

Upgrading of bio-oil by ex-situ catalytic pyrolysis and in-line esterification in fluidized bed reactor

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(Received 11 December 2019 • Revised 5 January 2020 • Accepted 28 February 2020)

Abstract—Ex-situ catalytic pyrolysis of *Quercus mongolica* over HZSM-5 and in-line esterification of pyrolysis/catalytic pyrolysis vapors with liquid phase *n*-butyl alcohol were carried out in a fluidized bed reactor. The ex-situ catalytic pyrolysis over HZSM-5 beads was performed to produce bio-oil containing aromatic hydrocarbons. The temperature of the ex-situ catalytic upgrading reaction was varied from 450 °C to 600 °C, and the maximum aromatic hydrocarbons yield was obtained at 450 °C. The selectivity for aromatic hydrocarbons as a function of catalytic reaction temperature varied depending on aromatic ring number, as the selectivity for mono-aromatic hydrocarbons decreased and that for poly-aromatic hydrocarbons increased with temperature. In-line esterification of the pyrolysis/catalytic pyrolysis vapors with liquid *n*-butyl alcohol was also carried out, and the GC/MS analysis results showed that the acids, aldehydes and ketones in the bio-oil were converted to esters and acetals.

Keywords: Ex-situ Catalytic Pyrolysis, Fluidized Bed Reactor, HZSM-5 Beads, In-line Esterification, *n*-Butyl Alcohol

INTRODUCTION

Renewable energy has received significant attention toward mitigating energy shortages, dwindling fossil fuels, and environmental problems. Lignocellulosic biomass is the only carbon source in renewable energy that has been considered for use in the petrochemical industry [1]. The pyrolysis of biomass is a thermochemical conversion method for replacing fossil fuels that involves thermal decomposition via heating at 400–600 °C under oxygen-free atmospheric conditions [2]. Biomass pyrolysis produces bio-oil, biochar, and gas, among which the liquid phase bio-oil is the main product. Bio-oil has advantages due to its liquid phase such as convenient storage and transport and potential for direct replacement of current fuels and chemicals [3]. However, the use of bio-oil produced by thermal pyrolysis of biomass is limited by its low quality as a fuel and chemicals because of its wide range of molecular weights, high oxygen-containing compound content, and properties such as acidic, corrosive, and thermally unstable [4]. Therefore, upgrading reactions including esterification, hydrodeoxygenation (HDO), and catalytic pyrolysis is essential for achieving a high quality bio-oil [5]. Among these, esterification and catalytic pyrolysis are advantageous in that the bio-oil can be upgraded without a hydrogen supply using a simple continuous process and atmospheric pressure [6].

Catalytic pyrolysis of biomass has been studied extensively using various reactors such as micro-scale pyrolysis reactors, lab-scale fixed beds, bench-scale fixed beds, and fluidized bed reactors and catalysts such as zeolite (HZSM-5, HY, HBeta, Mordenite) [7,8], mesoporous materials (Al-SBA-15, Al-MCM-41, Al-MCM-48, and Al-MSU-F) [9], and metal oxides (MgO, TiO₂, CeO₂, and Al₂O₃)

[10]. The upgrading capabilities, production of aromatic hydrocarbons, of HZSM-5 are known to be the most efficient due to its higher acidity and shape selectivity than other catalysts [11]. Jae et al. [12] previously reported the effect of zeolite pore structure and shape selectivity on the catalytic conversion of biomass to aromatic hydrocarbons and concluded that ZSM-5 with a medium pore size and moderate pore space resulted in the highest yield of aromatic hydrocarbons. Toward effective aromatic hydrocarbon production, studies on catalyst screening and the effects of operating parameters such as feedstock pretreatment (torrefaction) [13,14], catalyst acidity, catalytic upgrading mode (in-situ and ex-situ), and catalyst-to-feedstock ratio have been also reported. Paasikallio et al. [15] reported on the in-situ catalytic fast pyrolysis of beech wood over HZSM-5 with various catalyst-to-biomass ratios in a circulating fluidized bed reactor. Variations in catalyst-to-biomass ratio between 11 and 21 led to a limited change in product and elemental distributions. Iisa et al. [16] reported that in-situ and ex-situ catalytic pyrolysis of pine over HZSM-5 using a bench-scale fluidized bed reactor were conducted to evaluate the aromatic hydrocarbon yield and bio-oil quality. They reported that, compared with in-situ catalytic pyrolysis, the catalyst deactivation was relatively low in the ex-situ catalytic pyrolysis process.

Esterification is another bio-oil upgrading method for improving the physical and chemical properties of bio-oil, during which dehydration through reaction with alcohol simultaneously occurs [17]. The esterification of bio-oils with alcohol includes esterification of acids into esters and acetalization of aldehydes and ketones into acetals [18]. The reaction has been carried out at relatively low temperatures (50–120 °C) with various alcohols (methyl alcohol, ethyl alcohol, propyl alcohol, and butyl alcohol) to reduce the acidity and instability of the bio-oil [17,19]. For bio-oil esterification, various methods including esterification in olefins/alcohols, esterification coupled with pre-oxidation/hydrogenation, and reactive

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Table 1. Ultimate and proximate analysis results of *Quercus mongolica*

	Ultimate analysis (wt%)					Proximate analysis (wt%)			
	C	H	O	N	S	Moisture	Volatile matter	Fixed carbon	Ash
<i>Quercus mongolica</i>	49.39	6.59	43.72	0.25	0.05	3.31	78.04	18.2	0.46

distillation have been reported [20]. Most studies on esterification reactions were performed using dehydration by distillation. Although esterification of bio-oil has been extensively studied using recovered liquid-phase bio-oil with alcohol, research on gas-liquid phase esterification of pyrolysis vapors with liquid alcohol during pyrolysis or catalytic pyrolysis of biomass remains insufficient [21].

Therefore, in this study, an integrated reaction combining catalytic pyrolysis, and esterification of pyrolysis/catalytic pyrolysis vapors with liquid *n*-butyl alcohol was performed using a fluidized bed reactor for the first time. Mongolian oak (*Quercus mongolica*) was used as the feedstock for pyrolysis at 550 °C, and catalytic upgrading reaction was carried out using a bead type HZSM-5 zeolite catalyst. The effect of reaction parameters such as catalytic upgrading reaction temperature and catalyst deactivation and regeneration were investigated. In-line esterification was also performed on the thermal pyrolysis/catalytic pyrolysis vapors with liquid *n*-butyl alcohol, and the obtained bio-oil was qualitatively and quantitatively analyzed by gas chromatography/mass spectrometry (GC/MS).

MATERIALS AND METHODS

1. Materials

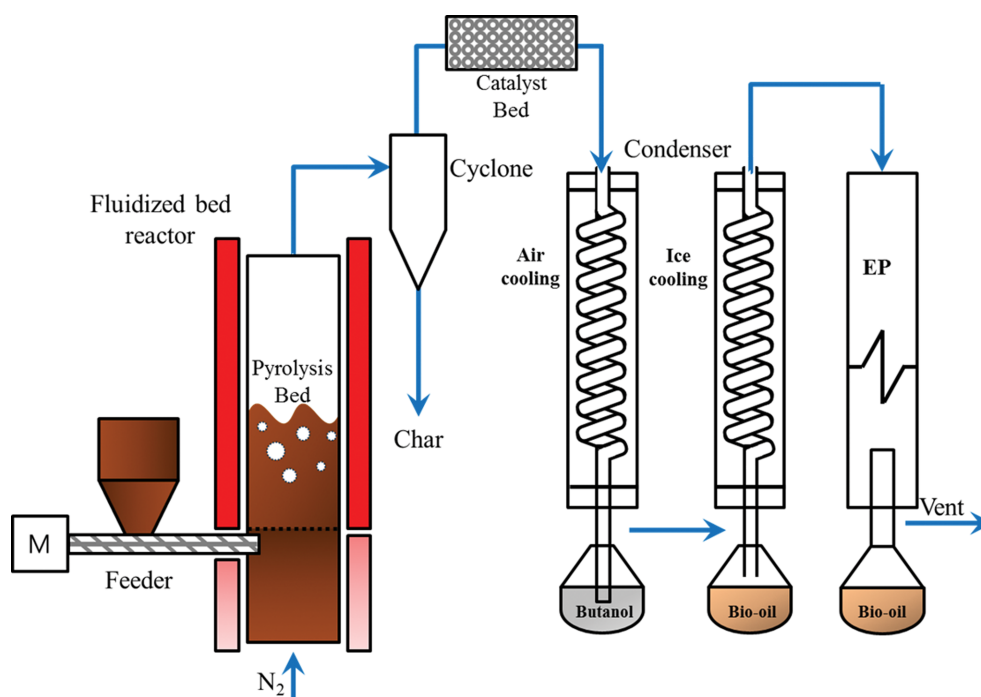
Quercus mongolica was used as the pyrolysis feedstock. The biomass feedstock was sieved to a particle size of approximately 1 mm,

then dried at 110 °C overnight before experimental use. The ultimate and proximate analyses of the biomass were conducted using an elemental analyzer (vario MACRO cube, Elementar) and thermogravimetric analyzer (TGA, Pyris 8000, PerkinElmer), respectively, according to literature procedures [22]. The results of the ultimate and proximate analysis are listed in Table 1. The content of carbon, hydrogen, oxygen, nitrogen, and sulfur obtained from the ultimate analysis was 49.39, 6.59, 43.72, 0.25, and 0.05 wt%, respectively. The content of moisture, volatile matter, fixed carbon, and ash obtained from the proximate analysis was 3.31, 78.04, 18.2, and 0.46 wt%, respectively. The biomass chemical compositions of feedstock were determined using the method of the National Renewable Energy Laboratory (NREL) [23]. The chemical composition of feedstock in this study was as follows: glucan: 45.78%, xylan: 20.16%, arabinan: 0.4%, lignin: 26.33% (acid-insoluble lignin: 24.3% and acid-soluble lignin: 2.03%) and extracts: 0.59%.

HZSM-5 beads (Zeolyst International, USA) with a diameter of 1 cm were used for ex-situ catalytic pyrolysis. The surface area and pore volume of HZSM-5 were characterized by N₂ adsorption-desorption using BELSORP-mini II (BEL, Japan). The Brunauer-Emmett-Teller (BET) surface area and total pore volume (at P/P₀=0.990) were 347 m²/g and 0.348 cm³/g, respectively.

2. Catalytic Upgrading Reaction

The thermal pyrolysis and catalytic pyrolysis of *Quercus mon-*

**Fig. 1. Schematic diagram of the fluidized bed pyrolysis reactor.**

golica were carried out using a fluidized bed pyrolysis reactor (Fig. 1) consisting of a feeding system, fluidized bed pyrolysis reactor, cyclone, ex-situ catalytic upgrading reactor, air- and ice-cooled condensing system, and electrostatic precipitator. The feedstock was supplied to the fluidized bed pyrolysis reactor with silica sand (50–70 mesh particle size, Sigma Aldrich) as a bed material through a screw-type feeder at a rate of 3–4 g/min. Nitrogen gas was supplied at a flow rate of 13 L/min as fluidizing gas. For catalytic pyrolysis, approximately 110 g of HZSM-5 beads (Zeolyst International, USA) with a diameter of 1 cm was used.

The condensing system consisted of two condensers (air- and ice-cooled) and an electrostatic precipitator. The first of the two condensers operated via air-cooled condensation to lower the vapor temperature to approximately 50–80 °C to recover the bio-oil from thermal pyrolysis/catalytic pyrolysis vapors or to perform esterification of thermal pyrolysis/catalytic pyrolysis vapors with liquid *n*-butyl alcohol (Junsei Chemical, Japan). The bio-oil was also recovered through heat exchange via condensing at –20 °C (2nd condenser, ice-cooled).

The produced bio-oil was qualitatively and quantitatively analyzed by GC/MS (7890A/5975C inert, Agilent Technologies, USA). For the separation of bio-oil compounds, a UA-1 GC capillary column (Ultra Alloy-1, Frontier Laboratories, 30 m length×0.25 mm inner diameter×0.25 μm film thickness) was used with a 30 mL/min helium flow. The oven temperature was programmed to increase from 35 °C (5 min) to 310 °C (7 min) at a heating rate of 10 °C/min with a 0.7 mL/min column flow rate. The GC/MS peaks of bio-oil were identified using the NIST 5th library. Quantitative analysis was performed by the internal standard method using fluoranthene (Sigma Aldrich). The yield of carbonaceous deposits, referred to as coke, on the HZSM-5 zeolite catalyst was measured by air-flow TGA. The deactivated catalyst was thermally treated under air flow at a heating rate of 20 °C/min up to 650 °C, at which the temperature was kept constant for 60 min.

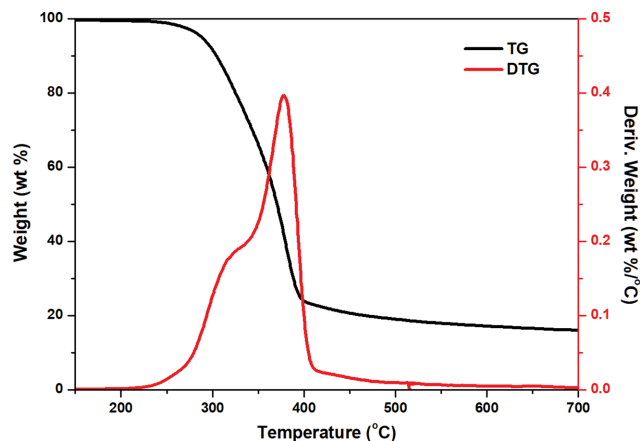


Fig. 2. TG and DTG curves of *Quercus mongolica*.

RESULTS AND DISCUSSION

1. Pyrolysis Properties of Feedstock

The thermogravimetry (TG) and derivative thermogravimetry (DTG) results of *Quercus mongolica* at a heating rate of 20 °C/min are shown in Fig. 2, which indicate the thermal degradation characteristics of the feedstock. Generally, hemicellulose, cellulose, and lignin decompose in the temperature ranges of 200–300 °C, 350–400 °C, and 250–500 °C, respectively [24]. Compared with cellulose and hemicellulose, lignin has a wider and higher decomposition temperature range due to its thermally resistant structure [25]. *Quercus mongolica* completely decomposed at approximately 550 °C, and thus the thermal pyrolysis temperature of *Quercus mongolica* was set at 550 °C in this study.

2. Thermal and Catalytic Pyrolysis

The results of thermal pyrolysis (550 °C) and ex-situ catalytic pyrolysis (550 °C for pyrolysis and 450–600 °C for catalytic upgrad-

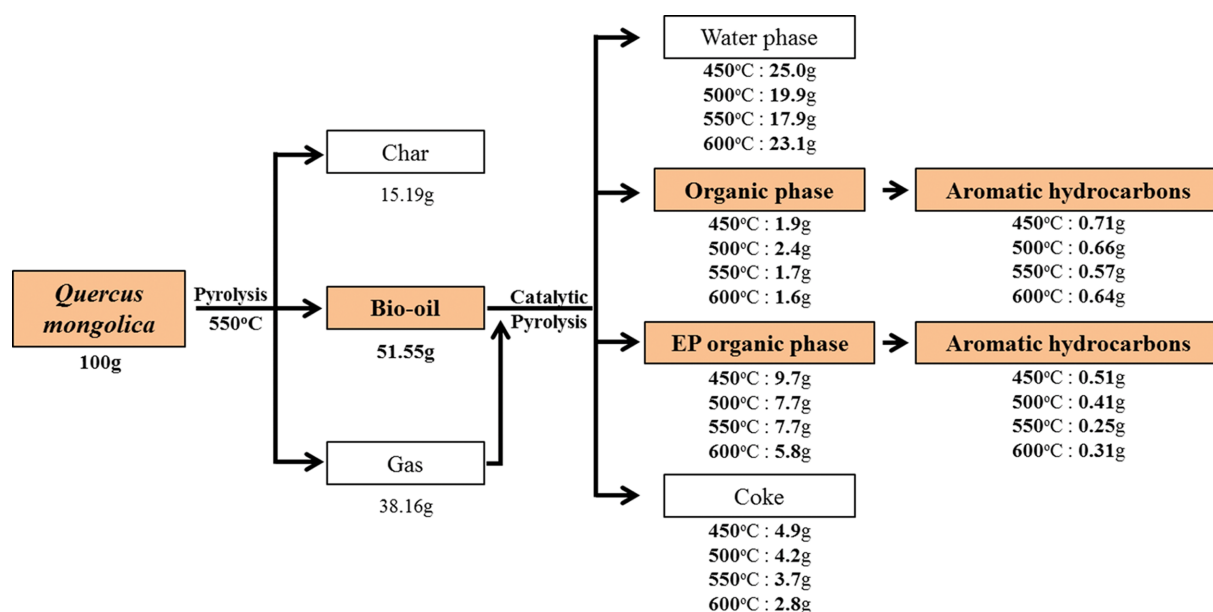


Fig. 3. Yield from thermal pyrolysis and catalytic pyrolysis.

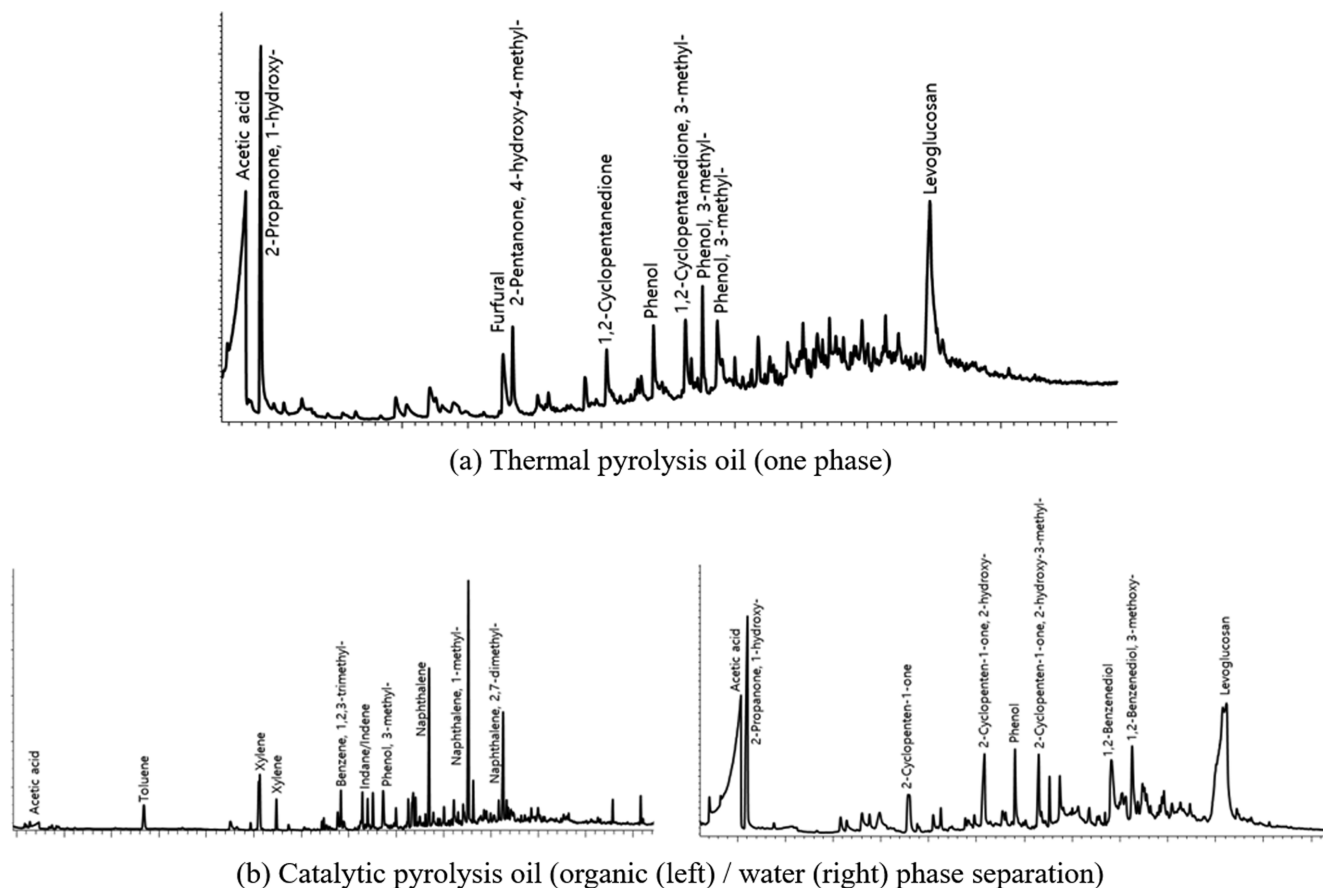


Fig. 4. GC/MS chromatograms of bio-oil obtained from (a) thermal pyrolysis and (b) catalytic pyrolysis.

ing reaction) of *Quercus mongolica* were compared. Compared to thermal pyrolysis, the bio-oil yield from the catalytic pyrolysis was decreased and gas product yield was increased due to ex-situ catalytic upgrading reactions such as catalytic cracking and deoxygenation (Fig. 3).

As indicated by the GC/MS analysis results in Fig. 4 of bio-oil produced from thermal pyrolysis and catalytic pyrolysis, the thermal pyrolysis oil contained acetic acid and hydroxy-propanone derived from hemicellulose pyrolysis, levoglucosan and furfural derived from cellulose pyrolysis, and phenolics derived from lignin pyrolysis. After the catalytic upgrading reaction, oxygen was removed from oxygenated compounds, and aromatic hydrocarbons such as toluene, xylene, naphthalene, and methyl-naphthalene were produced in the organic phase.

The conversion of cellulose and hemicellulose degradation products (levoglucosan, acetic acid, furans, and ketones) and lignin degradation products (phenolics) into aromatic hydrocarbons can be explained by two aromatic hydrocarbons formation mechanisms, the hydrocarbon pool mechanism and phenolic pool mechanism [26–28]. Levoglucosan derived from the pyrolysis of cellulose was converted to furan compounds via dehydration, decarbonylation, and decarboxylation on the catalyst. These furan compounds were converted to aromatic hydrocarbons over zeolite via a series of reactions of cracking, deoxygenation (dehydration to H_2O , decarboxylation to CO_2 , and decarbonylation to CO), oligomerization, and

aromatization [26]. The phenolic compounds were converted to aromatic hydrocarbons via the hydrocarbon pool and phenolic pool mechanisms. In the case of the hydrocarbon pool mechanism, light hydrocarbons derived from the cracking of lignin pyrolyzates were converted to aromatic hydrocarbons. The phenolic pool mechanism is related to the formation of a surface pool via phenolic condensation for aromatic hydrocarbons production. Aromatic hydrocarbons were then produced by cracking and H-transfer of the phenolic surface pool on zeolite [27,29].

3. Effect of Catalytic Upgrading Reaction Temperature

Quercus mongolica was pyrolyzed at 550 °C, and the temperature of ex-situ catalytic upgrading was adjusted from 450 to 600 °C to investigate the effect of temperature on aromatic hydrocarbons formation. The weights of the pyrolysis products (biochar, bio-oil, and gas) from 100 g of biomass are shown in Fig. 3. The bio-oil produced by catalytic pyrolysis was separated into water and organic phases, whereas thermal pyrolysis produced one-phase bio-oil. The organic phase of the bio-oil produced by catalytic pyrolysis contained upgraded bio-oil compounds such as aromatic hydrocarbons, whereas the water phase still consisted of oxygen-containing substances such as acetic acid, hydroxy-propanone, levoglucosan, and furfural (Fig. 4).

The yield and selectivity for aromatic hydrocarbons in the bio-oil from different catalytic upgrading temperatures are compared in Fig. 5. The aromatic hydrocarbons were categorized as BTEXs (ben-

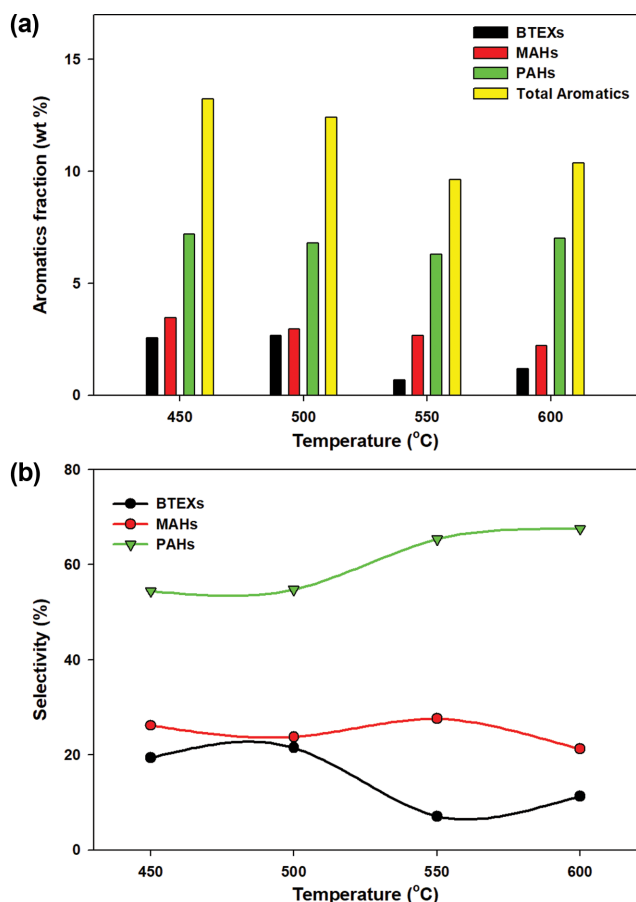


Fig. 5. Aromatic hydrocarbons production (a) yield and (b) selectivity.

zene, toluene, ethylbenzene, and xylene), MAHs (other mono-aromatic hydrocarbons such as trimethyl-benzene and indane/indene), and PAHs (polycyclic aromatic hydrocarbons such as naphthalene, methyl-naphthalene, and dimethyl-naphthalene).

The yield of total aromatic hydrocarbons in the bio-oil ranged from 9.63 to 13.22 wt%, where the highest yield was obtained at the lowest catalytic upgrading temperature of 450 °C. Aromatic hydrocarbons were classified into three groups, BTEXs, MAHs, and PAHs, and the selectivity for the respective groups (selectivity = corresponding aromatic hydrocarbons/total aromatic hydrocarbons) was also compared according to the catalyst upgrading temperature (Fig. 5(b)). In the temperature range of 450–600 °C, the selectivity for BTEXs was 7.0–21.5%, for MAHs was 21.5–27.6%, and for PAHs was 54.4–67.5%. As the catalytic upgrading reaction temperature decreased, the selectivity for BTEXs and MAHs, which are relatively small aromatic hydrocarbons, increased, and the selectivity for PAHs, which are relatively large aromatic hydrocarbons, decreased. Zhang et al. [30] previously described the catalytic pyrolysis reaction pathway: the vapor (bio-oil+gas) generated from biomass thermal pyrolysis adsorbs to the surface active sites of the catalyst, and cracking, deoxygenation, and aromatization proceed. Among the produced aromatic hydrocarbons, poly-aromatic hydrocarbons are formed by a secondary reaction on the catalyst surface [12]. As indicated by this catalytic pyrolysis pathway, the catalytic upgrading temperature could change the selectivity for PAHs

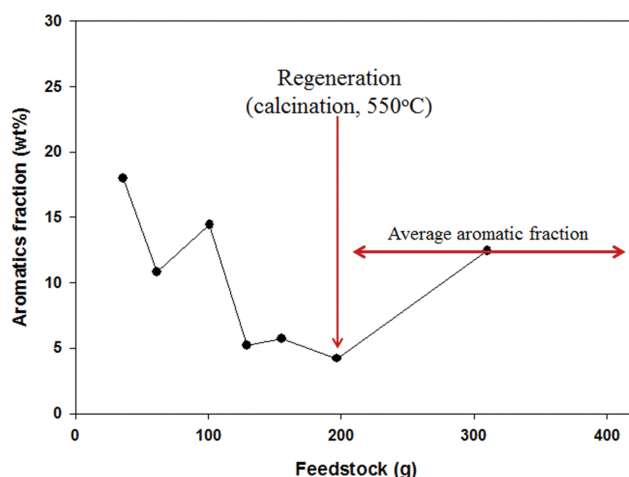


Fig. 6. Deactivation and regeneration of HZSM-5.

formed by polymerization after the formation of mono-aromatic hydrocarbons (BTEXs and MAHs).

Coke formation on the catalyst decreased from 4.9 to 2.8 wt% with increasing catalytic upgrading temperature (Fig. 3). This trend can be attributed to the conversion of oxygenated compounds via condensation. The typical behavior of paraffin or methanol conversion over zeolite results in coke formation on the catalyst increasing with catalytic reaction temperature because of a series of intermolecular reactions such as oligomerization, H-transfer, cyclization, and alkylation. For the conversion of oxygenated compounds such as phenolics and furans over zeolite, however, coke formation decreases with catalytic reaction temperature owing to the oligomeric compounds derived from oxygenated compounds via condensation reactions such as the Diels-Alder reaction and phenolic surface pool mechanism [29].

4. Catalyst Deactivation and Regeneration

The deactivation and regeneration of the ex-situ HZSM-5 catalyst were tested on the thermal pyrolysis (550 °C) and catalytic upgrading (550 °C) reaction condition according to the amount of biomass feedstock (Fig. 6). Catalyst deactivation and recovery of catalytic activity after regeneration are important factors in terms of the efficiency of catalytic pyrolysis process [31]. The catalytic activity of aromatic hydrocarbons production tended to gradually decrease with increasing biomass feedstock amount due to coke deposition and poisoning of active sites [32]. After 200 g of biomass was pyrolyzed, the catalyst was thermally regenerated at 550 °C for 3 h under air flow to burn the deposited coke. Regeneration of the deactivated catalyst could recover the initial catalytic activity for aromatic hydrocarbons production.

5. Upgrading of Bio-oil via In-line Esterification

In-line esterification was carried out on vapors generated from biomass pyrolysis/catalytic pyrolysis at approximately 50–80 °C with liquid *n*-butyl alcohol. Esterification is a promising upgrading method that improves the physical and chemical properties of bio-oil [33]. In this method, esterification converts acids in bio-oil with alcohols to esters, and acetalization converts aldehydes and ketones to acetals [34]. In a previous study, in-line esterification of pyrolysis vapor with methanol supplied by atomizer nozzle was carried out

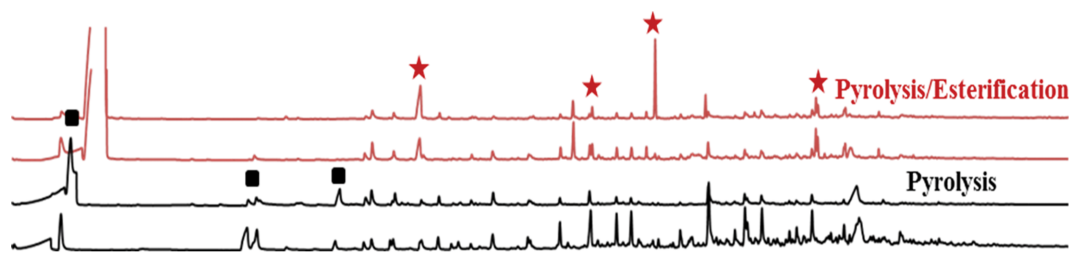


Fig. 7. Chromatograms of products of pyrolysis and esterification with *n*-butyl alcohol (■: acids, aldehydes and ketones; ★: esters and acetals).

using an auger pyrolysis reactor [21]. However, research on the in-line esterification of pyrolysis/catalytic pyrolysis vapors with liquid phase alcohol has rarely been reported. As previously discussed, the water phase of the bio-oil obtained from catalytic pyrolysis still consisted of acids and aldehydes/ketones. Therefore, it is possible to improve the bio-oil quality by converting the residual acids and aldehydes/ketones into esters and acetals through the esterification of pyrolysis vapors with liquid alcohol. Thus, the acids and aldehydes/ketones in the thermal pyrolysis bio-oil and water phase of catalytic pyrolysis bio-oil were esterified and acetalized with *n*-butyl alcohol to produce esters and acetals, respectively. Compared with the pyrolysis product chromatograms, the chromatograms of the products from pyrolysis with esterification showed new peaks (Fig. 7). The main substances were acetic acid from the acids group, acetaldehyde, hydroxy- from the aldehydes group and hydroxy-propanone and hydroxy-cyclopentenone from the ketones group. The esters/acetals produced by in-line esterification included acetic acid, butyl ester, acetaldehyde, dibutyl acetal, and so on. The acids, aldehydes/ketones, and esters/acetals were quantitatively analyzed using internal standard method. The esterification of pyrolysis/catalytic pyrolysis vapor with liquid *n*-butyl alcohol resulted in a decrease in the yield of acids and aldehydes/ketones and an increase in esters and acetals (Fig. 8). The thermal pyrolysis of *Quercus mongolica* produced acids and aldehydes/ketones at 3.57 and

6.09 wt% of bio-oil, respectively, which decreased to 1.69 and 2.40 wt% of bio-oil, respectively, via esterification with *n*-butyl alcohol. In the case of catalytic pyrolysis, the yield of acids and ketones was approximately 3.13 and 3.87 wt% of bio-oil, respectively, which decreased to 1.00 and 2.10 wt% of bio-oil, respectively, after esterification. The esterification of thermal pyrolysis and catalytic pyrolysis vapors with *n*-butyl alcohol produced esters and acetals at 2.02 and 4.80 wt% of bio-oil, respectively. The results confirmed the esterification of the pyrolysis/catalytic pyrolysis vapors with *n*-butyl alcohol.

CONCLUSIONS

Quercus mongolica pyrolysis oil was upgraded using a fluidized bed pyrolysis reactor. Aromatic hydrocarbons (BTEXs, MAHs, and PAHs) were produced by ex-situ catalytic pyrolysis of *Quercus mongolica* over HZSM-5 catalyst. The yield and selectivity for aromatic hydrocarbons were compared depending on the temperature of the catalytic reactor. When the temperature of the catalytic reactor decreased, the total aromatic hydrocarbon yield and selectivity for mono-aromatic hydrocarbons increased. The HZSM-5 was deactivated by coke deposition during catalytic upgrading, and the catalytic activity for aromatic hydrocarbons formation was recovered by thermal regeneration. The acids and aldehydes/ketones in the bio-oil obtained from thermal pyrolysis and catalytic pyrolysis were successfully converted to esters and acetals via the esterification of pyrolysis/catalytic pyrolysis vapors with liquid *n*-butyl alcohol.

ACKNOWLEDGEMENTS

This research was supported by the Research Program (FP0900-2019-01) of the National Institute of Forest Science (NIFoS, Seoul, Republic of Korea).

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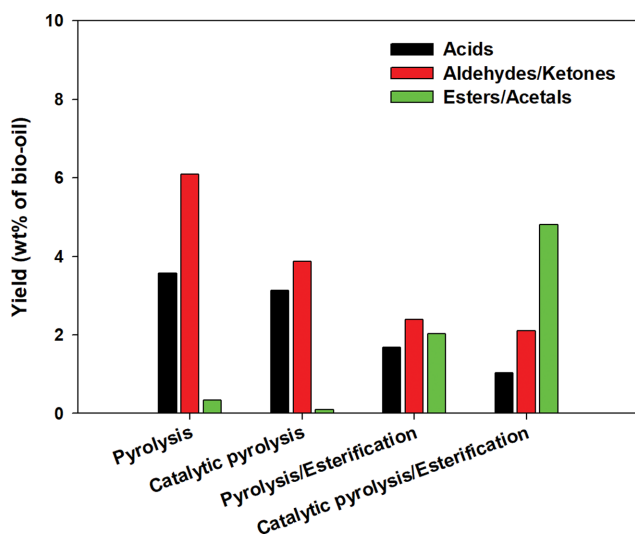


Fig. 8. Yield of esterification of pyrolysis vapor with *n*-butyl alcohol.

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