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Influence of Pyrolysis Temperature on Yields of Bio-oil Produced from Fast Pyrolysis of Cow Manure

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Abstract

This paper reports a study of bio-oil production via fast pyrolysis of cow manure in a bench-scale fluidized-bed reactor. The aim of this work is to investigate the influence of pyrolysis temperature on product yields. Results showed that the optimum pyrolysis temperature for obtaining highest bio-oil yields was around 401°C. The highest bio-oil yields was 53.75 wt% on biomass dry basis. The bio-oil products were also tested for their basic properties. Results showed that the water, solids and ash contents of the bio-oil were 34.23 wt%, 0.96 wt% and 0.16 wt%, respectively. Moreover, the density, pH value, low heating value (LHV) and viscosity measured to be 1,123 kg/m3, 3.6, 22.2 MJ/kg and 16.34 cSt, respectively.

Keywords: fast pyrolysis, cow manure, fluidized-bed reactor, bio-oil

1. Introduction

Biomass is a renewable resource of which its utilization has received great attention owing to environmental consideration and the increasing demand for energy. Biomass is clean, for it has negligible content of sulphur, nitrogen and ash, thereby giving lower emissions of sulphur oxides (SO), nitrogen oxides (NO_x) and soot than conventional fossil fuel. Zero net emission of carbon dioxide (CO_2) can be achieved because CO_2 released from biomass will be recycled into the plants by photosynthesis quantitatively [1, 2].

Biomass can be converted to energy via thermal, biological and physical conversion processes, such as direct combustion, pyrolysis and gasification [3, 4, 5]. As one of the thermochemical processes, fast pyrolysis is a promising tool for providing bio-oil that can be used as fuel or chemical feedstock. Fast pyrolysis is thermal decomposition at very high heating rates and very high heat transfer rates at the biomass particle occurring in the absence of oxygen [6]. The main product is called "bio-oil" ,which can be used as fuel for heat, power or combined heat and power (CHP), or as feedstock in the chemical industry [7, 8].

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Cow manure is one of the Thailand's main biomass residue resources. Cow manure is commonly used as raw material for production of compost and is not efficiently used for energy. By applying fast pyrolysis technology to cow manure for bio-oil production, the advantage that could be gained is not only on the fuel value aspect, but also on the environmental aspect. Cao et. al [9] studied production of bio-oil via fast pyrolysis of pig compost in a circulating fluidised-bed reactor and found that the bio-oil yield was 44.4 wt%. The objective of this research is to investigate the effects of pyrolysis temperature on the product yields. The main product, bio-oil, was also analysis for its properties.

2. Experimental methods

2.1 Biomass feedstock

Biomass sample used in this work is cow manure. The sample was sundried, ground and sieved to particle size range of 212-500 μm. Table 1 presents the results of the proximate and ultimate analysis of the biomass sample. The proximate analysis determines the moisture, volatile matter, fixed carbon and ash contents according to the ASTM standard methods (E1756-01, E872-82 and E1755-01). The ultimate analysis measures the contents of carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O). The heating values were calculated based on the ultimate analysis results and equations (1) and (2).

The higher heating value (HHV) of biomass was calculated from a correlation developed by Sheng and Azevedo [10] as shown by the following equation:

$$HHV_{dry}\ (MJ/kg) = -1.3675 + 0.3137C + 0.7009H + 0.0318O^* \tag{1}$$

where C, H are percentages on dry basis of carbon, hydrogen, respectively and O* is 100-C-H-Ash.

The lower heating value (LHV) was calculated from HHV and the hydrogen content by the following equation [11]:

$$LHV_{dry}\ (MJ/kg) = HHV_{dry} - [2.442 \times 8.936(H/100)] \tag{2}$$

Table 1. Characterization of cow manure

Analysis	Cow manure
Proximate (wt%, dry basis)	
Moisture (wet basis)	10.12
Volatile matter	74.11
Fixed carbon*	5.22
Ash	19.65
Ultimate (wt%, dry, ash-free basis)	
Carbon	56.72
Hydrogen	6.81
Nitrogen	2.52
Sulphur	0.23
Oxygen*	33.71
Heating value by calculation method (MJ/kg, dry basis)	
HHV	17.53
LHV	16.34

*Calculated by difference

2.2 Fast pyrolysis unit

Experiments were carried out in a fluidized-bed reactor unit. Its schematic diagram is shown in Fig. 1. The unit consists of a pre-heater, a biomass hopper, a two-staged feeder, a fluidised-bed reactor, two cyclone separators, a hot filter and a bio-oil product collection unit.

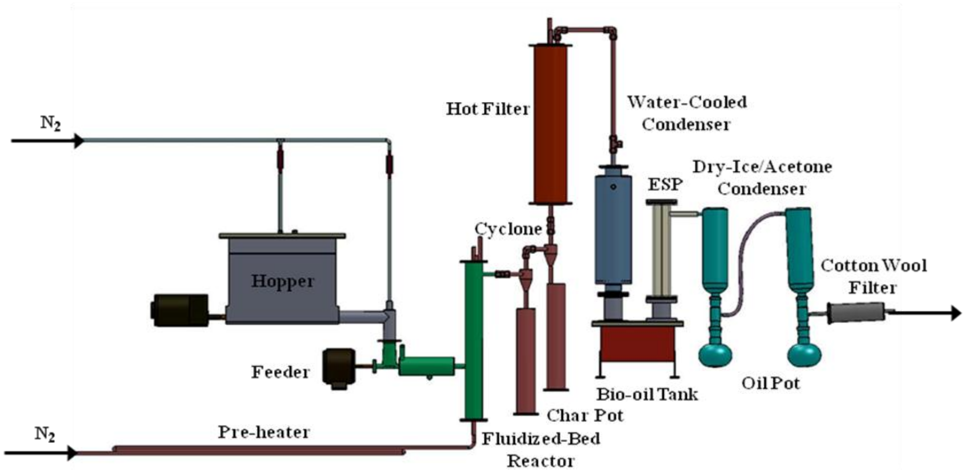

Fig. 1. Schematic diagram of fast pyrolysis unit.

2.3 Experimental design

Table 2 lists the different pyrolysis conditions for each experiment of. There were 5 levels of the setting temperatures including 350°C, 400°C, 450°C, 500°C and 550°C. The biomass particle size range was 212-500 µm. The feed rate of each experiment was around 200-300 g/hr. Nitrogen was used as the fluidizing medium at a flow rate of 7 L/min. Silica sand rested on a distributor plate, with a nominal diameter of 250–425 µm, acted as the fluidizing medium and heat carrier. The total time of each run was approximately 40-50 min. To achieve the goal of these variables, a total of 5 experimental runs were performed.

Table 2. Pyrolysis condition

Parameters	Run				
	1	2	3	4	5
Pyrolysis temperature (°C)	353	401	452	501	553
Particle size (µm)	212-500				
Feed rate (g/hr)	200-300				
Nitrogen flow rate (l/min)	7				
Heat transfer medium	Silica sand				
Time (min)	40	50	50	50	50

2.4 Bio-oil analysis

The characterization of bio-oil condensed in the water-cooled heat exchanger and an electrostatic precipitator (ESP) included water content, solids content, ash contents, density, pH, elemental composition, viscosity and heating value. Each analysis was performed in triplicate.

The water content of bio-oil was determined by the Center of Scientific and Technological Equipment (CSTE), Suranaree University of Technology, NakhonRatchasima, Thailand, using Karl-Fischer (KF) titration technique. The solids content of bio-oil was defined as ethanol insoluble and determined by vacuum filtration technique. This method is recommended by Oasmaa and Peacocke [12]. The ash content of bio-oil is indicated as the amount of residues when heating bio-oil to 775°C with oxygen supply[12, 13]. The density of bio-oil was the weight of bio-oil contained in a unit volume (g/ml), which is measured by using a density bottle at room temperature (about 30°C). The pH value of bio-oil was measured by a pH meter at room temperature. The carbon, hydrogen, nitrogen, and oxygen contents were determined using the same technique as those applied for the ultimate analysis of biomass. The viscosity of bio-oil (in cSt) was measured at 40°C using a Cannon-Fenske Routine Viscometer with a SDM viscosity bath (Art. 370) according to ASTM D445 and D446 standard methods. The heating values were expressed as higher heating value (HHV) and lower heating value (LHV). The higher heating value on dry basis (HHV_{dry}) of bio-oil was calculated based on the elemental analysis using a correlation developed by Channiwala and Parikh [14] as shown by equation (3). The lower heating value on dry basis (LHV_{dry}) of bio-oil was calculated from equation (2) [11]. For heating values on wet basis (HHV_{wet} and LHV_{wet}), equations (4) and (5) were used [11] by taking into account the water content of bio-oil (H_2O, wt%).

$$HHV_{dry}\ (MJ/kg) = 0.3491C + 1.1738H + 0.1005S - 0.10340O - 0.0151N - 0.0211A \quad (3)$$

The C, H, S, O, N and A in equation (3) are percentages of carbon, hydrogen, sulphur, oxygen nitrogen and ash in bio-oil on dry basis.

$$HHV_{wet}\ (MJ/kg) = HHV_{dry}\ [1 - (H_2O/100)] \quad (4)$$

$$LHV_{wet}\ (MJ/kg) = LHV_{dry}\ [1 - (H_2O/100)] - 2.442\ (H_2O/100) \quad (5)$$

3. Results and discussion

3.1 Effect of pyrolysis temperature on the product yields

Fig. 2. shows the effect of pyrolysis temperature on the product yields. The results showed that the optimum pyrolysis temperature for obtaining highest bio-oil yields was around 401°C. The highest bio-oil yields was 53.75 wt% on biomass dry basis. The char yield reduced with the temperature whereas the gas yield increased with temperature. The reduction of the char yields with increasing temperature could be due to the greater primary decomposition of the biomass at higher temperature and secondary thermal decomposition of the char formed before being entrained out of the reaction zone [15]. When pyrolysis temperature is too high, a secondary cracking of pyrolysis vapour could take place. Thus, reducing the bio-oil yield and increasing the gas yield. When comparing the bio-oil yields of the cow manure with pig compost [9], it is apparent that the bio-oil yields of cow manure were higher than that of pig compost (44.4 wt%, 500˚C).

3.2 Characterization of bio-oil

In this work, bio-oil samples were characterised by measuring water content, solids content, ash content, density, pH value, elemental composition, viscosity and heating value. The bio-oil analysis results are summarised in Table 3.

The water contents of cow manure bio-oil was 34.23 wt%. In contrast to the rice straw bio-oil [16], the water content of cow manure bio-oil was higher. These differences are possibly due to the different moisture content of biomass. The solids content of cow manure bio-oil was 0.96 wt%, which is in the acceptable range for burner fuel suggested by Oasmaa et al [17]. The ash content of bio-oil was approximately 0.16 wt%. The densities of bio-oil from pyrolysis cow manure were around 1,123 kg/m^3. This is a typical value of fast pyrolysis liquid. The pH value of the bio-oil products in this work was 3.6. When comparing the pH value of cow manure bio-oil with wood bio-oil [6], it is apparent that the pH values of the bio-oils are quite similar. Table 3 shows the elemental composition of cow manure bio-oil. The elemental composition of bio-oil was determined to find out the content of carbon, hydrogen, nitrogen and oxygen. The oxygen content of bio-oils was 34.14 wt.%, which is relatively high compared to that of fossil fuel. Interestingly, the high oxygen content results in a lower heating value (on dry basis) that is less than 50% of that for conventional petroleum fuel. The kinematic viscosity of bio-oil obtained from pyrolysis of cow manure was around 16.34 cSt. There values are much lower due to higher water content. Comparing the viscosity of cow manure bio-oils with cassava rhizome bio-oil [15], the viscosity of cow manure bio-oil are lower than that of cassava rhizome bio-oil because of the higher water content of the cow manure bio-oil. In addition, the lower heating value (LHV) of bio-oil was found to be 22.2 MJ/kg (water-free basis).

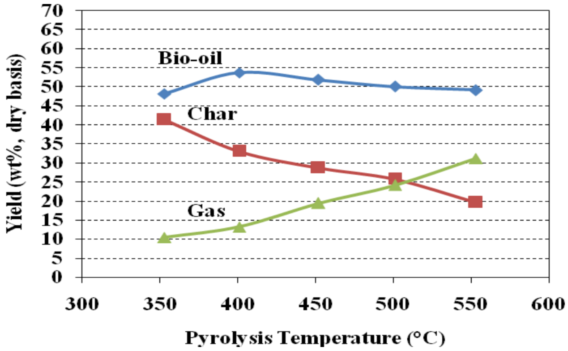

Fig. 2. Effect of temperature on product yields derived from fast pyrolysis of cow manure in a fluidized-bed reactor unit

Table 3. Properties of bio-oil obtained from pyrolysis of cow manure

Properties	Cow manure
Pyrolysis temperature (°C)	401
Elemental composition (wt.%, dry basis)	
Carbon	59.92
Hydrogen	5.04
Nitrogen	0.65
Oxygen*	34.14
Water content (wt%)	34.23
Solid content (wt%)	0.96
Ash content (wt%)	0.16
Density (kg/m^3)	1,123
pH value	3.60
Kinematic viscosity @ 40°C (cSt.)	16.34
Heating value by calculation method (MJ/kg)	
HHV (water-free basis)	23.30
HHV (as-produced basis)	15.33
LHV (water-free basis)	22.20
LHV (as-produced basis)	13.77

*Calculated by difference

4. Conclusions

Fast pyrolysis of cow manure was investigated using a bench-scale fluidized-bed reactor unit at different temperatures. The objective of this research was to investigate the effects of pyrolysis temperature on the product yields. The results showed that the cow manure bio-oil yields reached their maxima of 53.75 wt% (on dry biomass basis) at the corresponding pyrolysis temperatures of 401°C. The bio-oil products were also tested for their basic properties. Results showed that the water solids and ash contents of the bio-oil were 34.23 wt%, 0.96 wt% and 0.16 wt%, respectively. Moreover, the density, pH value, low heating value (LHV) and viscosity measured to be 1,123 kg/m^3, 3.6, 22.2 MJ/kg and 16.34 cSt, respectively. Further work are going to upgrading of bio-oil.

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