) bio-oil impregnation, char yield increased by 18.9% (spruce) and 19.1% (birch) on average from the raw woodchip pyrolysis. In addition, the char yield from bio-oil impregnated woodchips was higher than the interpolated char yield of raw woodchips and bio-oil, indicating that synergy effect exists by bio-oil impregnation compared with mere recycling of bio-oil. However, high heating rate corresponded to high temperature pyrolysis, i.e. above 400 ˚C, created cavities and breakages on woodchips, which minimized the secondary reaction. Neither carbon content nor heating value of char was influenced by bio-oil impregnation. Energy yield also showed improvement by increasing bio-oil recycling ratio. For example, energy yield of char from woodchips at the temperature of 340 ˚C increased from 48.4% with raw woodchips to 64.5% by woodchips with 25% of bio-oil impregnation.

Keywords: pyrolysis, biomass, biochar, bio-oil, blast furnace

1 INTRODUCTION

Global production of crude steel is expected to increase by 50% in 2050 in response to the increase of steel demand [1]. Energy consumption in steel industry is one of the most energy intensity, which consume averagely 20 GJ of energy per ton of crude steel [2]. Moreover, CO_2 emission from steel industry accounts for 6.7% of the global CO_2 emission [2]. In order to reduce consumption of fossil fuels and amount of CO_2 emission, biochar is a potential alternative fuel to introduce in blast furnaces. Biochar is the solid product obtained from pyrolysis. Pyrolysis is applied to convert biomass into carbonized solid and volatiles by heating in the absence of oxidizing agent. High values of carbon content and heating value in biochar made it comparable to coal and coke used in blast furnaces.

Due to requirements of blast furnace, biochar is recommended to have high carbon content, low volatiles, low ash content, high heating value, and satisfied mechanical properties [3]. Consequently, process parameters in pyrolysis such as temperature, heating rate, residence time, pressure, and particle size are crucial in particular to achieve high quality of biochar. Among the parameters, temperature is the most influenced parameter on biochar quality and yield. Increasing of pyrolysis temperature leads to produce better quality of biochar, i.e. higher carbon content, lower volatiles, lower ash content, and higher heating value. Whereas, biochar yield is lower when pyrolysis temperature is high, which correspond to poor economic performance of the pyrolysis processes.

To overcome the trade-off in pyrolysis temperature, an effort on increasing of biochar yield while maintaining its properties is required. It has been reported that residence time of volatiles plays an important role in mass yield of biochar. Longer residence time of the volatiles, influenced by high pressure, large particle size, and low gas flow rate, promotes the secondary reaction between volatiles and the char surface inside pore structure of solid residue [4][5].

The secondary reactions are likely to be promoted by pyrolysis volatile or bio-oil recycling, which can more undergo charring on the surface of biochar [6]. Hill et al. [7] investigated that biochar yield from pyrolysis of Aspen wood chips can be elevated by increasing concentration of pyrolysis volatile in woodchips bed during pyrolysis. Their result at pyrolysis temperature of 450 ˚C shows that char yield obtained from the bed with additional volatile is 26.9% by mass, while the normal bed gave char yield at 24.6% by mass. Moreover, the authors also found that deposition of volatile on biomass during pyrolysis do not result negative impact on microporosity and adsorption properties of biochar [7].

The aim of the present research is to increase mass/energy yield of biochar without negative effect on biochar quality. Bio-oil deposition on woodchip is the objective method to pursue the goal of this research. Changes of biochar yield were studied via a macro-thermogravimetric analyzer. Pyrolysis in oxygen-free isothermal environment was conducted. Characteristics of biochar such as carbon content and heating value were measured in particular to represent influence of pyrolysis conditions on biochar properties.

2 EXPERIMENTAL METHODS

2.1 Materials and preparation

Debarked chips of Norway spruce and birch were selected to study in this work. Dried woodchips were prepared in an oven at 105 ˚C for 24 hours. Fast pyrolysis oil was represented as bio-oil in this study. Characteristics of woodchips and bio-oil can be found in Table I.

Impregnated woodchips were prepared from dried woodchips covered by bio-oil before pyrolysis experiment. In the based case, impregnated woodchips with 20% (m/m) of bio-oil were prepared. In addition, 10 and 25% (m/m) of bio-oil impregnated woodchips were also prepared to study in selected temperatures.

Table I: Characteristics of raw materials

Characteristics	Unit	Spruce	Birch
Moisture content	%		
Before drying		3.1	2.8
After drying		0.4	0.1
Ultimate analysis	%, dry		
Carbon		49.5	47.1
Hydrogen		6.1	6.2
Nitrogen		0.25	0.27
Oxygen		42.8	43.6
H/C molar ratio	-	1.48	1.58
O/C molar ratio		0.65	0.69
HHV	MJ/kg	19.72	18.25

*% in mass basis

2.2 Experimental apparatus and method

Pyrolysis experiments were carried out in a macro-thermogravimetric analyzer. This method generally gives accessibility to measure mass decay of large particles during thermochemical conversion. The reactor is externally-heated cylinder made of stainless steel with internal diameter of 100 mm and 450 mm of length. Maximum temperature of the reactor is 900 ˚C. A wire mesh crucible, or ceramic crucible in case of liquid sample, connected with a precision balance is hung from the top of the reactor chamber, while type K thermocouple is placed at the center of the heating chamber to measure reactor temperature. Carrier gas can be fed into the reactor from the bottom and leave through the vacuum line at the top with volatiles generated during experiment. The schematic diagram of the macro-thermogravimetric reactor is shown in Fig. 1.

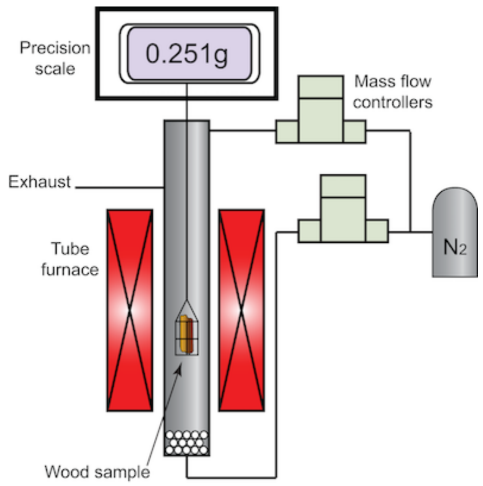

Figure 1: Macro-Thermogravimetric experiment

The samples, i.e. dried woodchip, pure bio-oil, and 20% (m/m) bio-oil impregnated woodchip, were individually introduced into reacting zone under inert atmosphere with N_2 (≥ 99.9995%) flow rate of 7 l min^{-1} at standard state. Experiments were carried out at isothermal temperatures of 300, 320, 340, 360, 380, 400, 425, 450, 500, 550 and 600 ˚C. Additional experiments were carried out with 10% and 25% (m/m) of bio-oil covered on woodchips at 300, 340, 400, and 500 ˚C to observe the effect of bio-oil content on char yield.

Char yields from different tests were calculated by

$$y_c = \frac{m_c}{m_w} \times 100\% \quad (1)$$

where, y_c is char yield (-), m_c is mass of char product (g), and m_w is mass of initial wood (or initial bio-oil in pure bio-oil experiments) (g).

2.3 Characterization of samples

Ultimate analysis, C, H, N and O content, of original woodchips, bio-oil, and biochar were examined via elemental analyzer, Euro EA3000. Higher heating value (HHV) of samples were measured by oxygen bomb calorimeter, IKA C200.

3 RESULTS AND DISCUSSION

3.1 Biochar yield

The yields of biochar produced at different temperature are shown in Fig. 2. In pure bio-oil pyrolysis, biochar yield decreased as temperature increased, which also means high heating rate, and stayed in plateau after pyrolysis temperature of 450 ˚C. The range of char yield produced from pure bio-oil pyrolysis is between 9.9% and 22%. In case of dried spruce and birch, char yield decreased continuously as the pyrolysis temperature increased, and spruce gave higher char yield than birch at all pyrolysis temperatures. Pyrolysis of spruce gave maximum char yield of 37.7% and minimum char yield of 18.5%. Meanwhile, 33.5% and 15.8% were maximum and minimum char yields from pyrolysis of birch.

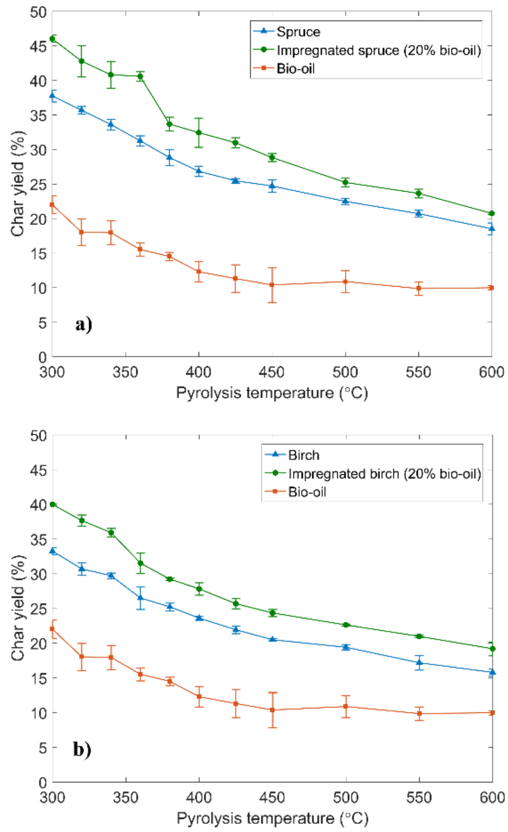

Figure 2: Char yield (mass basis) from isothermal pyrolysis at various temperature (a) spruce (b) birch

Impregnation of bio-oil on either spruce or birch chips gave higher char yield after pyrolysis than the result obtained from pyrolysis of dried materials. In spruce, char yield from pyrolysis of 20% (m/m) bio-oil covered on spruce had averagely 5.4% of char yield higher than pyrolysis of dried spruce. Likewise, average char yield increase by impregnation of bio-oil on birch was 4.6%. In this experiment, maximum char yield of 46.1% was obtained from pyrolysis of 20% (m/m) bio-oil impregnated spruce at temperature of 300 ˚C.

Char yields at various ratios of bio-oil impregnated on woodchip are represented in Fig. 3 for the temperature of 300, 340, 400, and 500 ˚C. Char yields in Fig. 3 are calculated by the ratio between final mass and total initial mass, which can be written by

$$\tilde{y}_c = \frac{m_c}{m_w + m_{bio-oil}} \times 100\% \qquad (2)$$

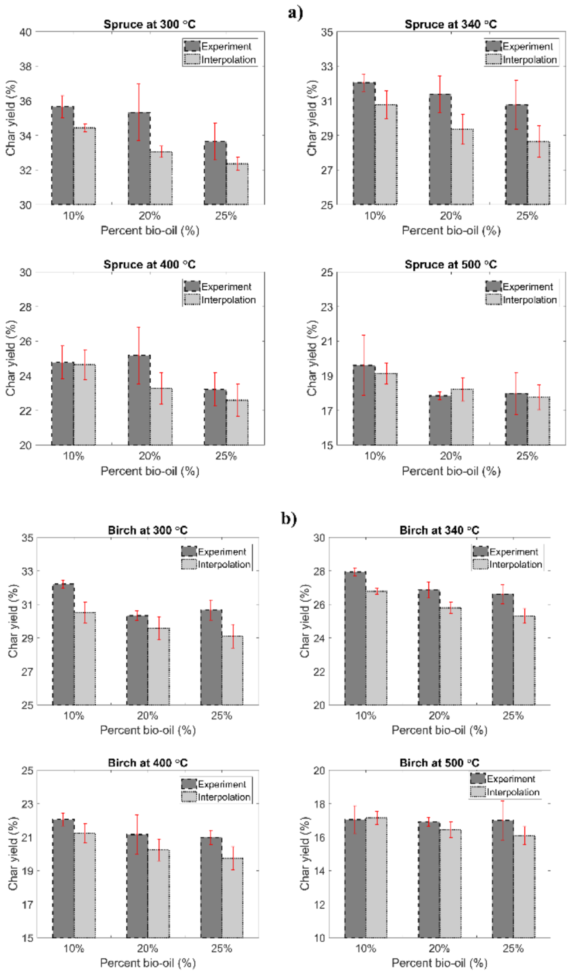

Figure 3: Comparison of char yields (mass basis) from isothermal pyrolysis of impregnated woodchip with different bio-oil ratio (a) spruce (b) birch

Higher ratio of bio-oil on woodchip gave lower char yield, because bio-oil pyrolysis generates char less than woodchip pyrolysis, according to the char yield result in the first section. At the temperature of 300 and 340 ˚C in both spruce and birch, the values of char yield interpolated from pyrolysis experiments of pure bio-oil and pure woodchip were significantly lower than experimental values. This means increasing of char yield by impregnation of bio-oil on woodchip caused by not only additional char from bio-oil but also synergy reaction promoted by bio-oil deposition on woodchip.

Nevertheless, the synergy effect did not significantly appear in pyrolysis at 400 and 500 ˚C. The reason of the diminished synergy effect could be explained by the physical changes as apparent from sample photos in Fig. 4. As observed from Fig. 4, increase of pyrolysis temperature, hence heating rate, led to physical disintegration of char particles. In case of spruce, char samples produced at 300 and 400 ˚C remained intact, while cracking and cavities were observed in spruce chars obtained at higher pyrolysis temperature. This behavior was also observed in birch; chars obtained at high pyrolysis temperature were fragmented into smaller pieces. Physical disintegration of woodchips during pyrolysis at high temperature/heating rate allowed volatile products including deposited bio-oil to be released from pore structure of woodchip and minimized the secondary reaction. Therefore, synergy effect between woodchip and bio-oil was not apparent in pyrolysis at high temperature, i.e. high heating rate.

Figure 4: Visual appearance of char produced from pyrolysis at different temperature

3.2 Characteristics of biochar

3.2.1 Ultimate analysis

Elemental compositions of biochar samples were measured (C, H, N, and O). The elemental content of biochar produced from spruce and birch are represented in Fig.5 a) and b), respectively. After pyrolysis, higher carbon content was obtained in biochar. In dry spruce, carbon content increased from 49.5% to the range between 72.5 and 89.7%. Meanwhile, carbon content of birch char increased from 47.1% to the range between 72.5 and 88.4%. High pyrolysis temperature led to biochar with higher carbon content and lower hydrogen and oxygen content. Biochar samples produced from bio-oil impregnated woodchip, 20% (m/m), contain similar amount of C, H, N, and O as char from dry materials. This means impregnation of bio-oil on woodchip had minor effect on elemental content of biochar.

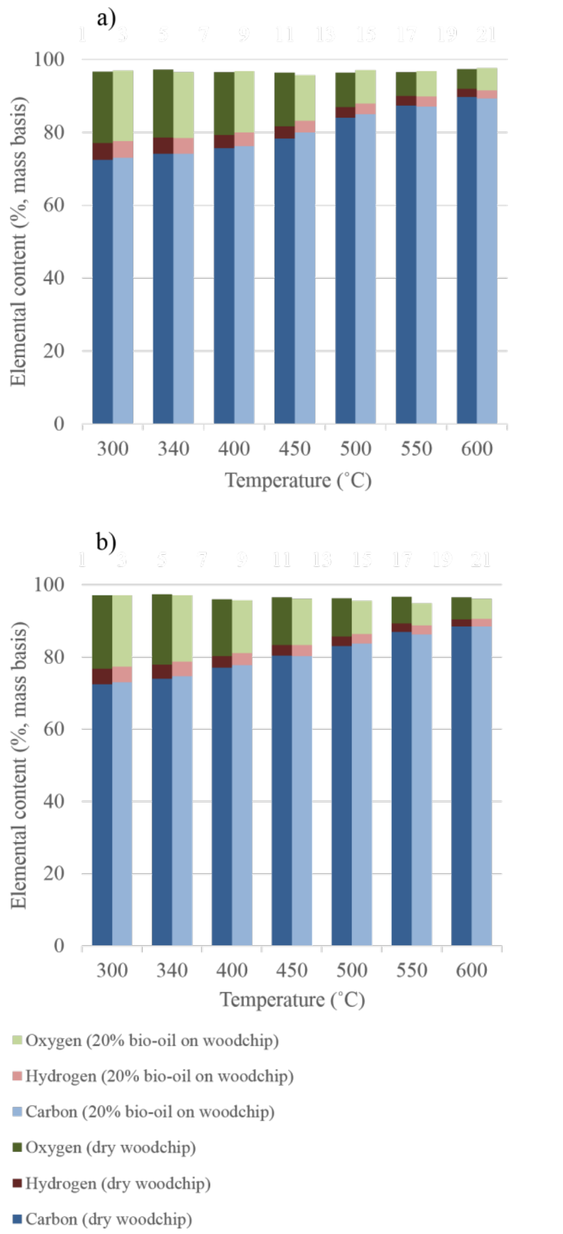

Figure 5: Mass content of C, H, and O in biochar samples (a) spruce (b) birch

3.2.2 HHV

According to HHV results of biochar represented in Fig. 6, heating value of biomass materials improved after pyrolysis. The heating value of char seems to increase by raising pyrolysis temperature. The range of HHV measured from spruce char was between 28.5 MJ/kg and 33.8 MJ/kg, which is approximately 45 to 72% increase from the original spruce. In birch, minimum and maximum HHV of char are 28.1 MJ/kg and 33.5 MJ/kg, respectively, or 54 to 84% higher than HHV of the original birch. Deposition of bio-oil on woodchip did not influence significant impact on HHV of biochar.

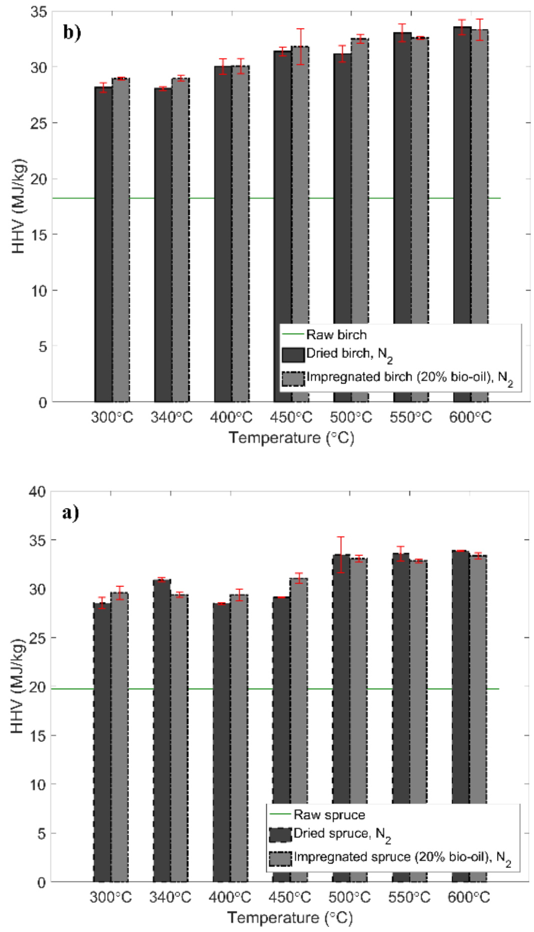

Figure 6: HHV results of char from pyrolysis at different temperature (a) spruce (b) birch

3.3 Energy recovery by bio-oil recycle

Acording to char yield and HHV obtained from the experiments, energy yield of pyrolysis at different conditions can be calculated by

$$y_E = y_c \frac{HHV_c}{HHV_w} \times 100\% \quad (3)$$

where, y_E is energy yield (-), *HHV* is higher heating value (MJ/kg), *c* and *w* are represented for char and wood respectively.

Energy yield calculated by the results from pyrolysis of spruce at 340 ˚C is shown in Fig. 7. Increasing of bio-oil ratio on woodchip improved energy yeild of char product. By 25% impregnation of bio-oil on woodchip, energy yield of char increases from 48.4% to 64.5%.

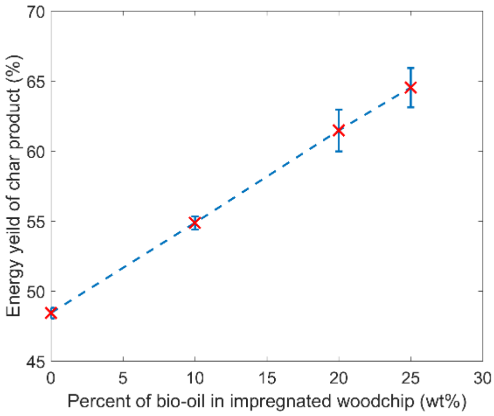

Figure 7: Energy yield of char produced at 340 ˚C with variety of bio-oil ratio

Comparison of energy balance between typical pyrolysis of dry woodchip and pyrolysis with bio-oil recycle process can be illustrated by Fig. 8. The result shows that pyrolysis with bio-oil recycle (25% of total feed) is expected to increase energy value of biochar by 35.4% from typical pyrolysis process.

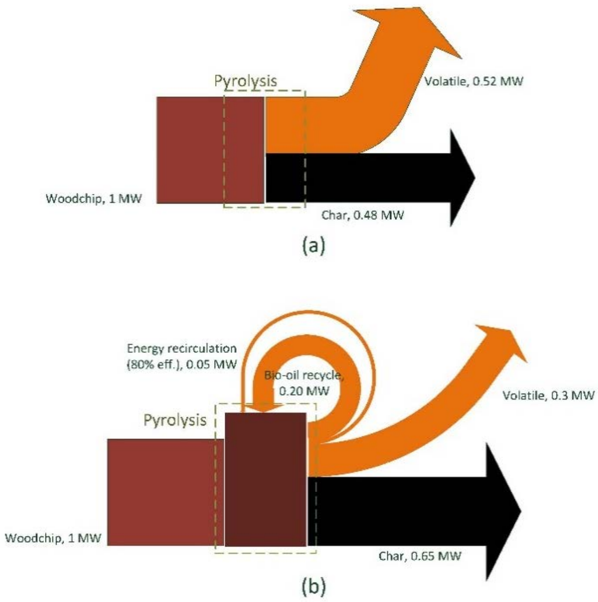

Figure 8: Energy balance (a) pyrolysis without bio-oil recycle at 340 ˚C (b) pyrolysis with 25% (m/m) bio-oil recycle at 340 ˚C

4 CONCLUSIONS

Pyrolysis of spruce and birch were studied in this work in particular to elevate char yield by bio-oil recycle. Impregnation of 20% (m/m) bio-oil on surface of dry woodchip was selected as the base case to compare char yield after pyrolysis with dry woodchip and pure bio-oil. On average, yield of biochar increased by the bio-oil impregnation 5.4% and 4.6% for spruce and birch, respectively. Synergy effect caused by secondary reaction between bio-oil and biomass was indicated by experimental results of additional impregnated bio-oil ratio woodchips (10 and 25%) pyrolysis. However, synergy effect did not appear at high pyrolysis temperature because of creation of cavities and breakage by high rate of heating.

Properties of biochar such as elemental content and higher heating value were measured. Increasing of pyrolysis temperature led to biochar with higher quality. Nevertheless, impregnation of bio-oil did not have significant impact on carbon content and HHV of biochar.

Energy yeild calculated from yield of biochar and HHV shows that by 25% bio-oil impregnation on woodchip, energy yield of char increased from 53.4% to 62.2%. As explained from the calculation of energy balance, pyrolysis with bio-oil recycle can be applied to increase performance of char production and more favorable to produce biochar from pyrolysis of biomass.

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