청정에너지기술

Catalytic Fast Pyrolysis of Tulip Tree (*Liriodendron*) for Upgrading Bio-oil in a Bubbling Fluidized Bed Reactor

Hoang Vu Ly[1,2], Jinsoo Kim[1,*], Seung-Soo Kim[2,*], Hee Chul Woo[3], and Suk Soon Choi[4]

[1]Department of Chemical Engineering, Kyung Hee University
1732 Daegyeong-daero, Giheung-gu, Yongin, Gyeonggi-do 17104, Korea
[2]Department of Chemical Engineering, Kangwon National University
346 Joongang-ro, Samcheok, Gangwon-do 25913, Korea
[3]Department of Chemical Engineering, Pukyong National University
365 Sinseon-ro, Nam-gu, Busan 48513, Korea
[4]Department of Biological and Environmental Engineering, Semyung University
65, Semyung-ro, Jecheon, Chungcheongbuk-do 27136, Korea

Abstract

The bio-oil produced from the fast pyrolysis of lignocellulosic biomass contains a high amount of oxygenates, causing variation in the properties of bio-oil, such as instability, high acidity, and low heating value, reducing the quality of the bio-oil. Consequently, an upgrading process should be recommended ensuring that these bio-oils are widely used as fuel sources. Catalytic fast pyrolysis has attracted a great deal of attention as a promising method for producing upgraded bio-oil from biomass feedstock. In this study, the fast pyrolysis of tulip tree was performed in a bubbling fluidized-bed reactor under different reaction temperatures, with and without catalysts, to investigate the effects of pyrolysis temperature and catalysts on product yield and bio-oil quality. The system used silica sand, ferric oxides (Fe_2O_3 and Fe_3O_4), and H-ZSM-5 as the fluidized-bed material and nitrogen as the fluidizing medium. The liquid yield reached the highest value of 49.96 wt% at 450 ℃, using Fe_2O_3 catalyst, compared to 48.45 wt% for H-ZSM-5, 47.57 wt% for Fe_3O_4 and 49.03 wt% with sand. Catalysts rejected oxygen mostly as water and produced a lower amount of CO and CO_2, but a higher amount of H_2 and hydrocarbon gases. The catalytic fast pyrolysis showed a high ratio of H_2/CO than sand as a bed material.

Keywords : Catalytic fast pyrolysis, Fluidized-bed reactor, tulip tree, upgrading bio-oil

1. Introduction

Fossil fuel has been historically used as the main energy sources supplied for human life [1]. However, fossil fuel is finite source and is becoming depleted. Consequently, the research for a sustainable and renewable energy source to replace the nonrenewable fossil fuels has been one of the challenges for our society [1-3]. Among all the renewable resources, biomass and waste plastics have attracted considerable attention including lignocellulose [4-6], non-lignocellulose biomass [7,8], and waste plastic [9]. Compared to fossil fuels, biomass has a good reputation for its abundance and carbon neutrality, can be used for producing value-added bioenergy and biomaterials [3,8].

Bioenergy generation can be achieved by conversion of biomass via thermochemical and biological processes. Among the thermochemical processes, pyrolysis is the most promising approach widely used for producing bio-oil which can be used as raw material to produce further biofuels and bio-gasoline, bio-diesel or bio-chemicals. Furthermore, the solid product of pyrolysis, which is known as bio-char, can be used as solid fuel, bio-fertilizer or activated carbon for water treatment [10]. Injection Characteristic of bio-oil using twin fluid nozzle has been researched for its gasification [11].

However, the bio-oils should be upgraded before it can be widely used as fuel sources. This is because the pyrolysis bio-oils from biomass generally contain high oxygenated compounds that

reduce the quality of the bio-oil. Moreover, the dominant presence of oxygen content in bio-oil can cause problems during thermal processing, such as low calorific value, high corrosiveness [12,13]. There are several methods for upgrading bio-oil have been developed in recent years. Among these methods, the catalytic cracking is the most convenient because it can be applied for pyrolysis vapour and liquid bio-oils [14]. The catalytic fast pyrolysis is a technique based on catalytic cracking. With the support of catalyst, the degradations of heavy molecules to lighter molecules are enhanced, and also the deoxygenation reactions to remove O-species in the form of CO_2, CO, and/or H_2O are promoted and thus, the properties of bio-oil are improved [15,16]. However, catalysts employed should be effective and inexpensive to be applied in industrial scales. Catalysts such as alumina (Al_2O_3), metallic oxides, zeolites, and activated carbon have been used for pyrolysis of biomass due to their high catalytic activity and relatively inexpensive materials. Ly et al. [17] studied the catalytic influence of HZSM-5 on the composition of pyrolysis bio-oil from macroalga (*Saccharina japonica*) in a fluidized-bed reactor. They found that HZSM-5 was effective in a reduction in the oxygenate compounds and in a formation of the aromatic hydrocarbons compared to the conventional (non-catalytic) fast pyrolysis. Park et al. [18] used spent HZSM-5 for direct catalytic upgrading of the pyrolytic vapor of Japanese larch in a fixed catalyst bed reactor. They reported that the spent HZSM-5 showed excellent activity for deoxygenation and high selectivity for valuable compound, compared to the fresh catalyst. Ly et al. [19] used two different types of catalysts: ZSM-5 zeolite and red mud (consisted of Fe_2O_3, Al_2O_3, CaO, TiO_2) in pyrolysis of bamboo for removal of oxygenates. They reported that HZSM-5 promoted formation of methoxy phenolic and aromatic compounds, whereas red mud enhanced the demethoxylation and improved the production of saturated phenols.

In previous work regarding to catalytic pyrolysis of tulip tree (*Liriodendron*) in a fluidized-bed reactor has been confirmed that dolomite rejected oxygen mostly through dehydration, instead of decarboxylation or decarbonylation [6]. The gas product released with high H_2/CO ratio in the gaseous product was observed. For this work, to further strengthen the results from our previous research, the pyrolysis of tulip tree was investigated with different types of catalyst: HZSM-5 and iron oxides: hematite and magnetite. These results were compared to study and clarify the influence of different catalysts on the pyrolysis of this biomass feedstock. The characteristics of bio-oil and biogas were analyzed using different techniques.

2. Experimental

2.1. Sample and catalysts preparation

Tulip tree biomass was supplied by Kangwon National University. The biomass chips with a size of $(0.8 \sim 1.2)$ mm was dried in air at 105 ℃ for 12 h before being used for experiment. All catalysts were ground and sieved particle size of $60 \sim 80$ mesh $(180 \sim 250 \ \mu m)$. The commercial ZSM-5 catalyst was supplied by Hyundai Petroleum Chem. Co. (South Korea). The two different types of iron oxides including hematite and magnetite were provided by WJ Science Supplier (South Korea). The compositions of each iron oxide was determined by X-ray florescence (XRF), showing that the hematite was mainly composed of Fe_2O_3 (90.6 wt%), CaO (1.92 wt%) and SiO_2 (5.97 wt%), whereas the magnetite contained main oxides of Fe_3O_4 (60.5 wt%), MgO (22.4 wt%), Al_2O_3 (1.45 wt%), MnO (2.88 wt%) and SiO_2 (10.5 wt%). Prior to using for experiment, the ZSM-5 catalyst and iron oxides were calcined at 550 ℃ at the heating rate of 2 ℃ min^{-1} for 5 h in a muffle furnace [17,19]. The specific surface area of catalysts was determined using the multipoint Brunauer-Emmett-Teller (BET). The crystallographic structure of these catalysts was specified by powder X-ray diffraction (XRD, MAC-18XHF, Rigaku, Japan) operating at the scanning rate of 5° min^{-1} from 5 to 80° [6].

2.2. Experimental setup and analytical method

In previous research, the pyrolysis experiments were carried out in a bubbling fluidized-bed reactor under nitrogen atmosphere. The schematic bubbling fluidized-bed reactor was shown in Figure 1. For the conventional (non-catalytic) pyrolysis, the silica sand was used as the bed material. The highest yield of liquid product was obtained at 450 ℃, and gas velocity was $2.0 \times U_{mf}$ (with the minimum fluidization velocity of sand, $U_{mf} = 7.5$ L min^{-1}). In this study, the HZSM-5, iron oxides catalysts were used to replace silica sand as the bed material (as catalytic medium), the reaction temperature was set constant at 450 and 500 ℃ and the fluidization velocity was applied at $2.0 \times U_{mf}$. The U_{mf} of each catalyst was determined to be 3.5 L min^{-1} for HZSM-5, 7.7 L min^{-1} for hematite, and 8.0 L min^{-1} for magnetite, respectively. The system was directly connected to the gas chromatography for analyzing the gases product. The detailed experimental procedure was shown in our previous literature [6,17]. The product yields were calculated based on the mass of each product after pyrolysis reaction and the mass of fed biomass sample.

The ultimate analysis (determination of carbon (C), hydrogen (H), nitrogen (N), oxygen (O) contents) of bio-oils were performed with Flash EA1112, CE Instrument [6]. A pH meter (Thermo Scientific Orion 3-Star) was used to measure the pH value of liquid products. The moisture content of bio-oil was analyzed by Karl-Fischer titration (CA-200, Mitsubishi). The bio-oil (organic phase) was separated from liquid product and an amount of 0.2 g bio-oil was diluted in methanol before the
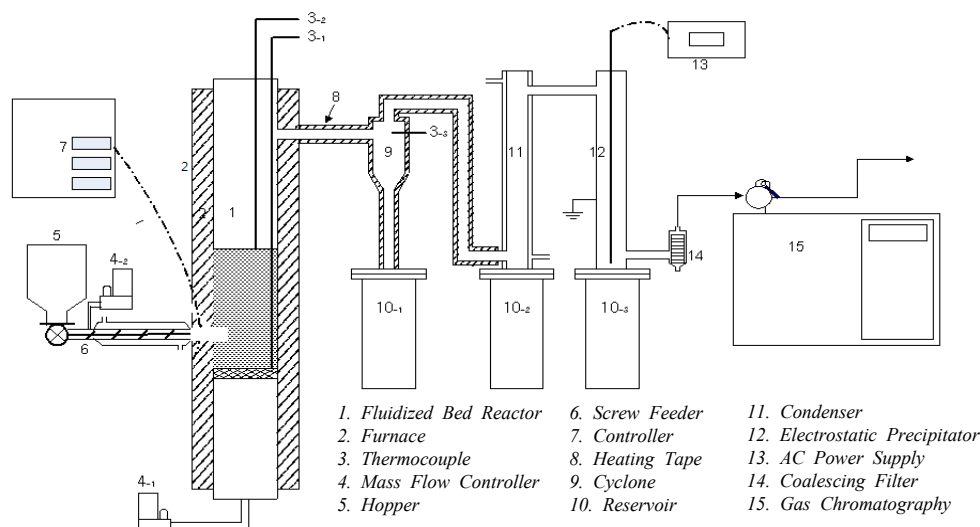
1. *Fluidized Bed Reactor* 6. *Screw Feeder* 11. *Condenser*
2. *Furnace* 7. *Controller* 12. *Electrostatic Precipitator*
3. *Thermocouple* 8. *Heating Tape* 13. *AC Power Supply*
4. *Mass Flow Controller* 9. *Cyclone* 14. *Coalescing Filter*
5. *Hopper* 10. *Reservoir* 15. *Gas Chromatography*

Figure 1. Schematic diagram of the bubbling fluidized-bed reactor.

analysis. The compositions of bio-oil were identified by Gas Chromatograph (GC-MS, Agilent 7890A) using helium carrier gas (flow rate of 1.0 mL min^{-1}) with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and coupled with 5975C mass spectrometer. The gas compositions including hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and hydrocarbon gases (C_1-C_4) were measured by gas chromatography (YL 6500GC) with a flame ionization detector (FID) using Porapak N column and a thermal conductivity detector (TCD) using Molecular sieve 13X column.

3. Results and discussion

3.1. Catalysts and Sample Characterization

The BET surface area (S_{BET}), the pore volume, and the average pore size of HZSM-5 were determined to be 132.49 m^2 g^{-1}, 0.14 cm^3 g^{-1}, and 6.70 nm, respectively. The hematite and magnetite catalysts showed the textual properties with specific surface area, the pore volume, the average pore size of 54.53 m^2 g^{-1}, 0.097 cm^3 g^{-1}, 4.11 nm for hematite and 145.17 m^2 g^{-1}, and 0.097 cm^3 g^{-1}, 3.91 nm for magnetite, respectively. The X-ray diffractogram of catalysts was reported in Figure 2. The XRD peaks for HZSM-5 were displayed at 7.83, 8.82, 22.86° and 23.89° [19,20]. The peaks at 2Θ = 21.62°, 33.37°, 40.19°, 53.36°, and 64.25° were associated with hematite (Fe_2O_3). The peaks of Fe_3O_4 appeared at 2Θ values of 30.27°, 35.67°, 43.21°, 57.16°, and 62.70°. These XRD results were consistent with those reported in previous studies [21,22].

3.2. Effect of catalysts on the product distribution and properties of bio-oil

The product distribution obtained from the catalytic fast
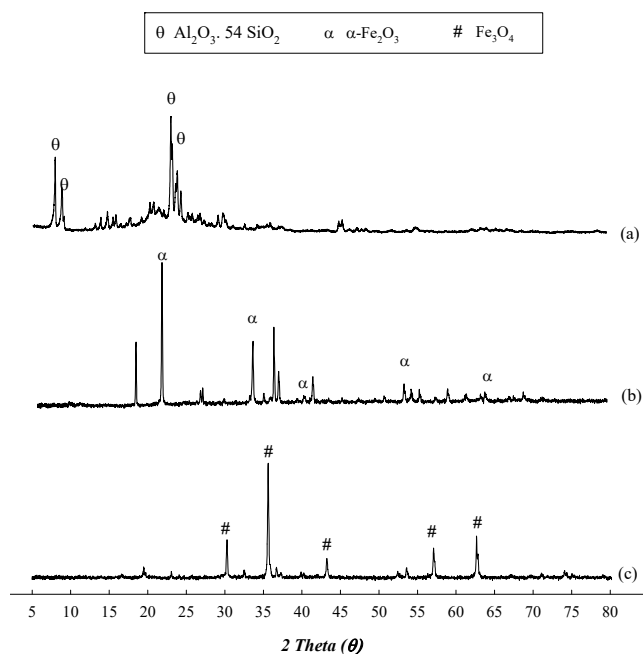

Figure 2. XRD patterns of calcined catalysts: (a) HZSM-5, (b) Hematite, and (c) Magnetite.

pyrolysis of tulip tree under the catalytic influence are shown in Table 1. As compared to non-catalytic pyrolysis, under the influence of thermal catalytic processes, the pyrolysis examined with catalysts showed higher gas yield but lower liquid yield. A decrease in liquid yield might be due to the catalytic cracking of the pyrolysis vapor to lower molecular weight compounds and non-condensable gas, followed by a series of deoxygenation reactions including dehydration, decarboxylation and decarbonylation [17,19]. Similar trends were reported by Ly et al. [6] and Lorenzetti et al. [23].

The product distribution in catalytic pyrolysis processes depends

Table 1. The effect of catalysts on product yield of tulip tree in a bubbling fluidized-bed reactor, feeding rate = 100 g hr^{-1}, 450 ℃, 2.0 × U$_{mf}$

Temperature [℃]		Sand (non-catalytic)		HZSM-5		Hematite		Magnetite	
		450	550	450	550	450	550	450	550
Product yield [wt%]	Gas	33.02	42.96	32.51	44.92	34.09	47.75	34.70	43.83
	Char	17.95	16.97	21.04	18.01	14.95	12.10	18.73	15.63
	Total liquid	49.03	40.07	48.45	37.08	49.96	40.15	47.57	40.55
	Moisture [wt%]	21.84	30.95	27.40	38.16	25.32	32.51	26.71	31.37
	Organic [wt%]	78.14	69.05	72.59	61.84	74.68	67.49	73.29	68.63
Elemental analysis of bio-oil [wt%]	C	54.17	58.49	58.31	62.21	57.48	59.23	55.84	57.85
	H	6.98	6.43	7.22	7.29	7.25	7.47	7.06	7.77
	N	0.27	0.38	0.25	0.30	0.19	0.25	0.25	0.35
	O	38.58	34.71	34.22	30.20	35.08	33.05	36.85	34.03
HHV of bio-oil [MJ kg^{-1}]		23.11	24.37	25.32	27.18	24.98	26.06	24.01	25.83
pH of bio-oil		2.53$_{\pm0.03}$	2.81$_{\pm0.01}$	3.31$_{\pm0.12}$	3.48$_{\pm0.16}$	2.91$_{\pm0.04}$	3.16$_{\pm0.01}$	2.98$_{\pm0.03}$	3.09$_{\pm0.05}$
Gas selectivity [mol%]	CO	33.21	32.25	39.28	43.34	33.92	37.25	35.69	39.80
	CO$_2$	59.03	56.60	40.70	30.66	48.11	32.65	47.23	34.24
	H$_2$	3.16	4.66	5.97	7.18	6.12	9.14	4.81	8.27
	CH$_4$	1.69	2.79	10.29	12.20	8.71	15.85	9.06	13.49
	C$_2$H$_4$	0.47	0.68	1.26	2.96	0.75	2.01	0.79	1.59
	C$_2$H$_6$	0.55	0.88	0.83	0.85	0.81	1.29	0.83	1.16
	C$_3$H$_8$	0.60	0.70	0.96	2.41	0.65	1.16	0.56	0.90
	> C$_4$ Hydrocarbons	1.28	1.44	0.72	0.39	0.94	1.29	1.03	0.54

on the reaction pathway of catalyst [19]. The high char yield was produced in case of HZSM-5 catalyst may be due to the formation of coke from aromatic compounds via polymerization and aromatization of organics in pyrolysis vapor. The increasing temperature favors the formation of coke by promoting the polymerization of these aromatic compounds [17,19].

The physicochemical properties of catalytic bio-oil are shown in Table 1. The higher heating value (HHV) of bio-oil products was theoretically calculated following the Channiwala and Parikh's equation based on the elemental analysis (the mass percentages, wt%, of C, H, O, and S) results [6,24]:

$$HHV \ (MJ \ kg^{-1}) = 0.3491 \times C + 1.1783 \times H - 0.1034 \times O$$
$$- 0.0151 \times N + 0.1005 \times S - 0.0211 \times A \quad (1)$$

A slight rise in the HHV of bio-oils was observed for catalytic pyrolysis results. The HHVs of catalytic pyrolysis bio-oils (at 450 and 550 ℃) were determined to be 25.32 ~ 27.18 MJ kg^{-1} (for HZSM-5), 24.98 ~ 26.06 MJ kg^{-1} (for hematite), 24.01 ~ 25.83 MJ kg^{-1} (for magnetite) compared to those of 23.11 ~ 24.37 MJ kg^{-1} (for sand) [6]. This is probably due to the removal of O contents from oxygenated compounds in the upgraded bio-oils to release CO, CO$_2$ gas and moisture under the catalytic effect. Indeed, in comparison with non-catalytic pyrolysis, the C content in bio-oils by catalytic pyrolysis was higher, while

the O content was lower. Especially, the O content was 30.20% (at 550 ℃) in bio-oil by pyrolysis with HZSM-5 as a catalyst (HZSM-5 bio-oil), lower than that of bio-oil by pyrolysis with sand as a bed material (sand bio-oil). This trend is similar to the literature reported by Ly et al. [19], Maisano et al. [25]. Maisano et al. [25] used dolomite and HZSM-5 catalysts in the pyrolysis of Posidonia Oceanica seagrass to produce high-quality bio-oil. They reported that, the HHV of bio-oil was 24.44 MJ kg^{-1} for non-catalytic pyrolysis. In the presence of catalysts, the HHVs increased to 26.39 MJ kg^{-1} (for dolomite) and 34.79 MJ kg^{-1} (for HZSM-5), respectively. Ly et al. studied the catalytic activity of two different catalysts (HZSM-5 and red mud) in the catalytic pyrolysis of bamboo tree. The authors concluded that the HHV increased from 25.89 MJ kg^{-1} (non-catalytic pyrolysis) to 27.98 MJ kg^{-1} and 27.26 MJ kg^{-1} with the aid of HZSM-5 and red mud, respectively. The pH values of catalytic pyrolysis bio-oil from tulip tree were between 2.91 and 3.48, higher than that of non-catalytic pyrolysis bio-oils. The elimination of oxygen from oxygenates via moisture formation was similar for all catalysts and higher than that of sand (non-catalytic pyrolysis).

3.2. Compositions of gas product

Table 1 presents that the gas products from the catalytic

pyrolysis process of tulip tree were made of mostly CO, CO_2, and a small fraction of H_2, CH_4 and other hydrocarbon gases such as ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), butane (i-C_4H_{10} and n-C_4H_{10}), which were similar to the conventional pyrolysis, but varied in their individual concentrations, depending on the conditions. It can be observed that, for conventional pyrolysis, with the increasing the temperature from 450 to 550 ℃, the CO_2 concentration decreased due to the rapid cracking of organic component to produce low molecular weight compounds; the concentration of CO increased as a result of decarbonylation of secondary pyrolysis vapor such as ketones, phenols, aldehydes [26,27].

The CO_2 and CO produced from catalytic pyrolysis could be formed by removing oxygen from O-containing compounds via catalytic cracking reactions or decarbonylation, decarboxylation under catalytic influence. These differences in concentrations of these gases are due to differences in reaction pathways depending on the activity of each catalyst. As known that HZSM-5 is an acid catalyst, due to Brønsted acid sites in zeolites structure, the decarbonylation was more dominant, producing more CO [19,28]. These accounted for the higher CO component produced from catalytic pyrolysis with HZSM-5 than other catalysts. Moreover, HZSM-5 also promoted the thermal cracking of longer chain hydrocarbons to release more hydrocarbon gases. Table 1 showed that the CO and CO_2 released from the catalytic reaction were obviously less than that of the non-catalytic reaction. On the contrary, the iron oxides favored decarboxylation reaction to produce more CO_2. In addition, the CO_2 released from catalytic the reduction reaction of hematite (Fe_2O_3) to magnetite (Fe_3O_4), to wustite (FeO) or to iron (Fe) occurred during catalytic pyrolysis process [29]. Furthermore, it can be seen that the high CH_4 yields of obtained from catalytic pyrolysis with hematite (Fe_2O_3) compared to other materials. This result might be attributed to the promoting effect of catalyst on the demethylation, demethoxylation and the thermal cracking of longer chain hydrocarbons during catalytic pyrolysis at high temperature [6].

3.3. Bio-oil analysis

The pyrolysis bio-oil is known as a complex mixture including hundreds of compounds with varied molecular weights. Table 2 shows the results of GC-MS analysis of bio-oil obtained from catalytic pyrolysis experiments at temperature of 450 ℃, at the same fluidization velocity ($2.0 \times U_{mf}$). The effect of HZSM-5 catalyst was revealed in formation of methoxy phenolic compounds, naphthalene, and indene. This result is in good agreement with other literature [17,19]. HZSM-5 promoted the production of the aromatic compounds by further recombination (repolymerization and aromatization reactions) of organic matters in pyrolysis vapor at high reaction temperature

[18,19,30]. In addition, the HZSM-5 catalyst also promoted the oxygen removal via the dehydration, showing higher water content in the liquid product than that of the others.

The major components detected in catalytic pyrolysis bio-oils with hematite and magnetite included furfural, derivatives of alkyl phenol and ketones. The formation of ketones accounts for promoting the decarboxylation and ketonization reactions during the pyrolysis processing in the presence of iron oxides catalyst [14,31]. Unlike HZSM-5, the iron oxide catalysts promoted the depolymerization reactions of pyrolysis vapor to produce the low-molecular compounds instead of aromatic compounds [19,31]. Moreover, the presence of iron oxides in pyrolysis promoted generation of saturated phenols (phenol, and alkyl phenols) through the demethylation and demethoxylation reactions of methoxy phenolic compounds. These results were similar to literature reported by Gupta et al. [14], and Wang et al. [31].

The pyrolysis bio-oils were also analyzed by thermogravimetric analyzer (TGA) with the concept of simulated distillation based on the boiling point of liquid product, to identify the carbon
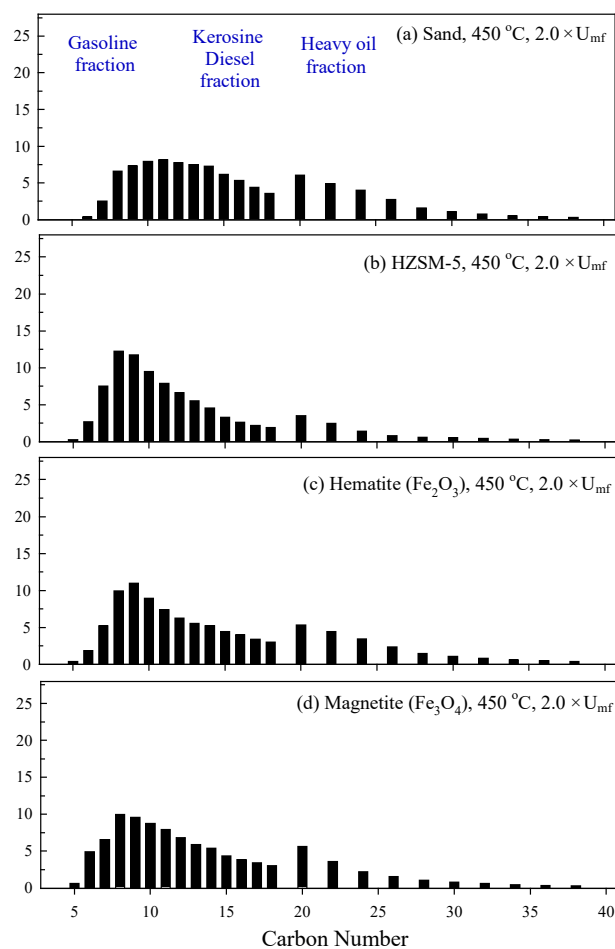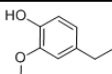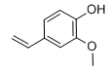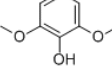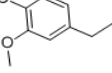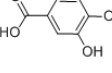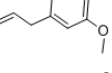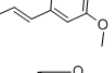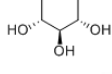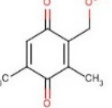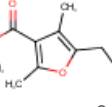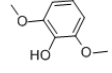

Figure 3. Carbon number distribution of bio-oil produced from pyrolysis and catalytic pyrolysis of tulip tree at 450 ℃, $2.0 \times U_{mf}$, and feeding rate of 100 g hr^{-1}.

Table 2. Compounds identified by GC-MS in bio-oil produced by catalytic pyrolysis of tulip tree at 450 ℃, $2.0 \times U_{mf}$, feeding rate = 100 g hr^{-1}

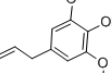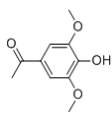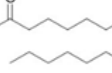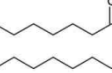| Composition	Sand	HZSM-5	Hematite	Magnetite	Structure
1-hydroxy-2-Propanone	1.96	2.45	3.05	3.21	
Furfural	1.49	2.5	3.23	2.92	
5-mehyl-2-Furfural			0.89	1.19	
2-Furanmethanol	0.40		1.04	1.78	
2-hydroxy-2-Cyclopenten-1-one	1.05	2.14	3.39	3.41	
2-hydroxy-3-methyl-2-cyclopenten-1-one	1.82	1.31	1.90	1.75	
2,3-dimethyl-2-Cyclopenten-1-one	0.49			0.22	
Phenol	0.37	1.12	1.68	1.85	
2-methyl-Phenol		1.2	1.78	1.44	
3-methyl-Phenol	0.46	1.18	1.89	1.56	
2-methoxy-Phenol	1.49	2.41	1.64	2.09	
2,4-dimethyl-Phenol	0.43	1.61	0.77	0.22	
3,5-dimethyl-Phenol			0.61	0.38	
2-methoxy-4-methyl-Phenol	1.58	3.10	1.19	1.79	
Naphthalene		1.43			
1-methyl-Naphthalene		2.81			
1,7-methyl-Naphthalene		2.55			
1,2-Benzenediol					
3-methyl-1,2-Benzenediol	1.4			0.66	
1-methyl-1H-indene		2.18			
2,4,6-trimethyl-Phenol		2.39			

Table 2. To be Continued

2-methoxy-4-ethyl-phenol	0.72	1.57	1.69	1.86	
2-methoxy-4-vinylphenol	1.17	2.94	1.66	2.08	
2,6-dimethoxy-Phenol	6.5	4.68	3.08	4.14	
2-methoxy-4-propyl-phenol	0.15	1.13	0.85	0.79	
4-Hydroxy-3-methoxybenzoic acid (Vanillic acid)	5.12	5.36	3.20	3.11	
2-methoxy-4-(2-propenyl)-Phenol (Eugenol)	1.63	1.14	0.57	0.65	
2-methoxy-4-(1-propenyl)-Phenol (Isoeugenol)		5.76	0.31	0.43	
Levoglucosan	10.76	1.70	2.9	2.33	
2-(methoxymethyl)-3,5-dimethyl-2,5-Cyclohexadiene-1,4-dione	4.28	4.41	3.39	3.0	
2,4-Dimethyl-3-(methoxycarbonyl)-5-ethylfuran	2.52	2.53	1.29	3.11	
4-hydroxy-3,5-dimethoxy-Benzaldehyde (Vanilline)	1.1	3.35	1.79	1.09	
2,6-Dimethoxy-4-allyl phenol	9.66	9.19	7.30	6.34	
1-(4-hydroxy-3,5-dimethoxyphenyl)-Ethanone (Acetovanilone)	1.06	2.41	1.97	1.33	
Palmitinic acid	0.77	0.32	0.57	0.36	
Oleic acid	1.57		0.50		

number distribution [6,17,19]. As shown in Figure 3, the carbon number of bio-oil was distributed in three fractions: C_5-C_{11}, C_{12}-C_{18} and small amount of C_{20}-C_{38} corresponding to gasoline, kerosene-diesel, and heavy oil fractions, respectively. The distribution of these fractions in the pyrolysis bio-oil (at 450 ℃) was 32.95 wt% (C_5-C_{11}), 41.99 wt% (C_{12}-C_{18}) and 22.48 wt% (C_{20}-C_{38}), respectively. However, the carbon number distribution showed significant changes with the replacement of sand by catalysts. The distribution of bio-oils concentrated in kerosene and diesel fraction. The fractions of C_5-C_{11}, C_{12}-C_{18}, C_{20}-C_{38} in HZSM-5 pyrolysis bio-oil were 51.80, 26.75, and 10.74 wt%, respectively. The bio-oil obtained from pyrolysis

with hematite contained 44.77 wt% of C_5-C_{11}, 31.87 wt% of C_{12}-C_{18}, and 20.37 wt% of C_{20}-C_{38}, compared to 48.33 wt% of C_5-C_{11}, 32.81 wt% of C_{12}-C_{18}, and 16.58 wt% of C_{20}-C_{38} of the bio-oil from pyrolysis with magnetite. These distributions are reasonable, considering the GC-MS data. These confirm the feasibility of upgrading tulip tree pyrolysis bio-oil to high quality bio-oil using natural catalysts, and the upgraded bio-oil can be used as a great source for manufacturing alternative biodiesel or valuable chemicals.

4. Conclusions

The catalytic fast pyrolysis process of tulip tree was systematically investigated in a bubbling fluidized-bed reactor at 450 and 550 ℃ with a fluidization velocity of $2.0 \times U_{mf}$ using HZSM-5 and hematite and magnetite catalysts as bed material. The HHVs of conventional pyrolysis bio-oils were in the range of $23.11 \sim 24.37$ MJ kg^{-1}. The liquid yield decreased but the quality of bio-oil increased when replacing sand by catalysts. The HHV of bio-oil from catalytic pyrolysis increased to $25.32 \sim 27.18$ MJ kg^{-1} for HZSM-5, and 24.98 ~ 26.06 MJ kg^{-1} for hematite catalysts, respectively. The reaction pathways were quite different between catalysts. HZSM-5 promoted the decarboxylation, decarbonylation and repolymerization. Meanwhile, iron oxides elevated the decarboxylation, ketonization and depolymerization reactions. The gas product with a high H_2/CO ratio can be used in the synthesis of liquid fuel. The weight fraction of bio-oil was mainly distributed in the range of gasoline fraction. This study proves the great potential of HZSM-5, hematite and magnetite catalyst for upgrading bio-oil to produce valuable products such as bio-fuel, biodiesel and/or bio-chemicals.

Acknowledgments

Nomenclature

HHV: high heating value (MJ kg^{-1})
U_{mf}: minimum velocity (L min^{-1})

References

1. Bach, Q.-V., Trinh, T. N., Tran, K.-Q., and Thi, N. B. D., "Pyrolysis Characteristics and Kinetics of Biomass Torrefied in Various Atmospheres", *Energy Convers. Manage.*, **141**, 72-78 (2017).

2. Hamzehkolaei, F. T., and Amjady, N., "A Techno-economic Assessment for Replacement of Conventional Fossil Fuel Based Technologies in Animal Farms with Biogas Fueled CHP Units", *Renew. Energy*, **118**, 602-614 (2018).

3. Maliutina, K., Tahmasebi, A, Yu, J., and Saltykov, S. N., "Comparative Study on Flash Pyrolysis Characteristics of Microalgal and Lignocellulosic Biomass in Entrained-flow Reactor", *Energy Convers. Manage.*, **151**, 426-438 (2017).

4. Mullen, C. A., Boateng, A. A., Goldberg, N. M., Lima, I. M., Laird, D. A., and Hicks, K. B., "Bio-oil and Bio-char Production from Corn Cobs and Stover by Fast Pyrolysis", *Biomass Bioenerg.*, **34**, 67-74 (2010).

5. Kim, S.-S., Shenoy, A., and Agblevor, F., "Themogravimetric and Kinetic Study of Pinyon Pine in the Various Gases", *Bioresour. Technol.*, **156**, 297-302 (2014).

6. Ly, H. V., Lim, D.-H., Sim, J. W., Kim, S.-S., and Kim, J., "Catalytic Pyrolysis of Tulip Tree (Liriodendron) in Bubbling Fluidized-bed Reactor for Upgrading Bio-oil using Dolomite Catalyst", *Energy*, **162**, 564-575 (2018).

7. Ly, H. V., Kim, S.-S., Kim, J., Choi, J. H., and Woo, H. C., "Effect of Acid Washing on Pyrolysis of Cladophora Socialis Alga in Microtubing Reactor", *Energy Convers. Manag.*, **106**, 260-267 (2015).

8. Ly, H. V., Kim, S.-S., Woo, H. C., Choi, J. H., Suh, D. J., and Kim, J., "Fast Pyrolysis of Macroalga Saccharina japonica in a Bubbling Fluidized-bed Reactor for Bio-oil Production", *Energy*, **93**, 1436-1446 (2015).

9. Yang, H.-S., Hyun, J.-H., Yoon, B.-Y., and Kim, H.-K., "Comparison of Yield of Pyrolysis Oil by Operating Condition in Batch Type Pyrolysis using Plastic Wastes", *J. Korea Soc. Waste Manag.*, **36**(4), 361-367 (2019).

10. Elkhalifa, S., Al-Ansari, T., Mackey, H. R., and McKay, G., "Food Waste to Biochars through Pyrolysis: A Review", *Resour. Conserv. Recy.*, **144**, 310-320 (2019).

11. Choi, M. K., Kang, S. J., Kim, H. S., Park, H. C., and Choi, H. S., "Numerical Study on Injection Characteristics of Bio-oil using Twin Fluid Nozzle for Bio-oil Gasification Reactor", *J. Korea Soc. Waste Manag.*, **36**(3), 267-277 (2019).

12. He, Z., and Wang, X., "Hydrodeoxygenation of Model Compounds and Catalytic Systems for Pyrolysis Bio-oils Upgrading", *Catal. Sustain. Energy*, **1**, 28-52 (2012).

13. Le, T. A., Ly, H. V., Kim, J., Kim, S.-S., Choi, J. H., Woo, H. C., and Othman, M. R., "Hydrodeoxygenation of 2-furyl Methyl Ketone as a Model Conpound in Bio-oil from Pyrolysis of Saccharaina japonica Alga in Fixe-bed Reactor", *Chem. Eng. J.*, **105**, 157-163 (2014).

14. Gupta, J., Papadikis, K., Kozhevnikov, I. V., and Konysheva, E. Y., "Exploring the potential of red mud and beechwood co-processing for the upgrading of fast pyrolysis vapours", J. Anal. Appl. Pyrol. **111**, 35-43 (2017).

15. Ly, H. V., Kim, J., Hwang, H. T., Choi, J. H., Woo, H. C., and Kim, S.-S., "Catalytic Hydrodeoxygenation of Fast Pyrolysis Bio-Oil from Saccharina japonica Alga for Bio-Oil Upgrading", *Catalysts*, **9**, 1043 (2019).

16. Graça, I., Lopes, J. M., Cerqueira, H. S., and Ribeiro, M. F., "Bio-oils upgrading for second generation biofuels", *Ind. Eng. Chem. Res.*, **52**, 275-287 (2013).

17. Ly, H. V., Choi, J. H., Woo, H. C., Kim, S.-S., and Kim, J., "Upgrading Bio-oil by Catalytic Fast Pyrolysis of Acid-washed Saccharina japonica Alga in a Fluidized-bed Reactor", *Renew. Energy*, **133**, 11-22 (2019).

18. Park, H. J., Heo, H. S., Yim, J. H., Jeon, J. K., Ko, Y. S., Kim, S. S., and Park, Y. K. "Catalytic Pyrolysis of Japanese Larch using Spent HZSM-5", *Korean J. Chem. Eng.*, **27**(1), 73-75 (2010).

19. Ly, H. V., Park, J. W., Kim, S.-S., Hwang, H. T., Kim, J., and Woo, H. C., "Catalytic Pyrolysis of Bamboo in a Bubbling Fluidized-bed Reactor with Two Different Catalysts: HZSM-5 and Red Mud for Upgrading Bio-oil", Renew. Energy in press.

20. Wang, B., Wang, H., Liu, G., Li, X., and Wu, J., "Conversion of Dimethyl Ether to Toluene under an O_2 Stream over W/HZSM-5 Catalysts", *Catal. Sci. Technol.*, **5**, 1813-1820 (2015).

21. Tirupanyam, B. V., Srinivas, C., Meena, S. S., Yusuf, S. M., Kumar, A. S., Sastry, D. L., and Seshubai, V., "Investigation of Structural and Magnetic Properties of Co-precipitated Mn-Ni Ferrite Nanoparticles in the Presence of α-Fe_2O_3 phase", *J. Magn. Magn. Mater*, **392**, 101-106 (2015).

22. Ebadi, M., Buskaran, K., Saifullah, B., Fakurazi, S., and Hussein, M. Z., "The Impact of Magnesium-Aluminum-Layered Double Hydroxide-Based Polyvinyl Alcohol Coated on Magnetite on the Preparation of Core-Shell Nanoparticles as a Drug Delivery Agent", *Int. J. Mol. Sci.*, **20**(15), 3764 (2019).

23. Lorenzetti, C., Conti, R., Fabbri, D., and Yanik, J., "A Comparative Study on the Catalytic Effect of H-ZSM5 on Upgrading of Pyrolysis Vapors Derived from Lignocellulosic and Proteinaceous Biomass", *Fuel*, **166**, 446-452 (2016).

24. Channiwala, S. A., and Parikh, P. P., "A Unified Correlation for Estimating HHV of Solid, Liquid and Gaseous Fuels", *Fuel*, **81**, 1051-1063 (2002).

25. Maisano, S., Urbani, F., Mondello, N., and Chiodo, V., "Catalytic Pyrolysis of Mediterranean Sea Plant for Bio-oil Production", *Int. J. Hydrog. Energy,* **42**, 28082-28092 (2017).

26. Idem, R. O., Katikaneni, S. P. R., and Bakhshi, N. N., "Thermal Cracking of Canola Oil: Reaction Products in the Presence and Absence of Steam", *Energy Fuels*, **10**, 1150-1162 (1996).

27. Kantarelis, E., "Catalytic Steam Pyrolysis of Biomass for Production of Liquid Feedstock", KTH-Royal Institute of Technology 162. ISBN 978-91-7595-023-5 (2014).

28. Liu, T.-L., Cao, J.-P., Zhao, X.-Y., Wang, J.-X., Ren, X.-Y., Fan, X., Zhao, Y.-P., and Wei, X.-Y., "In situ Upgrading of Shengli Lignite Pyrolysis Vapors over Metal-loaded HZSM-5 Catalyst", *Fuel Process. Technol.*, **160**, 19-26 (2017).

29. López, A., Marco de, I., Caballero, B. M., Laresgoiti, M. F., Adrados, A., and Aranzabal, A., "Catalytic Pyrolysis of Plastic Wastes with two Different Types of Catalysts: ZSM-5 zeolite and Red Mud", *Appl. Catal. B.*, **104**, 211-219 (2011).

30. Sweygers, N., Somers, M. H., and Appels, L., "Optimization of Hydrothermal Conversion of Bamboo (Phyllostachys aureosulcata) to Levulinic Acid via Response Surface Methodology", *J. Environ. Manage.*, **219**, 95-102 (2018).

31. Wang, S., Xi, Z., Bai, X., Yi, W., and Fu, P., "Catalytic Pyrolysis of Lignin in a Cascade Dual-catalyst System of Modified Red Mud and HZSM-5 for Aromatic Hydrocarbon Production", *Bioresour. Technol.*, **278**, 66-72 (2019).