Performance Analysis of a Vacuum Pyrolysis System

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Abstract

Purpose: The purpose of this study was to investigate the performance of a vacuum pyrolysis system, to analyze bio-oil characteristics, and to examine the applicability for farm-scale capacity. **Methods:** The biomass was pyrolyzed at 450, 480, and 490℃ on an electric heat plate in a vacuum reactor. The waste heat from the heat exchanger of the reactor was recycled to evaporate water from the bio-oil. The chemical composition of the bio-oil was analyzed by gas chromatography-mass spectrometry (GC-MS). **Results:** According to the analysis, the moisture content (MC) in the bio-oil was approximately 9%, the high heating value (HHV) was approximately 26 MJ/kg, and 29 compounds were identified. These 29 compounds consisted of six series of carbohydrates, 17 series of lignins, and six series of resins. **Conclusions:** Owing to low water content and the oxygen content, the HHV of the bio-oil produced from the vacuum reactor was higher by about 6 MJ/kg than that of the bio-oil produced from a fluidized bed reactor.

Keywords: Bio-oil, Vacuum pyrolysis, Fluidized bed reactor

Introduction

Many pyrolysis processes are being developed for better production of bio-oil. Researchers have been studying the production and component analysis of bio-oil (Bridgwater et al., 1999; Oasmaa et al., 1997; Oasmaa et al., 2003; Kaltschmitt and Bridgwater, 1997; Oasmaa and Peacocke, 2001). Sugarcane bagasse was converted to bio-oil of 30-34 wt% by vacuum pyrolysis. A series of aging tests indicated that the bagasse-derived bio-oil had a normal bio-oil thermal stability (Garcìa-Pèrez et al., 2002).

Vacuum pyrolysis is a thermal decomposition technique for converting biomass as well as rubber, plastic, and wastes of valuable substances to bio-oil, biogas, and bio-char. In vacuum pyrolysis, pyrolysis is accomplished under reduced pressure. Organic materials, having a complicated structure, are broken down to a more basic structure when heated in a reactor. Polymers that are decomposed into a basic structure are quickly removed from the reactor using a vacuum pump, and are collected in a condenser in the form of pyrolysis oil. When the reactor interior is a vacuum, steam is quickly removed, and the polymer will stay inside the reactor. As a result, a second thermal cracking can reduce decomposition, repolymerization, and recondensation. The reaction rate can be increased and vacuum circumstance rather than under atmospheric pressure condition (Lopez et al., 2009). In addition, pyrolysis occurs between 400-500℃ and 15-20 kPa. The low pressure of the vacuum is an important factor in determining the composition and quality of the bio-oil. In a vacuum system, carrier gas is not required, and the pyrolysis temperature is reduced by about 100℃ more than in a fluidized bed reactor. A

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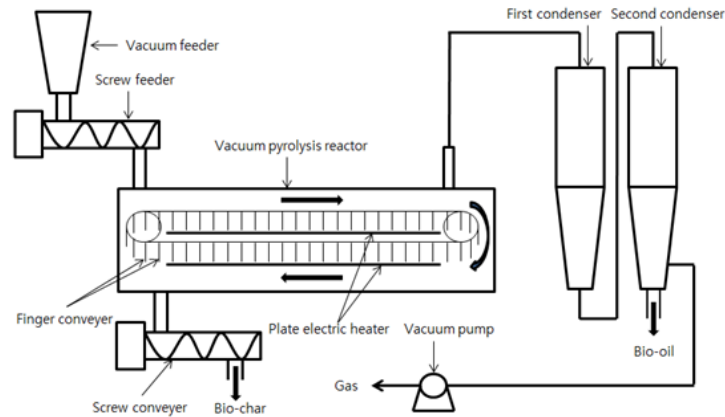
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Figure 1. Two-dimensional schematic diagram of vacuum pyrolysis system
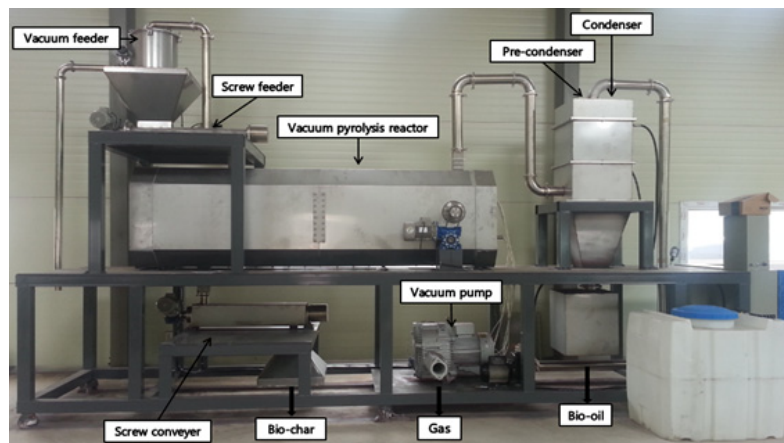

Figure 2. Vacuum pyrolysis system

vacuum transfers only the vapor without char, and therefore it is possible to produce almost-char-free bio-oil. Compared to fluidized bed pyrolysis, vacuum pyrolysis produced 2% more carbon at 450℃, which was a lower temperature than that of fluidized bed pyrolysis (550℃) (Kim et al., 2007).

Continuous transfer in a heat plate system and pyrolysis of biomass is possible in a reactor. An upside-down effect of the top heat plate is possible when using a multistage conveying system. A finger conveyer system is used to transfer biomass and to clean the surface of the top heat plate. A waste heat recovery system is installed in the heat exchanger of the reactor through the pipeline, and is used to evaporate water from the bio-oil.

The advantages of vacuum pyrolysis are relatively short residence and reaction time required, less carrier gas needed, and higher energy density produced. In this paper, a vacuum pyrolysis system to produce bio-oil from biomass is developed to investigate the possibility of applying this method up to farm-scale capacity. Bio-oil

was analyzed by GC-MS to investigate the components of the compound. The elemental analysis, pH, high heating value (HHV), moisture content (MC), and viscosity of bio-oil were analyzed as well.

Materials and Methods

Vacuum pyrolysis system

Vacuum pyrolysis can reduce the residence time and reaction time compared to other pyrolysis systems owing to differences in pressure that enhances the escape rate of the pyrolysis product (Guedes et al., 2017). From an economic point of view, vacuum pyrolysis does not require a large amount of carrier gas (Fan et al., 2018) and increases the energy density of the resulting bio-oil (Marathe et al., 2017). In this study, a vacuum pyrolysis system was assembled at Eco D & S Co., Ltd., in the Republic of Korea. The system can handle 50-100 kg/h of biomass. As shown in Figure 1 and Figure 2, the vacuum

pyrolysis system consists of a vacuum feeder, a screw feeder, two electric heating plates, a vacuum pyrolysis reactor, two condensers, a vacuum pump, a finger-type conveyer, and a screw conveyer. The vacuum feeder supplied biomass materials and blocked the oxygen to maintain the vacuum. The two electric heating plates were adjusted between 400 and 500℃ in order to decompose the biomass particles injected into the heat transfer plate. In the first condenser, at least 80% of the syngas was condensed in the range of 0-20℃. In the second condenser, volatile matter was condensed in the range of 0-20℃. The suction-type vacuum pump was used to maintain a pressure of about 15-20 kPa in the reactor and to emit exhaust gas. Numerous finger conveyers conveyed the biomass particles. The screw conveyer conveyed the bio-char.

The proximate and elementary analytical data of the lignocellulosic biomass employed in this study are shown in Table 1, with particle sizes ranging from 100 to 500μm.

A schematic diagram of the automatic control technology of the pyrolysis system is shown in Figure 3. A screw feeder and rotary valve fitted with an air locking system made the pyrolysis air-free. Raw material was discharged by the discharge screw conveyer. The waste heat recovery pipeline connected the pyrolysis reactor with the heat exchanger. By recycling the waste heat generated during the pyrolysis reaction, the efficiency of the pyrolysis reaction was increased and dried the raw material introduced in the reactor. and is possible to preheating.

The operating control procedure for condensation of the pyrolysis of the biomass, condensation of gas, and the waste heat recovery system is as follows. ⑤ and ⑨ are cooled by the refrigeration system.
1) ①-⑩ times set in sequence: only actions ⑤ and ⑨, and in the ON condition.
2) In ④, when the temperature reaches the set value, ① and ⑤ operate.
3) ① by vacuum transfer, after completion, operates the air lock device.
4) Completion of ② and ③ starts operation.
5) In ④ → ⑦ → ⑧ → ⑨ and ⑩ sequences, the waste thermal transfer suction pump operates.

Bio-oil analysis

GC-MS analysis of the bio-oil was conducted by a mass selective detector (Agilent 5975C, Agilent Technologies, USA) and gas chromatograph (Agilent 7890B, Agilent Technologies, USA). A DB-5 column was used in the analysis, and the conditions were as follows: split ratio was controlled at 1:20 at an injector temperature of 250℃,

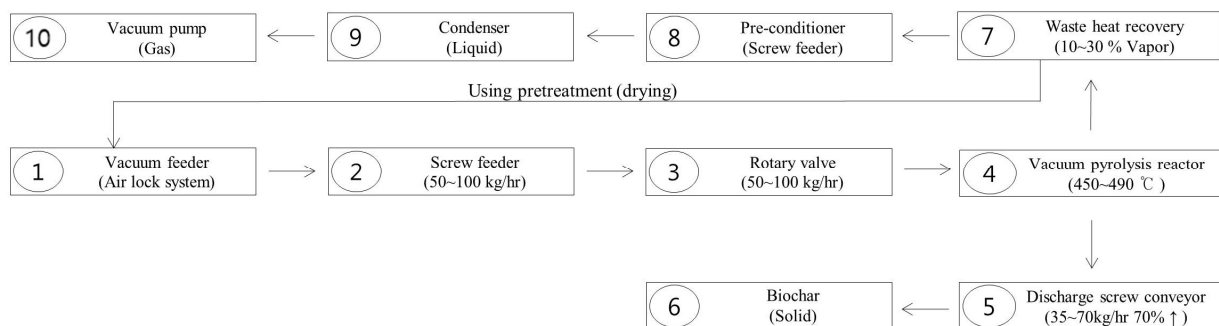| Table 1. Proximate and ultimate analyses of lignocellulosic biomass			
Technical analysis (%)		Elementary analysis (%)	
Water content	4.73	Carbon (C)	52.30
Volatile	77.50	Hydrogen (H)	6.50
Ash	2.56	Nitrogen (N)	0.00
Fixed carbon	15.20	Oxygen (O)	38.00
-	-	Sulfur (S)	0.03
High heating value (MJ/kg)		Low Heating value (MJ/kg)	
19.08		17.49	

Figure 3. Pyrolysis reactor control diagram using waste heat for dryer

and flame ionization detector (FID) analysis was conducted at 300℃. After that, the oven temperature was held for 5 min at 50℃, and the temperature was raised to 140℃ at a constant rate of 3℃/min. This temperature system was maintained for 10 min. After that, the heating rate was fixed at 2℃/min to increase the temperature to 280℃, and this final temperature was maintained for 20 min. An analysis sample was prepared by 10-fold dilution with acetone, and the analysis results were obtained by dividing each peak area by the respective total peak area.

The MC was analyzed by a KF titrator (V20, Mettler Toledo, USA), and the viscosity was analyzed by a Vibro Viscometer (SV-10, A&D Company Ltd., Japan).

Results and discussion

Comparison of bio-oil properties generated from vacuum system and fluidized bed system

Table 2 lists the physical properties and elemental composition of the bio-oil obtained at three different temperatures: 450, 480, and 490℃. It was found that there was no change in the pH of the bio-oil produced at the three different temperatures. The bio-oil yield produced at 480℃ was highest. The MC at 480℃ was highest, resulting in the lowest HHV. The difference in viscosity at the three temperatures was about 3.82 cST. The composition of the bio-oil was different than that of crude oil. Crude oil consists mainly of hydrogen, carbon, and a very small amount of oxygen. However, bio-oil contains a large amount of oxygen in hydroxyl, carboxyl, carbonyl, and several other functional groups such as oxy groups. An elemental analysis of the bio-oil showed C, H, O, and N. The C content of the bio-oil produced at 480℃ was lowest, which resulted in the lowest HHV at that temperature. Generally, the heating value of the bio-oil influences the oxygen and moisture content. In this study, the moisture content and O content were highest at 480℃, resulting in the lowest HHV at that temperature.

The amount of carbon in the bio-oil produced in the vacuum pyrolysis system was greater than that of the fluidized bed system at the same temperature (Table 2). In addition, the oxygen and MC were lower, resulting in a higher HHV value in the vacuum pyrolysis system. Based on the experimental results from the fluidized bed reactor, the range of the suitable reaction temperature is from 450 to 500℃. With this result, the optimized reaction temperature of the vacuum reactor was found to be 480℃ in terms of the liquid yield (Table 2).

GC-MS analysis detected a total of 29 compounds at 480℃, as shown in Table 3 and Figure 4. Three types of bio-oil were analyzed. These 29 compounds consisted of 6 series of carbohydrates, 17 series of lignins, and 6 series of resins. Furfural, 5-methyl-furfural, 2-Cyclopenten-1-one, and 2-hydroxy-3-methyl- were the major carbohydrates. In the lignins, the H units (p-hydroxyphenyl types) consisted mainly of 2, 4-Dimethyl-phenol, and the G units consisted mainly of 2-Methoxy-phenol, 4-Ethyl-2-methoxy-phenol, 2-Methoxy-4-vinyl-phenol, and (Z)-2-Methoxy-4-(1-propenyl)-phenol. Among the six resins, dehydroabietic

| Table 2. Physical properties and elemental composition of bio-oil (wet basis)							
Properties	Vacuum reactor			Fluidized bed reactor			
	450℃	480℃	490℃	400℃	450℃	500℃	550℃
pH	2.20	2.20	2.20	1.9	2.2	2.5	2.9
Liquid yield (%)	65.3	65.9	64.7	47.0	54.8	64.9	55.8
Moisture content (wt%)	8.01	9.60	8.68	26.1	23.6	18.8	11.9
Viscosity (cST)	10.86	8.30	7.04	10.2	10.3	34.5	-
Elemental analysis (wt%)							
C	59.96	51.40	59.94	38.6	43.1	44.1	49.1
H	6.62	7.60	6.97	6.9	6.6	6.8	6.4
O	33.38	40.30	33.05	54.5	50.4	49.1	44.5
N	0.04	0.04	0.04	N/D	N/D	N/D	N/D
High heating value(MJ/kg)	26.5	25.7	26.2	16.6	17.2	18.0	19.3
Low heating value(MJ/kg)*	24.8	23.7	24.4	14.4	15.1	15.9	17.6

* Calculated based on moisture content and high heating value
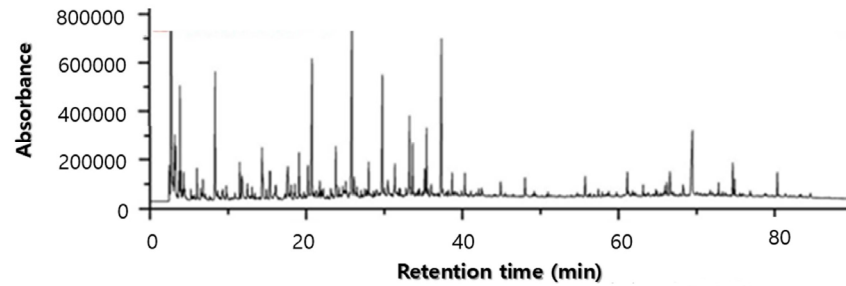
a. Bio-oil sample 1 (numbered peaks are listed in Table 3)
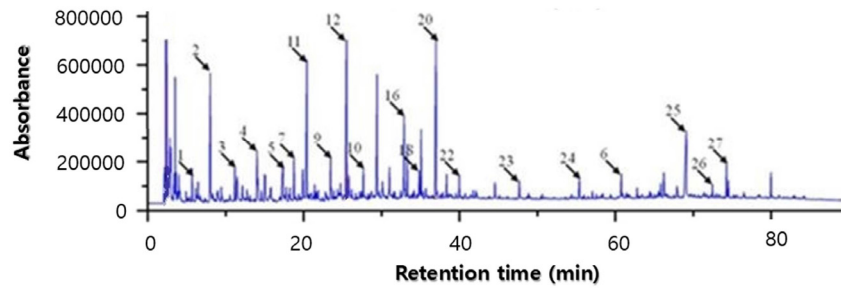
b. Bio-oil sample 2 (numbered peaks are listed in Table 3)
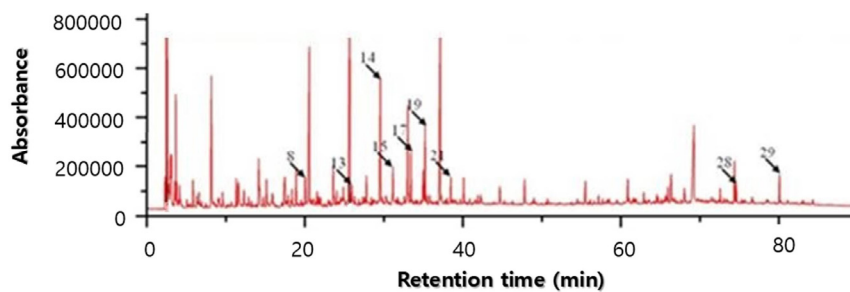
c. Bio-oil sample 3 (numbered peaks are listed in Table 3)

Figure 4. Gas chromatogram result of bio-oil

acid and 10, 11-Dihydro-10-hydroxy-2,3-dimethoxydibenz (b,f) oxepin were the main types found.

The carbohydrate compounds (cellulose and hemicelluloses) and lignins (H and G) of the fluidized bed reactor (550 ℃) were greater than those in the vacuum reactor (480 ℃), but no resins were found in the bio-oil produced in the fluidized bed (Table 4). It was concluded that the number of resin and lignin components produced were the highest at 480 ℃ in the vacuum atmosphere compared to the fluidized bed, and thus the energy density was enhanced.

Conclusion

In this paper, biomass was pyrolyzed at three different temperatures (450, 480, and 490 ℃) in a vacuum pyrolysis system. The results showed that the bio-oil generated from vacuum pyrolysis was of higher quality. It was further found that the yield of bio-oil was affected by the oxygen and moisture content. A heat recovery system that recycled the heat generated from the reactor was installed to dry raw materials for better pyrolysis as a pretreatment in order to enhance the system performance efficiency.

The results also showed that a rise in temperature increases the moisture content owing to the influence of temperature on producing water from the biomass. Compared with a fluidized bed reactor, owing to low thermal decomposition temperatures, fewer secondary reactions occurred, resulting in a bio-oil almost free from char, metals, and minerals. Viscosity is an important parameter in determining the flow case of bio-oil, and the

Table 3. Main compounds of bio-oil (H unit: p-hydroxyphenyl types, G unit: guaiacyl types)

		Compounds	Ratio of peak area (peak area/total peak area)		
			480°C #40 sample		
			1	2	3
Carbohydrates	1	Acetic acid	0.017	0.004	0.002
	2	Furfural	0.051	0.051	0.052
	3	2-Cyclopenten-1-one, 2-methyl-	0.011	0.000	0.012
	4	5-methyl-furfural	0.029	0.012	0.015
	5	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.024	0.021	0.030
	6	Hexadecanoic acid	0.023	0.024	0.027
Lignin / H unit	7	2-Methyl-phenol	0.016	0.010	0.013
	8	4-Methyl-phenol	0.014	0.012	0.015
	9	2,4-Dimethyl-phenol	0.072	0.085	0.085
	10	3-(1-Methylethyl)-phenol	0.023	0.019	0.025
Lignin / G unit	11	2-Methoxy-phenol	0.105	0.127	0.127
	12	2-Methoxy-4-methyl-phenol	0.023	0.010	0.003
	13	4-Hydroxy-3-methoxy-benzeneacetic acid	0.012	0.009	0.012
	14	4-Ethyl-2-methoxy-phenol	0.056	0.057	0.064
	15	2-Methoxy-4-vinyl-phenol	0.113	0.020	0.014
	16	2-Methoxy-4-(2-propenyl)-pheno	0.024	0.038	0.031
	17	2-Methoxy-4-propyl-phenol	0.019	0.020	0.022
	18	4-Hydroxy-3-methoxy-benzaldehyde	0.008	0.011	0.011
	19	2-Methoxy-4-(1-propenyl)-phenol	0.021	0.027	0.028
	20	(Z)-2-Methoxy-4-(1-propenyl)-phenol	0.075	0.090	0.093
	21	1-(4-Hydroxy-3-methoxyphenyl)-ethanone	0.008	0.009	0.010
	22	4-Hydroxy-3-methoxyphenylethyl-alcohol	0.008	0.009	0.010
	23	4-Hydroxy-2-methoxy-cinnamaldehyde	0.008	0.012	0.011
Resins	24	Estra-1,3,5(10)-trien-17βol	0.020	0.031	0.023
	25	Dehydroabietic acid	0.140	0.189	0.167
	26	7-Oxodehydroabietic acid, methyl ester	0.011	0.013	0.013
	27	10,11-Dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin	0.034	0.046	0.040
	28	Dibenz[b,d]cycloheptanone, 1,2,9-trimethoxy-	0.014	0.016	0.016
	29	3-Benzofuranmethanol, 2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-5-(3-hydroxy-1-propenyl)-7-methoxy-	0.023	0.028	0.028
		Total	1.000	1.000	1.000

Table 4. Relative percentage of compounds of bio-oil

Properties	Vacuum	Fluidized bed (Kim et al., 2012)			
Pyrolysis temperature (°C)	480°C	400°C	450°C	500°C	550°C
Carbohydrate (%)	13.5	65.8	66.4	67.5	67.7
Lignin (H) (%)	13.0	4.5	3.8	3.7	5.0
Lignin (G) (%)	45.2	29.7	29.8	28.9	27.3
Resin (%)	28.4	-	-	-	-
Total (%)	100	100	100	100	100

H unit: p-hydroxyphenyl types, G unit: guaiacyl types

viscosity of the bio-oil at 490°C was found to be lowest. The reduction of viscosity was the result of an increase in the moisture content of the bio-oil.

It is concluded that the quality of bio-oil produced from a vacuum reactor was better than that produced from a fluidized bed reactor, owing to fewer carbohydrates and more lignins and resins.

Conflict of Interest

Acknowledgement

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