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Upgrading of Bio-oil obtained from Fast Pyrolysis of Biomass Using a Vacuum Distillation Method

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Abstract

This paper reports on a study of upgrading of bio-oil obtained from a fast pyrolysis of biomass using a vacuum distillation method. In this work, a fast pyrolysis unit with a fluidized-bed reactor was operated with a feed rate 300 g/hr. This fast pyrolysis experiment was conducted at a reaction temperature of 425°C using sugarcane leaves and tops with particle sizes of 0.250-0.500 mm. The experimental distillation was completed at a temperature of 80°C and using a 200 ml bio-oil sample. The results showed distillation yields of 57.0 wt.% (organic phase) from vacuum distillation of fast pyrolysis bio-oil. The basic properties of pyrolysis oil products were determined. The bio-oils produced by pyrolysis of sugarcane leaves and tops had improved properties in terms of carbon, oxygen and water content, pH value and heating value after distillation.

Keywords: Upgrading, Fast pyrolysis, Sugarcane leaves and tops, Vacuum distillation, Fluidized-bed reactor

1. Introduction

Bio-oil is a kind of biofuels obtained from fast or rapid pyrolysis of biomass. Bio-oil is also referred to as pyrolysis oil, liquid wood, bio-oil, pyrolysis liquid, pyrolytic liquid and pyrolytic oil, etc [1, 2]. Usually, pylolysis oil is dark brown and free-flowing liquids with an acrid [3]. The components of bio-oil include acids, alcohols, esters, phenols, aldehydes, furans, sugars, ketones and multifunctional compounds [4]. The chemical compositions of pyrolysis oils are determined by many factors including biomass type, reactor type, pyrolysis conditions, feedstock pretreatment and condensation type, etc. The pyrolysis oil can be used as a renewable fuel and feedstock of chemicals [5-7]. Pyrolysis oil has the content of water as high as 15-35 wt.% due to dehydration reaction and the content of oxygen is usually 35-40% [8]. The heating value of pyrolysis oil that much lower than that of fossil fuel. The pyrolysis oil contains organic acids, resulting the high acidity (pH 2-3) and is therefore corrosive. The pyrolysis oil of viscosity vary in a large range. The pyrolysis oil produced obtained from rapid pyrolysis of biomass is unstable. Therefore pyrolysis oil's utilization as a fuel requires some form of upgrading to attain suitable storage stability and heating value.

There are many routes to upgrading the properties of pyrolysis oil. These include hydrogenation, hydrodeoxygenation, hot filtration, emulsification, catalytic pyrolysis, catalytic cracking, solvent addition, vacuum distillation, ethanol addition, steam reforming, and esterification [9]. Pidtasang et al. [10] studied upgraded of pyrolysis oil from rapid pyrolysis of eucalyptus bark in a free-fall reactor with alcohol addition. It was found that the pyrolysis oil produced in this manner had better quality in terms of viscosity, stability and heating value. Zheng and Wei. [11] upgraded fast pyrolysis bio-oil by reduced pressure distillation. It was found that bio-oils produced in this studied had higher heating value, lower corrosivity and better stability.

Therefore, it is the aim of the current work to investigate the upgrading of pyrolysis oil produced from rapid pyrolysis of sugarcane leaves and tops in a fluidized-bed reactor using a vacuum distillation method.

2. Experimental method and analysis

2.1 Materials

Sugarcane leaves and tops were collected from plantations in the north-east Thailand. The sample was sundried in ambient atmosphere, ground by hammer milling technique and sieved to the size range of 0.250-0.500 mm. The feedstock particle was oven dried for 24 h at 105°C prior to fast pyrolysis experiment. The proximate and ultimate analysis, heating value and bulk density of the biomass sample is presented in Table 1. The heating value of biomass sample was calculated using equations (1) [12] and (2) [13]. The bulk density of biomass was calculated using equation (3).

$$□□□\left(\frac{□□}{□□}\right) = -1.3675 + 0.3137□ + 0.7009□ + 0.0318□^{*} \quad (1)$$

$$\square\square\square\left(\frac{\square\square}{\square\square}\right) = \square\square\square - 2.442 \times 8.936\left(\frac{\square}{100}\right) \qquad (2)$$

$$\square\left(\frac{\square\square}{\square^3}\right) = \frac{\square}{\square} \qquad (3)$$

2.2 Unit of rapid pyrolysis

The schematic diagram of rapid pyrolysis unit is presented in Fig. 1. The experimental unit consists of a fluidized-bed reactor, a hopper, nitrogen gas cylinder, nitrogen gas pre-heater, two-staged feeder, two cyclones, two char pot, a hot filter, a water-cooled condenser, an electrostatic precipitator (ESP), a dry-ice condenser, a bio-oil bottle, an oil pot and a cotton wool filter. The fluidized-bed reactor was made from a stainless-steel pipe, 0.045 m in diameter, with a 0.45 m long cylindrical section. The temperature of the pyrolysis unit was adjusted using PID temperature controllers and was monitored using K-type thermocouples. The cyclones were used to separate char particles from the hot vapour. Pyrolysis hot vapour was condensed into bio-oil product by a water-cooled condenser, an electrostatic precipitator (ESP), a dry ice/acetone condensers and a cotton wool filter. Fig. 2 shows a photograph of the laboratory equipment used.

Table. 1 Characteristics of sugarcane leaves and tops

Characteristics	Sugarcane leaves and tops	Sugarcane leaves*	Sugarcane tops*
Particle size (mm)	0.250-0.500	0.250-0.450	0.250-0.450
Proximate (wt.%, as-received basis)			
Moisture	9.32±0.08	6.7	6.6
Volatile matter	74.45±0.09	79.0	74.9
Fixed carbon[a]	20.07±0.04	8.6	12.5
Ash	4.61±0.07	5.7	6.0
Ultimate (wt.%, dry ash-free basis)			
Carbon	46.99±0.13	48.9	49.0
Hydrogen	7.75±0.09	6.5	6.6
Nitrogen	0.68±0.02	0.2	0.6
Sulfur	0.15±0.02	NA	NA
Oxygen[a]	39.80±0.25	44.4	43.8
H/C molar ratio	1.98±0.02	1.58	1.60
O/C molar ratio	0.64±0.01	0.68	0.67
Molecular formula	$CH_{1.98}O_{0.64}$	$CH_{1.58}O_{0.68}$	$CH_{1.60}O_{0.67}$
Heating value (MJ/kg, dry basis)			
HHV	20.10±0.08	18.4	18.3
LHV	18.41±0.07	17.0	17.0
Density (kg/m^3)			
Bulk density	134.02±2.29	230	160

[a]Calculated by difference.
*Pattiya et al. [14].

2.3 Vacuum distillation method

Production of bio-oil from sugarcane leaves and tops was conducted in a fluidized-bed reactor. Rapid pyrolysis experiments were conducted at a reaction temperature was 425°C [15] using a biomass sample particle size of 0.250-0.500 mm, feed rate of 300 g/h, hot nitrogen gas flow rate of 6 litres/min.

Fig. 3 shows a photograph of the upgrading equipment by a vacuum distillation method. The experimental apparatus consists of an electric heater, a flask (250 ml), a capillary, a thermometer, a cooling water, a cooling ice, two oil pot and a vacuum pump. The experimental distillation was completed at a temperature in the flask of 80°C, the residual pressure in the flask is -15 mmHg and 200 ml bio-oil sample was used for test.

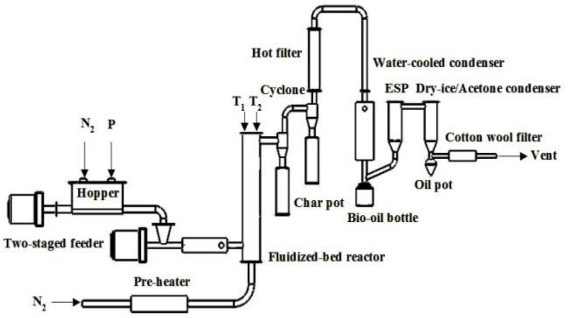

Fig. 1 Scheme of the laboratory plant for the sugarcane leaves and tops batch fast pyrolysis.

Fig. 2 A photograph of the laboratory equipment used.

Fig. 3 A photograph of a vacuum distillation experiments.

2.4 Pyrolysis oil property analysis

In order to compare the bio-oil of vacuum distillation with the rapid pyrolysis bio-oil. The properties of vacuum distillation pyrolysis oil were tested. These properties include elemental composition, water and ash contents, density, pH and heating values. Each analysis were performed in three times. The pyrolysis oils elemental composition were to determine its carbon, hydrogen, nitrogen, sulfur and oxygen contents. The H/C and O/C molar ratio of pyrolysis oil was calculated using hydrogen, oxygen and carbon content. The pyrolysis oils water content were determined by using Karl-Fischer (KF) titration technique. The pyrolysis oils ash content were determined as the amount of residues after heating bio-oil to 775°C in the presence of oxygen [16]. The pyrolysis oils density were measured using a density bottle at room temperature. The pyrolysis oils pH value were measured with a pH meter at room temperature. The pyrolysis oils heating value were determined by calculation. The higher heating value on dry or water-free basis (HHV_{dry}) was calculated based on the elemental analysis as shown by equation (4) [17]. The lower heating value on dry or water-free basis (LHV_{dry}) was calculated using equation (2) [13]. To determine higher and lower heating values on wet or as-produced basis (HHV_{wet} and LHV_{wet}), equations (5) and (6) were used [13] to account of the pyrolysis oil water content.

$$\square\square\square_{\square\square\square}\left(\frac{\square\square}{\square\square}\right) = 0.3491\square + 1.1738\square + 0.1005\square - 0.10340\square - 0.0151\square - 0.0211\square \quad (4)$$

$$\square\square\square_{\square\square\square}\left(\frac{\square\square}{\square\square}\right) = \square\square\square_{\square\square\square}\left(1 - \frac{\square_2\square}{100}\right) \quad (5)$$

$$\square\square\square_{\square\square\square}\left(\frac{\square\square}{\square\square}\right) = \square\square\square_{\square\square\square}\left(1 - \frac{\square_2\square}{100}\right) - 2.442\left(\frac{\square_2\square}{100}\right) \quad (6)$$

3. Results and discussion

3.1 Product yields of vacuum distillation

Fig. 4 shows the product yields of vacuum distillation from fast pyrolysis of sugarcane leaves and tops at temperature of 80°C, using a 200 ml pyrolysis oil sample. There were three products of vacuum distillation from fast pyrolysis bio-oil including organic phase, aqueous phase (water phase) and residue. The results showed distillation yields of 57.0 wt.% (organic phase) from vacuum distillation of fast pyrolysis bio-oil. The aqueous phase and residue yields of 31.1 and 11.9 wt.%, respectively. This result is consistent with the result reported by Zheng and Wei [11]. In that study, the distilled bio-oil yields of 61 wt.%, was achieved for rice husk fast pyrolysis in a fluidized-bed reactor.

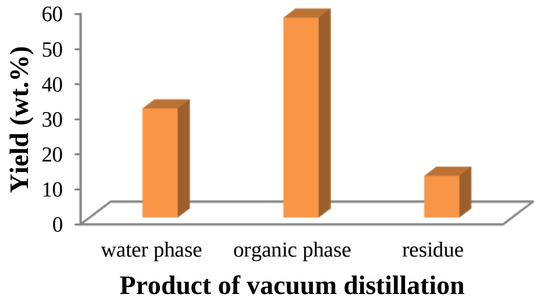

Fig. 4 Product yields of vacuum distillation from fast pyrolysis of sugarcane leaves and tops

3.2 Characteristics of vacuum distillation pyrolysis oil

Fig 5 shows the pyrolysis oil and products of vacuum distillation from fast pyrolysis of sugarcane leaves and tops including organic phase and aqueous phase (water phase). Basic properties of bio-oil products were determined. Results of these tests showed that pyrolysis oil from fast pyrolysis of sugarcane leaves and tops met to ASTM burner fuel standards [18].

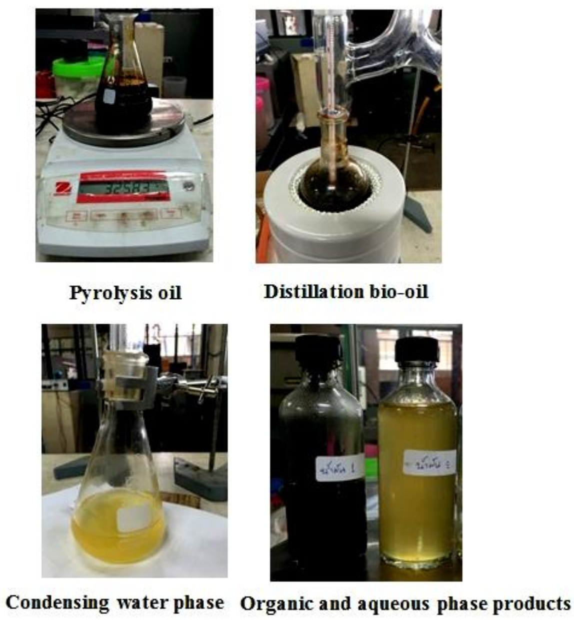

Fig. 5 Pyrolysis oil and products of vacuum distillation from fast pyrolysis of sugarcane leaves and tops.

Table 2 shows characteristics of rapid pyrolysis bio-oil and vacuum distillation pyrolysis oil (organic phase) from fast pyrolysis of sugarcane leaves and tops. Its includes the elemental composition, molecular formula, H/C molar ratio, O/C molar ratio, water content, ash content, pH value, densities and heating value. Results show that the carbon content of vacuum distillation pyrolysis oil of 68.66 wt.% whereas the carbon content of fast pyrolysis bio-oil of 46.01 wt.% and the oxygen content of vacuum distillation pyrolysis oil of 22.21 wt.% whereas the oxygen content of fast pyrolysis bio-oil of 46.49 wt.%. The H/C and O/C molar ratios of vacuum distillation pyrolysis oil are 1.53 and 0.23, while the H/C and O/C molar ratios of rapid pyrolysis bio-oil are 0.97 and 0.31, respectively. The vacuum distillation bio-oil water content of 0.94 wt.% (fast pyrolysis bio-oil of 31.07 wt.%). The vacuum distillation bio-oil pH value of 6.23. The heating value of vacuum distillation bio-oil product has higher heating value of 32.37 MJ/kg by calculation method. The differences are possibly related the carbon and oxygen content of the pyrolysis oil.

Table. 2 Characteristics of rapid pyrolysis bio-oil and vacuum distillation pyrolysis oil from fast pyrolysis of sugarcane leaves and tops.

Characteristics	Fast pyrolysis bio-oil	Vacuum distillation bio-oil
Elemental composition (wt.%, as-produced basis)		
Carbon	46.01±0.31	68.66±0.28
Hydrogen	7.18±0.17	8.84±0.06
Nitrogen	0.18±0.01	0.16±0.01
Sulfur	0.11±0.01	0.10±0.01
Oxygen[a]	46.49±0.24	22.21±0.31
H/C molar ratio	0.97±0.03	1.53±0.01
O/C molar ratio	0.31±0.02	0.23±0.01
Molecular formula	$CH_{0.97}O_{0.31}$	$CH_{1.53}O_{0.23}$
Water content (wt.%)	31.07±11.6	0.94±0.03
Ash content (wt.%)	0.02±0.01	0.02±0.01
Density (kg/m^3)	1,135.9±50.62	1,289.6±2.76
pH value	2.85±0.13	6.23±0.05
Heating value (MJ/kg)		
HHV (water-free basis)	26.87±0.74	32.37±0.16
HHV (as-produced basis)	18.51±0.11	32.06±0.16
LHV (water-free basis)	25.69±0.73	30.44±0.15
LHV (as-produced basis)	16.94±0.09	30.13±0.15

[a]Calculated by difference.

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4. Conclusions

Upgrading of pyrolysis oil from fast pyrolysis of sugarcane leaves and tops using a vacuum distillation method was confirmed that it was effective method to get higher quality. Production of fast pyrolysis bio-oil was conducted in a fluidized-bed reactor, feed rate 300 g/hr. This fast pyrolysis experiment was conducted at a reaction temperature of 425°C using biomass sample with particle sizes of 0.250-0.500 mm. The product yields of vacuum distillation from fast pyrolysis of sugarcane leaves and tops was obtained at temperature of 80°C, using a 200 ml pyrolysis oil sample. They were three products of vacuum distillation from fast pyrolysis bio-oil including organic phase, aqueous phase (water phase) and residue. The results show that distillation yields of 57.0 wt.% (organic phase) from vacuum distillation of fast pyrolysis bio-oil. The aqueous phase and residue yields of 31.1 and 11.9 wt.%, respectively. The basic properties of bio-oil products were clarified. The bio-oils produced by pyrolysis of sugarcane leaves and tops had improved properties in terms of carbon, oxygen and water content, pH value and heating value after vacuum distillation

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