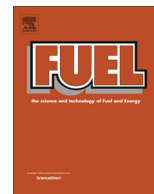




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Comparison of oil-tea shell and Douglas-fir sawdust for the production of bio-oils and chars in a fluidized-bed fast pyrolysis system

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ABSTRACT

Oil-tea shell, a fertilized agro-waste, was compared with Douglas-fir sawdust, a non-fertilized woody waste, for the production of bio-oils and chars in a fluidized-bed fast pyrolysis system. Comparison of the metal contents in biomass, derived bio-oil and bio-char indicated that most of the metals retained in the char after the fast pyrolysis process. The bio-oils were almost free of metals. The water contents of oils from Douglas-fir-sawdust and oil-tea-shell were as high as 23.8 wt.% and 38.1 wt.%, respectively. Combustion of water-fuel emulsion, formed by the high moisture content of Douglas-fir-sawdust oil (11 wt%) mixed in the heavy fuel oil (89 wt%), led to the lower NO_x emission of 231 ppm@6% O₂ as compared to 265 ppm@6% O₂ of 100 wt% heavy-fuel-oil combustion. The water-fuel-emulsion suppressed the peak flame temperature in boiler and hence reduced the thermal NO_x emission. To elucidate the metal-concentrated effect from biomass to char, a measured R_c was defined as the ratio of the metal content in char to the metal content in biomass. The average measured R_c from oil-tea-shell and Douglas-fir-sawdust chars were 8.3 and 8.0, respectively. A simple predicted R_c was proposed based on the bio-char yield. The predicted R_c for oil-tea-shell and Douglas-fir-sawdust chars were 7.7 and 8.9, respectively which were in agreement with the results of average measured R_c . The predicted R_c will be useful for the provision of additional information to double checking the measured metals in bio-char obtained from the fast pyrolysis process when bio-oil contained very low metal contents. The oil-tea-shell char contained a very high potassium content of 12,700 mg kg⁻¹ due to the metal-concentrated effect from biomass, making it suitable for soil amendment but unqualified for energy application. Both the Douglas-fir-sawdust and oil-tea-shell oils with low sulfur content, almost free of metal and water-fuel-emulsion effect, can be considerable as potential fungible fuels for energy application, but necessary precautions should be taken to against the low pH value of the bio-oils which they may corrode the facility.

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1. Introduction

Concerns over climate change related to carbon emissions are a great challenge for researchers. To reduce the carbon dioxide emissions, it is imperative to use sustainable fuels instead of fossil fuels. Biofuel considered as a carbon-neutral fuel has been attracting intense attention lately as a potential renewable energy source for replacing part of the fossil fuels and reducing dioxide emission. There are some technologies that can convert biomass into biofuel. Among these, fast pyrolysis technology, a thermo-chemical process, is a promising technology for converting biomass into an alternative fuel oil or solid fuel [1]. Many biomass materials can be considerable for the production of bio-oil and bio-char by fast

pyrolysis technology. Demirbas [2] reported that the wood and woody materials tend to be low in ash contents while the agricultural materials can have high ash content. The high ash contents in agricultural materials arise from fertilizers. Most fertilizers contain high alkali and alkaline earth metals, while taken by plants they form nutrients in plants and finally become ashes in biofuel combustion. It is well studied that alkali and alkaline earth metals, in combination with other fuel elements such as silica and sulfur, and facilitated by the presence of chlorine, are responsible for many undesirable reactions in combustion furnaces and power boilers [3]. Most studies of the fast pyrolysis technologies focused on the conversion of biomass into bio-oil, char and the subsequent upgrading of the bio-oil [4]. Research for analyzing the ash contents in bio-oil and bio-char [5] and the consequent effects on application is limited.

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In this study, it is therefore interesting to compare the oil-tea shell, a fertilized and high ash-content agro-waste, with Douglas-fir (*Pseudotsuga menziesii*) sawdust, a non-fertilized and low ash-content woody waste, when they were used as feedstocks for the production of bio-oil and char by fast pyrolysis technology. Douglas-fir wood and other soft wood have been widely used in making pallet and construction materials in developing countries in Asia. The Douglas-fir waste is abundant and can be potentially considerable as the feedstock for the pyrolysis technology. Oil-tea tree (*Camellia oleifera*) whose seed contains wealth of oil and can be extracted as camellia oil is one of the important cultivation in China. Camellia oil, like olive oil in Mediterranean countries, is notable as an important source of edible oil in Asia. Oil-tea shell, an agro-waste after camellia oil extraction, can be considerable as a feedstock for fast pyrolysis technology since extraction of one kilogram of camellia oil produces one kilogram of camellia shell waste.

The objective of this study is twofold. Firstly, pyrolysis oil and char produced from oil-tea shell and Douglas-fir sawdust were investigated experimentally. Secondly, based on metal analyses, the pyrolysis oils and chars derived from oil-tea shell and Douglas-fir sawdust were compared and some suggestions were made for their applications.

2. Experimental setup

Fig. 1 shows the bubbling fluidized bed (BFB) fast pyrolysis system. Typical feeding rates of biomass were $3\text{--}6\text{ kg h}^{-1}$. The BFB reactor with an internal diameter of 10 cm and height of 45 cm was heated by electric power and operated at near atmospheric pressure. There were three k-type thermocouples in the BFB reactor. One was in the freeboard; the other two were in the dense phase to check the temperature uniformity of the BFB reactor. The pyrolysis temperature of the reactor was decided by the average value of the two thermocouples in the dense phase. The pyrolysis temperatures of the BFB reactor were in the range of $703\text{--}793\text{ K}$ with an accuracy of $\pm 3\text{ K}$. A stream of preheated gas was introduced at the bottom of the BFB reactor to fluidizing the silica sand in the reactor. The average particle size of the silica sand was $350\text{ }\mu\text{m}$. The flow rate of the fluidizing gas was adjusted with a rotameter. Two cyclones connected in series were used to collect char after the BFB reactor. The temperature of the cyclone was kept

at $400\text{ }^{\circ}\text{C}$ to prevent any condensable gas condensed in the cyclones.

After char was collected, the bio-oil vapor (condensable gas) and product gas (non-condensable gas) were quenched by two condensers connected in series. Each condenser was constituted by a spraying column followed by a shell-tube-type cooler. Each shell-tube-type cooler equipped with a chilling machine with a coolant temperature of $288\text{ K} \pm 1\text{ K}$ to control the temperature of the shell-tube-type cooler. Bio-oils were collected in the two condensers. The bio-oil temperatures in the first and second condensers were $313\text{--}323\text{ K}$ and 293 K , respectively. Aerosol escaped from the condensers was captured by an electrostatic precipitator. The product gas after the electrostatic precipitator was vented or was utilized as a fluidizing gas in the BFB reactor as required. After each test, the char for analysis was the char mixed from the two cyclones and the bio-oil was the oil mixed from the two condensers and the electrostatic precipitator. The bio-oil distributions in the first condenser, second condenser and electrostatic precipitator were $88.3\text{ wt}\%$, $9.8\text{ wt}\%$, $1.9\text{ wt}\%$ for the Douglas-fir sawdust and $81.4\text{ wt}\%$, $16.9\text{ wt}\%$, $1.7\text{ wt}\%$ for the oil-tea shell. Each run of pyrolysis test lasted for two hours. After test, a cleanup process was conducted to prevent coke clogging problem in the piping for the next run.

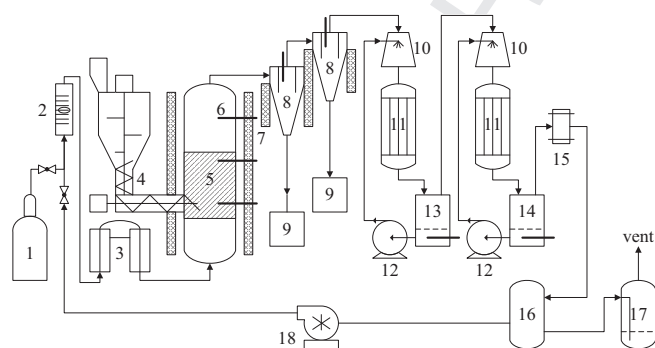
The collected bio-oil and char contained some silica sand fines entrained from the BFB reactor. The specific gravity of the silica sand was 2.33, which was higher than those of the bio-oils ($1.13\text{--}1.2$) and chars ($0.6\text{--}0.8$). It was then easy to separate the bio-oil and char from the silica sand fines by gravity settling method and a pneumatic separator, respectively before calculating the bio-oil yield and char yield. The pneumatic separator was a fluidized-bed separator operated at room temperature, separating the char and sand fines due to different gravities. Yield of product gas was obtained by subtracting bio-oil and char yields from $100\text{ wt}\%$.

3. Results and discussion

3.1. Product yields

The oil-tea shell investigated in this study had been taken from a camellia oil factory. Prior to use, the oil-tea shell was oven-dried to have a mean moisture content of $11\text{ wt}\%$. The sample was shredded and sieved to obtain particle sizes less than 2 mm . Douglas-fir sawdust was collected from a domestic pallet plant. The Douglas-fir sawdust was dried and ground with a mean moisture content of $12\text{ wt}\%$ and a maximum particle size of 2 mm . After shredding and drying, the oil-tea shell and Douglas-fir sawdust particles were ready for use as feedstocks for fast pyrolysis experiments. The results for proximate analysis, ultimate analysis and heating values measurement of Douglas-fir sawdust and oil-tea shell are given in Table 1. The measured oxygens (by Elementar Model Vario-el elemental analyzer) of Douglas-fir sawdust and oil-tea shell were $43.83\text{ wt}\%$ and $38.43\text{ wt}\%$, respectively which were in good agreement with the balanced oxygens in Table 1. The ash and nitrogen contents of oil-tea shell were much higher than those of Douglas-fir sawdust, mainly arising from fertilizer. Douglas-fir sawdust and oil-tea shell had very close calorific values (HHV and LHV) when considered for use as biofuel.

Pyrolyses of Douglas-fir sawdust and oil-tea shell were to determine the pyrolysis conditions that gave the maximum bio-oil yield with a minimum of char and gas. Particular investigated process variables were pyrolysis temperatures ($703\text{--}793\text{ K}$), fluidizing gas flow rates ($45\text{--}105\text{ NL min}^{-1}$), biomass feeding rates ($3\text{--}5\text{ kg h}^{-1}$) and under two pyrolysis atmospheres (nitrogen gas and product gas).



- | | | |
|--------------------------|----------------------------|--------------------------------|
| 1. N_2 cylinder | 7. heater | 13. first bio-oil tank |
| 2. flow meter | 8. cyclone | 14. second bio-oil tank |
| 3. pre-heater | 9. char pot | 15. electrostatic precipitator |
| 4. screw feeder | 10. spraying column | 16. buffer tank |
| 5. BFB reactor | 11. shell-tube-type cooler | 17. water sealing tank |
| 6. thermal couple | 12. recycling pump | 18. blower |

Fig. 1. Fast pyrolysis system.

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