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청정에너지기술

# Hydrodeoxygenation of Spent Coffee Bio-oil from Fast Pyrolysis using HZSM-5 and Dolomite Catalysts

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## Abstract

Spent coffee is one of biomass sources to be converted into bio-oil. However, the bio-oil should be further upgraded to achieve a higher quality bio-oil because of its high oxygen content. Deoxygenation under hydrotreating using different catalysts (catalytic hydrodeoxygenation; HDO) is considered as one of the promising methods for upgrading bio-oil from pyrolysis by removal of O-containing groups.

In this study, the HDO of spent coffee bio-oil, which was collected from fast pyrolysis of spent coffee (460 ℃, $2.0 \times U_{mf}$), was carried out in an autoclave. The product yields were 72.16 ~ 96.76 wt% of bio-oil, 0 ~ 18.59 wt% of char, and 3.24 ~ 9.25 wt% of gas obtained in 30 min at temperatures between 250 ℃ and 350 ℃ and pressure in the range of 3 to 9 bar. The highest yield of bio-oil of 97.13% was achieved at 250 ℃ and 3 bar, with high selectivity of D-Allose. The carbon number distribution of the bio-oil was analyzed based on the concept of simulated distillation. The $C_{12} \sim C_{14}$ fraction increased from 22.98 wt% to 27.30 wt%, whereas the $C_{19} \sim C_{26}$ fraction decreased from 24.74 wt% to 17.18 wt% with increasing reaction time. Bio-oil yields were slightly decreased when the HZSM-5 catalyst and dolomite were used. The selectivity of CO was increased at the HZSM-5 catalyst and decreased at the dolomite.

**Keywords :** Spent coffee waste, Upgrading bio-oil, Hydrodeoxygenation, HZMS-5, Dolomite

## 1. Introduction

The emission of carbon dioxide has been gradually increased since fossil fuel has continuously been using. Fossil fuel is a limited resource as well. The research for renewable energy sources and solving global warming has been actively carried out. Research for renewable energy is under investigation in forms which suit each country's environment, and the U.S., Japan and European countries have already replaced much of those fossil fuels to renewable energies, and even some of technologies commercialized. Especially, supply of bioenergy is rapidly increased over OECDs. The bioenergy within renewable energy was consumed 460.1 Mtoe in 2017, which was 50% of consumption within total renewable energy [1].

Biomass is a renewable energy source whose reserve is not limited unlike fossil fuel. It also has a worldwide distribution, and can solve the disadvantages of fossil fuels such as greenhouse gases by photosynthesis of plants growing [2]. U.S. and Canada are developing it to have more practicality and economical efficiency as a next generation energy source because of these potential powers.

Various researches have been tired to produce bio-fuels from the fast pyrolysis of lignocellulosic and algae biomass [3,4,5]. The bio-oil produced from fast pyrolysis of biomass has received a lot of attention as an attractive replacement for fossil fuel. The research for pyrolysis kinetic of microalgae residue reported that value-added chemicals were extracted from microalgae [6].

The amount of 135,480 ton coffee was imported in domestic at 2017/2018. The weight of ground coffee beans lost 19 wt% during extraction, and the remaining was used as fertilizer and deodorant, but most of them were thrown out as waste [7,8]. Ground coffee beans lost 19 wt% during extraction, and the remaining were thrown out as waste. Such as waste biomass

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can be used as resource for bio-energy feedstock, and those of waste have an advantage for the production of bioenergy in terms of decreasing of expense for the waste treatment. Ktori et al. researched for the recovery of energy from spent coffee, and reported that a maximum yield of bio-oil was 36 wt% at 540 ℃ [9]. Luz et al. reported that the results of model and experimental were well matched from the important variables such as mass flow, pyrolysis temperature, inert gas flow, and biomass composition in screw reactor [10]. Bubbling fluidized bed reactor is generally used for the fast pyrolysis to produce of bio-oil from spent coffee. It is known that the content of oxygen is higher in a comparison with that of carbon in bio-oil through the production of fast pyrolysis [5,11]. Catalytic pyrolysis is one of the technologies to decrease oxygen content in bio-oil, and the upgrading of bio-oil’s quality has been actively researched [12]. Yim et al. reported that coffee ground oil-butanol blended fuel was applied in a diesel tractor [13]. The 30 wt% content of coffee ground oil in diesel showed slightly high carbon monoxide (CO) and nitrogen oxide ($NO_x$), but particulate matter (PM) emission was significantly decreased because of the high oxygen content in the blended fuels.

Hydrodeoxygenation of bio-oil, which was produced by fast pyrolysis of spent coffee, was carried out in this research for the effective reuse of waste. An autoclave was used for hydrodeoxygenation of spent coffee bio-oil with a variation of temperature, pressure, and catalysts, and that of compositions were analyzed systematically. For the analysis of liquid bio-oil, there are several analysis methods applied such as elemental analysis, carbon number distribution, higher heating value, and GC-MS. The compositions of produced gases were analyzed by gas chromatography.

## 2. Experimental

### 2.1. Sample and catalysts preparation

Coffee, which was grown in Columbia, was imported from Kirkland to Korea. Spent coffee sample was collected after extraction, and it was washed three times with distilled water at 80 ℃. The washed samples were subjected to primary drying at room temperature, followed by secondary drying at 90 ℃ for 4 h to equilibrium moisture before being used as biomass material in experiments. The bio-oils (organic phase) obtained from fast pyrolysis experiments at the temperature of 460 ℃, and the fluidization velocity of $2.0 \times U_{mf}$ was used as the experimental sample for hydrodeoxygenation.

The ultimate and proximate analyses of biomass sample and bio-oil were determined using American Society for Testing and Materials, ASTM standard method [3,5]. The thermal decomposition of the SCW and bio-oil were determined using thermogravimetric analyzer (TGA N-1000, SINCO) in a nitrogen flow rate of 20 mL $min^{-1}$, from room temperature up to 700 ℃ at the heating rate of 10 ℃ $min^{-1}$.

All catalysts were ground and sieved particle size of 70 – 100 mesh (150 – 212 μm). The commercial ZSM-5 catalyst was supplied by Hyundai Petroleum Chem. Co. (South Korea). Before using ZSM-5 catalyst, it was calcined at 550 ℃ for 5 h to convert ZSM-5 into the protonated form of HZSM-5 [3]. Prior to use as a catalyst, natural dolomite (Seungshin Corp., Korea) was activated by calcination at 900 ℃ in 3 h to convert dolomite from carbonate form $CaMg(CO_3)_2$ into oxide form CaO and MgO [5]. The characteristics of HZSM-5 and activated dolomite catalyst were reported in our previous studied [3,14].

### 2.2. Experimental setup and analytical method

A bubbling fluidized bed reactor was used for the fast pyrolysis of spent coffee (Figure 1). More detailed explanation for the bubbling fluidized bed reactor can be seen in our previous paper [14,15].

The upgrading of spent coffee bio-oil (SCO) was carried out in an autoclave reactor, as shown in Figure 2. The system consisted of a salt bath, a temperature controller, a mechanical stirrer and a reactor with an inner volume of 100 ml. A molten salt bath, which has excellent heat transfer properties, was prepared utilizing a eutectic salt of $KNO_3$ (59 wt.%) and $Ca(NO_3)_2$ (41 wt.%) [2,4]. The temperature of the salt bath was kept constant during a run, but various temperatures (250, 300, 350 ± 1 ℃). The initial pressure of the system was set up from 3 to 9 bar using hydrogen. In all experiments, a 10 g bio-oil sample (and 1 g of catalyst, for catalytic upgrading experiment) was placed into the reactor, and then autoclave was immersed in the molten salt bath. The residence time of reactant in the salt bath was 30 min for each reaction temperature. After each run, the reactor was removed from the bath and cooled down to room temperature.

The products of upgrading by hydrogeoxygaenation were collected and the product yields were calculated based on the ratio between the mass of each product produced after pyrolysis reaction and the mass of fed biomass sample products. The gas yield was obtained by weighing the reactor before and after the gas release. Other products were separated into liquid and solid after solvent extraction with acetone, using a micro filter paper (pore size: 0.45 μm). The solid yield was calculated by weighing the solid and filter after drying. The liquid yield was given by difference of solid product from the total amount of liquid and solid product.

The elemental compositions of the upgraded bio-oils were characterized by Flash EA1112, CE Instrument [3]. The pH and

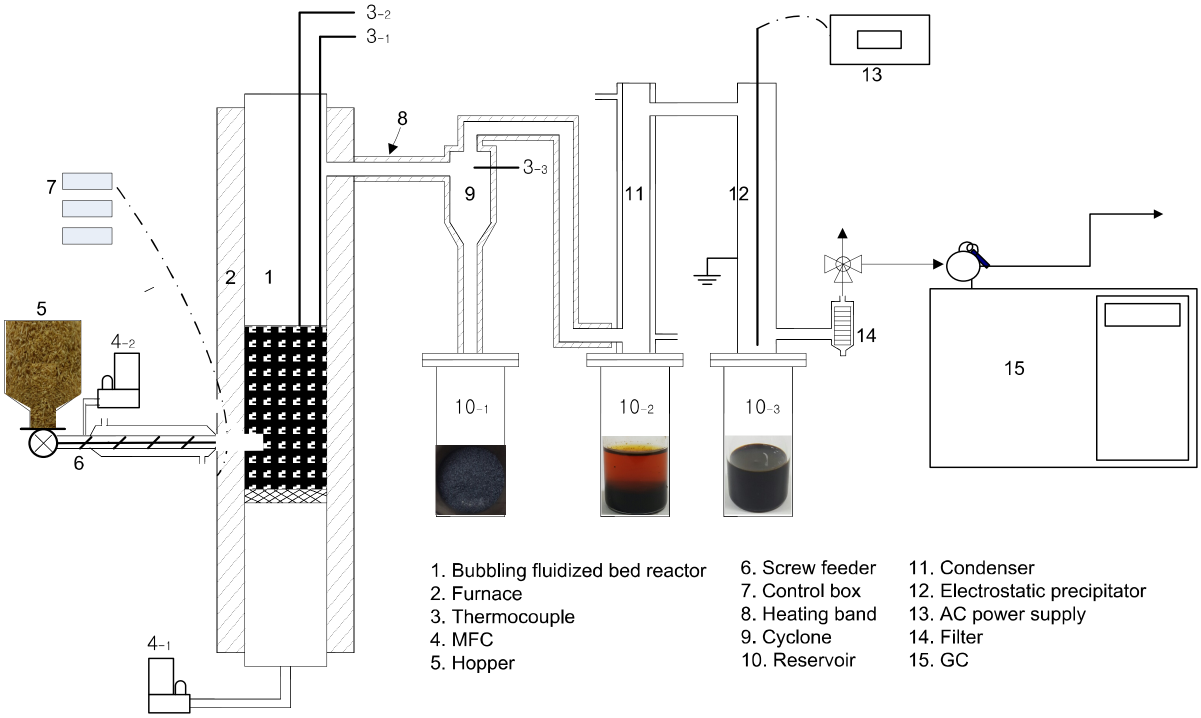


**Figure 1.** Schematic diagram of a bubbling fluidized bed reactor for fast pyrolysis.

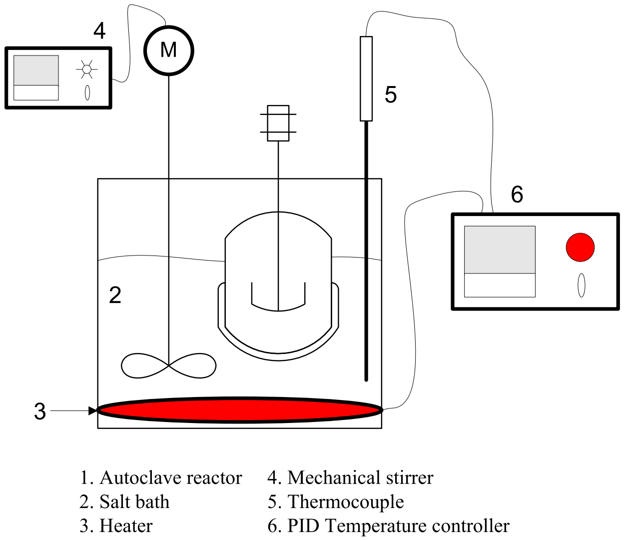


**Figure 2.** Schematic diagram of an autoclave reactor.

moisture content were analyzed by a Thermo Scientific Orion 3-Star pH meter and Karl-Fischer (CA-200, Mitsubishi), respectively. The upgraded bio-oils (0.2 g) were diluted in methanol before analysis by Gas Chromatograph/Mass Spectrometry (GC–MS Agilent 7890A). The gas compositions were analyzed by the gas chromatography (YL 6500GC) equipped with a flame ionization detector (FID) using Porapak N column to determine hydrocarbon gases ($C_1$–$C_4$) and a thermal conductivity detector (TCD) using Molecular sieve 13X column to identify hydrogen ($H_2$), carbon monoxide (CO), carbon dioxide ($CO_2$) and methane ($CH_4$).

## 3. Results and discussion

### 3.1. Material characterization

The characteristics of spent coffee and SCO are reported in Table 1. The moisture and the ash contents of spent coffee were 8.56 and 0.64 wt%. The HHV of SCW and CWO was determined using a bomb calories meter (DSC715, SUNDY Science & Technology). As shown in Table 1, the HHV of SCO was determined to be 35.73 MJ/kg, which is higher than those of waste biomass and woody biomass such as spent coffee (21.52 MJ/kg) and woody biomass *Pinyon* pine (18.94 MJ/kg) [4], tulip tree (18.87 MJ/kg) [3].

### 3.2. Thermogravimetric analysis of biomass samples

The TGA results can be considered as a function of the conversion as depending on temperature. Conversion from the thermogravimetric analysis is calculated based on the initial weight of the biomass sample, the weight of the pyrolyzed sample, and the final residual weight, as reported in our previous studies [3,14]. The TGA and DTG behavior of spent coffee is shown in Figure 3(a). The main thermal conversion occurred at a temperature between 170 and 520 ℃, corresponded to the degradation of organic compounds in spent coffee. The small signal in DTG curves at temperatures between 70 and 130 ℃ was attributed to the evaporation of

**Table 1.** Characteristics of spent coffee and spent coffee bio-oil

| Proximate analysis (wt%) | Moisture[a] | Ash[b] | Volatile matter[c] | Fixed carbon[c] | Elemental analysis[d] (wt%) | | | | HHV (MJ/kg) d.a.f.b | pH |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | O[e] | | |
| Spent coffee | **8.56**<br>± 0.03 | **0.64**<br>± 0.28 | 83.62 | 7.18 | 50.80 | 7.58 | 2.13 | 38.85 | 21.52 | - |
| Spent coffee bio-oil | **3.90**<br>± 0.36 | - | 94.05 | 2.05 | 70.32 | 10.41 | 1.12 | 18.14 | 35.73 | 3.92 |

[a] ASTM E1756, Standard test method for the determination of the total solids of biomass.
[b] ASTM E1755, Standard test method for determination of ash content of biomass.
[c] Calculating based on sample after drying
[d] On dry, ash free basis (for biomass material)
[e] By difference.

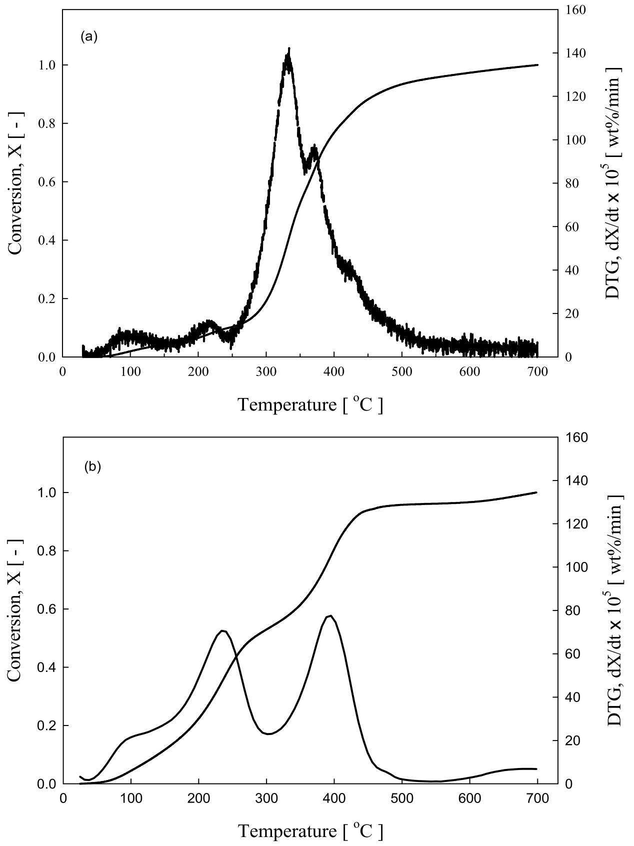


**Figure 3.** Thermogravimetric (TG) and differential thermogravimetric (DTG) curves for the spent coffee (a) and spent coffee bio-oil (b) at heating rate of 10 ℃ min$^{-1}$.

moisture adsorbed on the surface of biomass. In a temperature range of 170 and 520 ℃, the DTG profile could be separated into four peaks. The first peak starting from 170 to 240 ℃ corresponded to the volatilization of the remaining extractives in spent coffee after treatment. The next stage included three peaks with the maximum value for each peak of 331.50 ℃, 375.97 ℃, and 425.18 ℃, which is attributed to the degradation of hemicellulose, cellulose, lignin and proteins, respectively. This result is in good agreement with other literatures [4].

### 3.3. Effect of reaction conditions on product distribution

The hydrodeoxygenation (HDO) of SCO was performed in the autoclave reactor at the temperature between 250 ℃ and 350 ℃. Table 2 shows the product distributions obtained from the HDO of SCO at different temperatures without catalyst. Total liquid yield decreased from 97.06 to 70.10 wt% with increasing the temperature from 250 to 350 ℃. The char yield increased from 0.81 to 17.03 wt%, whereas the gas yield increased from 2.51 to 12.87 wt%. The increase in yield of gases is corresponded to the decrease in the yield of liquid with increasing reaction temperature. That of result is similar to hydropyrolysis under atmospheric pressure in the literature. This is attributed to secondary thermal cracking of the vapors, followed by a series of decarboxylation, deoxygenation, dehydrogenation, and decarbonylation, alkylation, the pyrolyzed volatiles are cleaved into smaller organic matters [15], and release $CO_2$, CO, and hydrocarbon gases [11,16].

The effect of initial pressure on the HDO of SCO was also investigated. In these experiments, reaction temperature and reaction time were kept constant at 250 ℃ and 60 min respectively. Effect of pressure on HDO is related to the suppression of volatiles by the physical effect of increasing gas pressure. Güell *et al.* reported that the liquid yield was decreased with the formation of char (coke) and water content when hydrogen pressure increased [12]. The difference in char yields in 3 bar and 9 bar experiments is attributed to the suppression of hydrogen pressure, which led carbon and hydrogen reaction to the production of moisture. The moisture content was increased with increasing pressure and temperature due to hydrogenation.

Table 2 also show the characteristic of HDO spent coffee bio-oils. The C content was increased with increasing temperatures and pressure. The C content was in range of 70.48-73.91 wt%. The mol ratio of C *vs.* H was increased with increasing pressure and temperature, whereas that of C vs. O

**Table 2.** The effect of different reaction conditions on product distribution of SCO in an autoclave reactor, at reaction time of 60 min

| Reaction conditions | | **250** ℃<br>3 bar | **300** ℃<br>3 bar | **350** ℃<br>3 bar | **250** ℃<br>6 bar | **250** ℃<br>9 bar | **250** ℃ - **3** bar | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | **Dolomite** | **HZSM-5** |
| Product yield [wt%] | **Gas** | 2.51 | 7.57 | 12.87 | 2.40 | 2.37 | 6.62 | 6.62 |
| | Char + Coke | 0.81 | 5.99 | 17.03 | 1.85 | 3.59 | 7.87 | 7.87 |
| | **Total liquid** | 96.68 | 86.44 | 70.10 | 95.75 | 94.04 | 85.51 | 85.51 |
| Organic content in total liquid [wt%] | | 95.22 ± 0.68 | 93.78 ± 0.32 | 90.68 ± 0.22 | 94.91 ± 0.24 | 92.98 ± 0.12 | 93.60 ± 0.11 | 92.86 ± 0.12 |
| Moisture content in total liquid [wt%] | | 4.78 ± 0.68 | 6.22 ± 0.32 | 9.32 ± 0.22 | 5.09 ± 0.24 | 7.02 ± 0.12 | 6.40 ± 0.11 | 7.14 ± 0.12 |
| Elemental analysis of bio-oil [wt%] | **C** | 70.48 | 71.92 | 73.64 | 71.29 | 72.60 | 73.73 | 74.28 |
| | **H** | 10.26 | 10.08 | 9.87 | 9.86 | 9.73 | 9.54 | 9.92 |
| | **N** | 1.39 | 2.25 | 2.16 | 1.31 | 1.34 | 2.41 | 1.21 |
| | **O** | 17.87 | 16.38 | 14.33 | 17.54 | 16.33 | 14.34 | 14.69 |
| Mol ratio | **C/H** | 0.57 | 0.59 | 0.62 | 0.60 | 0.62 | 0.64 | 0.62 |
| | **C/O** | 5.26 | 5.85 | 6.85 | 5.42 | 5.93 | 6.86 | 6.74 |
| HHV of bio-oil [MJ/kg] | | 34.82 | 35.32 | 35.72 | 35.11 | 35.96 | 37.54 | 38.09 |
| pH of bio-oil | | 3.48 ± 0.02 | 3.44 ± 0.04 | 3.51 ± 0.11 | 3.43 ± 0.05 | 3.68 ± 0.07 | 5.02 ± 0.03 | 4.56 ± 0.03 |
| Gas selectivity [mol%] | **CO** | 1.92 | 1.37 | 1.09 | 1.99 | 2.89 | 2.11 | 6.19 |
| | $CO_2$ | 97.38 | 97.61 | 97.85 | 97.44 | 96.38 | 97.18 | 92.59 |
| | $CH_4$ | 0.13 | 0.10 | 0.08 | 0.11 | 0.15 | 0.18 | 0.25 |
| | $C_2H_4$ | 0.12 | 0.15 | 0.12 | 0.14 | 0.14 | 0.17 | 0.26 |
| | $C_2H_6$ | 0.02 | 0.17 | 0.20 | 0.03 | 0.05 | 0.21 | 0.19 |
| | $C_3H_8$ | 0.14 | 0.26 | 0.31 | 0.11 | 0.13 | 0.09 | 0.31 |
| | $C_4H_{10}$ | 0.29 | 0.34 | 0.35 | 0.18 | 0.26 | 0.06 | 0.22 |

was increased. These results can be explained that deoxygenation was increased by hydrogen pressure and reaction temperature, thus led to higher moisture content from 4.78 wt% to 9.32 wt%. The N content increased from 1.51 to 2.31 wt%, with increasing temperatures. This result was due to the decomposition of N-containing organic compounds in bio-oil. The higher heating value (HHV) of bio-oils was measured by the bomb calories meter. The HHV of pyrolysis bio-oils was in the range 34.84-35.96 MJ/kg. The HHV increased with increasing reaction temperatures and pressure. The produced bio-oils have high HHV compared with that of woody pyrolysis bio-oil as well as non-lignocellulose pyrolysis bio-oil, such as tulip tree (24.37 MJ/kg) [3], *S.japonica* (26.1 – 28.27 MJ/kg) [15], palm kernel cake (13.9 MJ/kg) [17].

The effect of catalysts on the HDO of SCO was investigated. The catalytic pyrolysis of SCO was performed in an autoclave reactor at a pressure of 3 bar, using dolomite and HZSM-5 catalysts (10 wt% weight loading). The reaction temperature was fixed constant at 250 ℃. The product distributions are shown in Table 2. In comparison with hydrogenation of spent coffee bio-oil without catalyst, the liquid yield decreased, whereas the gas yield increased for all catalytic experiments. This might be due to the catalytic cracking reaction to produce lower molecular weight compounds and non-condensable gas, followed by a series of deoxygenation reactions [14]. The product distribution depends on the reaction pathway of catalyst. When HDO was applied catalysts, the char yield was higher than those of without catalyst process. This might be due to the polymerization and aromatization of organics component to produce aromatic compounds and coke, thus increasing the char yield [14].

The C content of catalytic bio-oil in HDO of SCO was higher than that of SCO without catalyst. The O content of catalytic HDO of SCO was lower than that of SCO without catalyst due to the rejection of O content as CO gas and moisture under the catalytic effect. The high C content and low O content accounts for the high HHV of catalytic HDO bio-oil. The HHV of catalytic pyrolysis bio-oils was determined to be 37.54 MJ/kg (for dolomite), 38.09 MJ/kg (for HZSM-5) which was higher than those of initial SCO.

**Table 3.** Composition of bio-oil produced by HDO of SCO at 250 ℃, 3 bar with dolomite and HZSM-5 catalysts

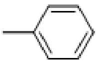
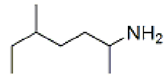
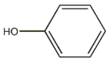
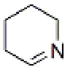
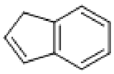
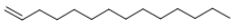
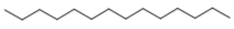
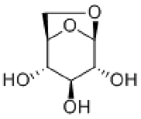
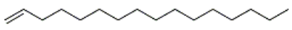
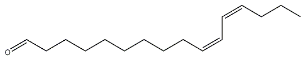
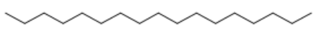
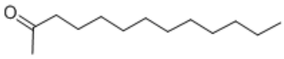
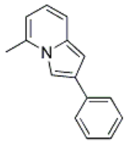
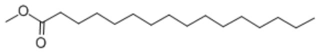
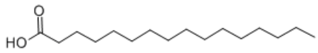
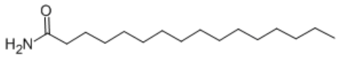
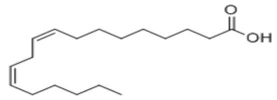
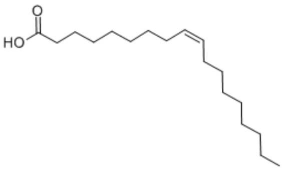
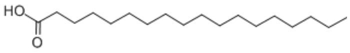
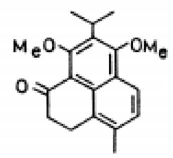
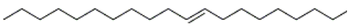
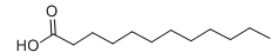
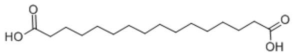
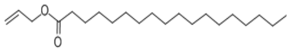
| Composition | Bio-oil at 460 ℃ 2.0 × $U_{mf}$ | 250 ℃ 3 bar | 250 ℃ 3 bar Dolomite | 250 ℃ 3 bar HZSM-5 | Structure |
|---|---|---|---|---|---|
| Heptane | | 1.88 | 0.81 | |  |
| Toluene | | 0.63 | | 1.17 |  |
| 5-methyl-2-Heptanamine | | | | 0.30 |  |
| Phenol | 3.27 | | 2.01 | |  |
| Butyl Benzene | | | 0.70 | 0.66 |  |
| 1-Undecene | | 1.24 | 0.56 | 0.39 |  |
| Pentyl Benzene | 0.44 | 1.16 | 1.91 | 1.24 |  |
| 1-Piperideine | | | | 7.46 |  |
| 1H-Indene | | | | 1.80 |  |
| 1-Dodecene | 0.39 | 0.82 | 0.94 | 0.67 |  |
| 1-Tetradecene | 0.66 | 0.90 | 1.28 | 0.93 |  |
| Tetradecane | 0.54 | 0.96 | 0.94 | 0.95 |  |
| Levoglucosan | | 3.94 | 20.21 | |  |
| 1-Pentadecene | | 2.25 | | 0.82 |  |
| Pentadecane | 3.34 | 6.24 | | 5.58 |  |
| Hexadecane | 0.30 | | 0.85 | |  |
| 1-Tridecene | | 3.59 | 0.56 | |  |
| Tridecane | | 0.60 | 0.68 | |  |
| 8-Heptadecene | 1.63 | 1.49 | 3.69 | 3.11 |  |
| Heptadecane | 1.16 | 1.65 | 2.03 | 1.70 |  |
| Nonadecane | | 1.77 | 1.99 | 4.92 |  |
| 2-Tridecanone | 1.17 | | | |  |
| 5-methyl-2-phenylindolizine | | | | 1.29 |  |

**Table 3.** To be Continue

| Composition | Bio-oil at 460 ℃ $2.0 \times U_{mf}$ | 250 ℃ 3 bar | 250 ℃ 3 bar Dolomite | 250 ℃ 3 bar HZSM-5 | Structure |
|---|---|---|---|---|---|
| Methyl palmitate | 0.72 | | | 0.57 |  |
| Palmitinic acid | 38.52 | 24.61 | 5.56 | 22.8 |  |
| Hexadecanamide | | | 1.64 | |  |
| Linoleic acid | 20.73 | | 13.68 | 10.03 |  |
| Octadecane | | 4.68 | | |  |
| Stearic acid | 7.74 | 1.35 | | |  |
| 7,9-Dimethoxy-8-isopropyl-4-methyl-1H-phenalen-1-one | | | 7.32 | |  |
| 9-Eicosene | | | 4.94 | 6.03 |  |
| Dodecanoic acid | | | | 9.17 |  |
| Hexadecanedioic acid | | 5.46 | 1.08 | |  |
| Allyl stearate | | | | 7.72 |  |

### 3.4. Compositions of gas product

Gas products from HDO and catalytic HDO of SCO are shown in Table 2. The compositions of gas are mostly contained CO, $CO_2$, $CH_4$ and other hydrocarbon gases with different concentration, depending on the reaction conditions. Among these produced gases, $CO_2$ is a major component that is produced from the decarboxylation reactions of carboxyl groups presented in the compositions of the spent coffee pyrolysis bio-oil [18]. The CO component produced from HDO with HZSM-5 was higher than that of others. Besides promotion the thermal cracking of longer chain hydrocarbons to release more hydrocarbon gases, the HZSM-5 is known as an acid catalyst, due to Brønsted acid sites in zeolites structure, which dominates the decarbonylation to produce more CO [19,20]. There was no effect of dolomite catalyst on gas compositions at low temperature.

### 3.5. Bio-oil analysis

Table 3 shows the GS-C-MS analysis data of the bio-oils obtained from experiments at different conditions. The bio-oil compositions included fatty acids such as palmitic acid, linolic acid, and stearic acid and alkanes. These fatty acids may be derived from the decomposition of lipid, which is one of the main ingredients of coffee bean. As a result of analysis from HDO of SCO, palmitic acid, linoleic acid, and stearic acid and alkanes (tetradecane, pentadecane, heptadecane) and alkenes (8-heptadecene, tetradecene) are also main compositions of bio-oil, however, those of components showed different selectivity. The selectivity of fatty acids was observed to decrease. Conversely, the selectivity to alkanes and alkenes increased. This result indicated that these alkanes and alkenes were formed from the fatty acids via decarboxylation and decarbonylation. Decarboxylation of fatty acids produces alkanes and decarbonylation of fatty acid produces alkenes [21]. The effect of HZSM-5 catalyst was revealed in the formation of alkenes, alkanes and aromatic compounds such as indene. HZSM-5 promoted the production of the aromatic compounds [22]. Besides the alkanes and alkenes, some

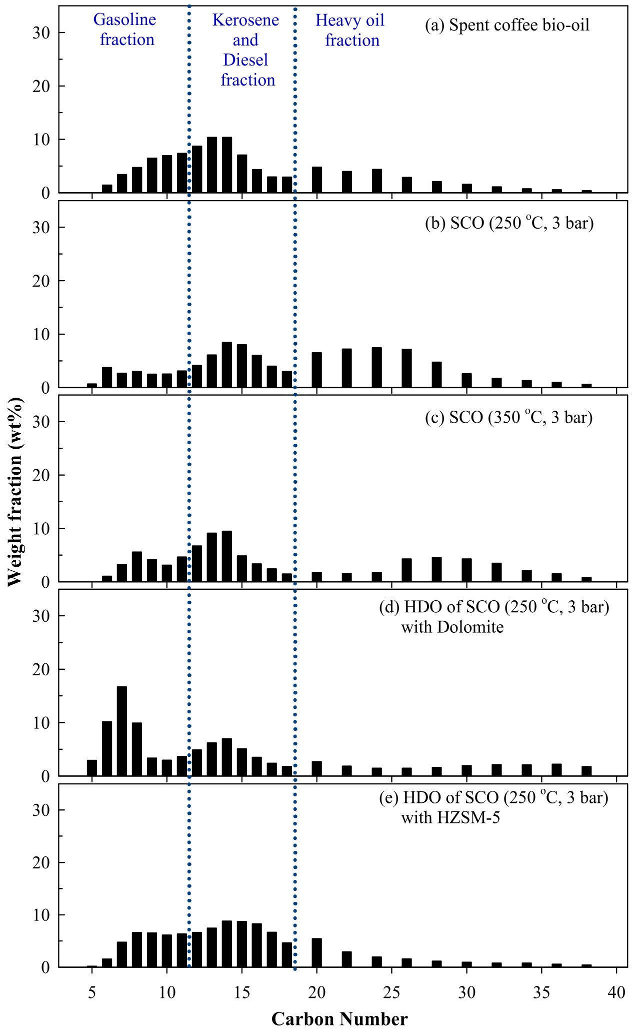


**Figure 4.** Carbon number distribution of spent coffee bio-oil and HDO of spent coffee bio-oil at different reaction conditions.

derivatives of amine were also found in dolomite bio-oil. Indeed, the dolomite bio-oil contained alkanes, alkenes, phenol and derivatives of benzene. Unlike HZSM-5, the dolomite contains metal oxides (CaO, MgO) which promoted the decarboxylation and depolymerization reactions of vapor to produce the low-molecular compounds instead of aromatic compounds [22].

The simulated distillation of SCO and catalytic SCO has been tried for the bio-oil using TGA, which was based on the boiling point of carbonaceous liquid [23]. Figure 4. shows that the carbon number distribution of bio-oil. It was identified three groups such as $C_5 - C_{11}$, $C_{12} - C_{18}$ 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 spent coffee bio-oil (at 460 ℃) was 30.41 wt% ($C_5 - C_{11}$), 46.73 wt% ($C_{12} - C_{18}$) and 22.44 wt% ($C_{20} - C_{38}$), respectively. However, the carbon number distribution showed significant changes with HDO reaction conditions and with different catalysts. The fractions of $C_5 - C_{11}$, $C_{12} - C_{18}$, $C_{20} - C_{38}$ in dolomite bio-oil were 49.73, 30.85, and 19.30 wt%, respectively. The HZSM-5 bio-oil consisted of 32.17 wt% of $C_5 - C_{11}$, 51.15 wt% of $C_{12} - C_{18}$, and 16.64 wt% of $C_{20} - C_{38}$. These distributions are reasonable, considering the GC-MS data. These confirm the feasibility of upgrading SCO to high quality bio-oil using natural catalysts, and the upgraded bio-oil can be used as a great source for manufacturing alternative bio-fuel and/or valuable chemicals.

## 4. Conclusions

The hydrodeoxygenation process of spent coffee bio-oil was systematically investigated in an autoclave reactor. The HHVs of HDO bio-oils were in the range of 34.82-35.96 MJ/kg without catalyst. The major components of the bio-oil were palmitic acid, linoleic acid, and stearic acid, alkanes and alkenes. The liquid yield decreased, but the quality of bio-oil increased when using dolomite and HZSM-5 catalysts applied in catalytic HDO of SCO. The selectivity of fatty acids was observed to decrease, whereas the selectivity to alkanes and alkenes increased. The HHV of HDO bio-oils were increased to 37.54 MJ/kg and 38.09 MJ/kg with dolomite and HZSM-5 catalysts, respectively. The reaction pathways of HZSM-5 promoted the decarbonylation, and repolymerization, whereas dolomite elevated the depolymerization reactions. The weight fraction of bio-oil's carbon number was mainly distributed in the range of gasoline, kerosene and diesel fraction.

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## References

1. Renewables 2018, https://www.iea.org/renewables2018/.
2. Biomass, https://www.sciencedirect.com/topics/engineering/biomass.
3. 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).
4. Kim, S.-S., Shenoy, A., and Agblevor, F. A., "Thermogravimetric and Kinetic Study of Pinyon Pine in the Various Gases," *Bioresour. Technol.*, **156**, 297-302 (2014).
5. Ly, H. V., Kim, S.-S., Kim, J. Kim, Choi, J. H., and Woo, H. C., "Effect of Acid Washing on Pyrolysis of Cladophora Socialis Alga in Microtubing Reactor," *Energ. Convers. Manage.*, **106**, 260-267 (2015).

6. Kim, S.-S., Ly, H. V., Kim, J, Lee, E. Y., and Woo, H. C., "Pyrolysis of Microalgae Residue Biomass Derived from Dunaliella Tertiolecta after Lipid Extraction and Carbohydrate Saccharification," *Chem. Eng. J.*, **263**, 194-199 (2015).
7. International Coffee Organization, Word Coffee Consumption, http://www.ico.org/prices/new-consumption-table.pdf
8. Kim, T.-S., Kim, K.-H., Han, G.-S., Choi, I.-G., and Choi, J.-W., "Evaluation of Possibility of Spent Coffee Grounds for Biodiesel Production," *J. Korea Soc. Waste Manage.*, **27**(8), 694-699 (2010).
9. Ktori, R., Kamaterou, P., and Zabaniotou, A., "Spent Coffee Grounds Valorization through Pyrolysis for Energy and Materials Production in the Concept of Circular Economy," *Materials Today: Proceeding*, **5**, 27582-27588 (2018).
10. Luz, F. C., Cordiner, S., Manni, A., Mulone, V., and Rocco, V., "Biomass Fast Pyrolysis in Screw Reactors: Prediction of Spent Coffee Grounds Bio-oil Production through a Monodimensional Model," *Energ. Convers. Manage*, **168**, 88-106 (2018).
11. Venkatakrishnan, V. K., Degenstein, J. C., Smeltz, A. D., Delgass, W. N., Agrawal, R., and Ribeiro, F. H., "High-pressure Fast-pyrolysis, Fast-hydropyrolysis and Catalytic Hydrodeoxygenation of Cellulose: Production of Liquid Fuel from Biomass," *Green Chem.*, **16**(2), 792-802 (2014).
12. Güell, A. J., Li, C. Z., Herod, A. A., Stokes, B. J., Hancock, P., and Kandiyot, R., "Effect of $H_2$-pressure on the Structures of Bio-oils from the Mild Hydropyrolysis of Biomass," *Biomass Bioenerg.*, **5**(2), 155-171 (1993).
13. Yim, J., Yoon, G. S., Lee, S., Kim, G., "A Feasibility Study of using Coffee Ground Oil-butanol Blended Fuel in a Diesel Tractor," *Transactions of KSAE*, **27**(2), 77-84 (2019).
14. Ly, H. V., Choi, J. H., Woo, H. C. Woo, 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. Energ.*, **133**, 11-22 (2019).
15. 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).
16. He, Z., and Wang, X., "Hydrodeoxygenation of Model Compounds and Catalytic Systems for Pyrolysis Bio-oils Upgrading," *Catal. Sustain. Energy*, **1**, 28-52 (2012).
17. Ngo, T.-A., Kim, J., and Kim, S.-S., "Fast Pyrolysis of Palm Kernel Cake using a Fluidized Bed Reactor: Design of Experiment and Characteristics of Bio-oil," *J. Ind. Eng. Chem.*, **19**, 137-143 (2013).
18. Ngo, T.-A., Kim, J., and Kim, S.-S., "Fast Pyrolysis of Spent Coffee Waste and Oak Wood Chips in a Micro-Tubular Reactor," *Energ. Source Part A*, **37**, 1186-1194 (2015).
19. Yathavan, B. K., and Agblevor, F. A., "Catalytic Pyrolysis of Pinyon−Juniper using Red Mud and HZSM5," *Energ. Fuel*, **27**, 6858-6865 (2013).
20. Liu, T.-L., Cao, J.-P., Zhao, X.-Y., and Wang, J.-X., Ren, X.-Y., Fan, X., Zhao, Y.-F., 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).
21. Ngo, T.-A., Kim, J., and Kim, S.-S., "Fast Pyrolysis of Spent Coffee Waste and Oak Wood Chips in a Micro-Tubular Reactor," *Energ. Source Part A*, **37**, 1186-1194 (2015).
22. López, A., Marco, 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).
23. Kim, S.-S., Chun, B. H. Chun, and Kim, S. H., "Non-isothermal Pyrolysis of Waste Automobile Lubricating Oil in a Stirred Batch Reactor," *Chem. Eng. J.*, **93**, 225-231 (2003).