

## Article

# Upgrading of Coffee Biocrude Oil Produced by Pyrolysis of Spent Coffee Grounds: Behavior of Fatty Acids in Supercritical Ethanol Reaction and Catalytic Cracking

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**Abstract:** Spent coffee grounds contain lipids (fatty acids) in addition to cellulose, hemicellulose, and lignin. The reaction process for upgrading biocrude oil produced from spent coffee grounds is different from that followed for upgrading biomass pyrolysis oil, such as processes that utilize sawdust. The feasibility of upgrading coffee biocrude oil through a supercritical ethanol reaction with plastic pyrolysis oil and through catalytic cracking for the improvement of the undesirable properties of biocrude oil, caused by the presence of oxygenated compounds, was evaluated. The initial oxygen content of the coffee biocrude oil was 16.9 wt%. The oil comprised a total content of 40.9% fatty acids, as found by analyzing the GC-MS peak area. After the supercritical ethanol reaction at 340 °C, the oxygen content was decreased to 9.9 wt%. When the MgNiMo/AC catalyst was applied to the supercritical reaction, the oxygen content was further decreased to 8.5 wt%. The esterification of the fatty acids in the biocrude oil with ethanol converted them to esters. After the supercritical reaction of coffee biocrude oil with plastic pyrolysis oil (1:2 (*w/w*)), the oxygen content was 6.4 wt%. After the catalytic cracking of the biocrude oil by Ni/MCM-41 at 400 °C, the fatty acids were converted to hydrocarbons, C9 to C21, and the oxygen content decreased to a final value of 2.8 wt%.

**Keywords:** spent coffee grounds; waste plastic; pyrolysis oil; supercritical ethanol; catalytic cracking; oxygen content



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## 1. Introduction

Due to issues such as the depletion of fossil fuels, global warming, and environmental pollution, interest in renewable energy has increased. Biomass is a sustainable energy source that reduces carbon dioxide emissions by absorbing carbon dioxide for photosynthesis. Given that lignocellulosic biomass is the most abundant non-food biomass in the world, the production of biocrude oil through the fast pyrolysis of lignocellulosic biomass is a particularly attractive process [1–3]. Biocrude oil can be applied to furnaces or boilers, through direct combustion, and to engines and turbines by upgrading to high-quality hydrocarbon fuels, and to high-value-added chemicals [4]. Although biocrude oil is one of the most promising clean and renewable energy resources as a replacement for fossil fuel, it has undesirable properties, such as high moisture content, high oxygen content, high acid value, low heating value, and high reactivity, which is caused by the presence of oxygenated and unsaturated compounds [5,6]. Aldehydes and phenolic species tend to easily polymerize and increase oil viscosity. The high moisture content and oxygenated compounds result in low heating values and immiscibility with conventional fossil fuels. These highly acidic compounds result in thermally unstable and highly corrosive oil [7].

Upgrading biocrude oil to oil with lower oxygen and acidic species contents is required in order to improve its storage stability and, thus, suitability as a viable fossil fuel replacement. Biocrude oil upgrading techniques, such as emulsification, catalytic cracking, hydrodeoxygenation, and catalytic deoxygenation, have been reported [8,9]. The catalytic

cracking of biocrude oil efficiently converts hydrocarbons by removing oxygen in the presence of the zeolite catalyst [8]. The resultant hydrocarbon products have the potential to be used as platform chemicals for the production of fuels, lubricants, and other valuable petrochemicals. Catalytic deoxygenation also upgrades biocrude oil by reducing the oxygen content in several chemical reactions, including decarbonylation, decarboxylation, and hydrodeoxygenation. In fact, relatively inexpensive transition metal catalysts, such as nickel, have shown excellent catalytic activity that is comparable to novel metal catalytic activity for hydrodeoxygenation [10].

Another biocrude oil upgrade route is through organic acid removal by esterification with alcohol and an acid catalyst. Decreased acidity and viscosity can enhance the quality of biocrude oil. Esterification using supercritical fluids, such as water, methanol or ethanol, for the removal of organic acids in biocrude oil with or without catalysts has been intensively researched, due to the supercritical fluid system's unique properties, which include faster rates of mass and heat transfer, liquid-like density and dissolving power, and gas-like diffusivity and viscosity [10–13]. In supercritical ethanol, ethanol reacts with carboxylic acids in biocrude oil and produces the corresponding esters by esterification, even without catalysts. Supercritical ethanol acts as an effective reactant medium by reducing the viscosity of biocrude oil. Ethanol can also produce hydroxyl and hydrogen radicals in reactions with biocrude oil in the supercritical state [14,15].

Among lignocellulosic biomass, coffee has a huge potential for biomass feedstock, simply because it is one of the most popular beverages worldwide. Typically, most coffee grounds are disposed of as waste, while only a small amount is employed as compost or for use in deodorants. Because the rate of coffee consumption is continuously increasing, spent coffee grounds could be a promising biomass resource for production of biocrude oil [4]. However, spent coffee grounds contain additional lipids besides cellulose, hemicellulose, and lignin (the major components of lignocellulosic biomass); the reaction process for upgrading biocrude oil that is produced from spent coffee grounds is predicted to be very different from that followed for upgrading pyrolysis oil from lignocellulosic biomass, such as sawdust [16,17]. Lipids can be extracted from spent coffee grounds using organic solvents and subsequently converted to biodiesel by transesterification [18,19]. Coffee biocrude oil has been found to contain highly acidic substances originating from lipids, the major compounds of which are palmitic acid, oleic acid, and stearic acid [16]. The catalytic cracking of fatty acids in coffee biocrude oil for lowering the oxygen and acid contents can be utilized to improve the oil's properties. However, studies on upgrading biocrude oil produced from spent coffee grounds by fast pyrolysis are rare.

Meanwhile, waste plastic is one of the most common wastes in the world, its global production has been steadily increasing for more than 50 years. The short-lived use of plastic products causes a drastic accumulation of waste plastic worldwide, and waste plastic accounts for 10–12% of municipal solid waste [20]. Appropriate management of waste plastic is now a significant public concern, especially given the dire environmental risk and the necessity of meeting increasingly stringent waste-separation regulations. The plastic waste to energy conversion process via pyrolysis, for example, has demonstrated the potential to produce high-value-added products, such as chemicals and fuels [20]. Plastic pyrolysis oil's abundance of aliphatic and aromatic hydrocarbons is expected to improve the low-grade properties of oxygen-rich biocrude oil when combined with the latter [21].

In the present study, coffee biocrude oil produced by the pyrolysis of spent coffee grounds was upgraded with three methods: (i) a supercritical ethanol reaction with and without catalyst, (ii) a supercritical ethanol reaction with plastic pyrolysis oil, and (iii) catalytic cracking with Ni/MCM-41. The changes in the properties of coffee biocrude oil, including the lipids (fatty acids), through each upgrading method, were compared for their reduced oxygen and acid contents and increased heating values.

## 2. Materials and Methods

### 2.1. Materials

Coffee biocrude oil, prepared through the fast pyrolysis of spent coffee grounds, was provided by the Korea Institute of Machinery and Materials [4]. Prior to the experimentation, the oil was evaporated at 150 °C to remove water and volatile compounds. Spent coffee grounds with a moisture content of 57.8% were dried in an oven overnight at 105 °C for analysis of their fatty acid contents. Concurrently, plastic pyrolysis oil was prepared from mixed-waste plastics by the Korea Institute of Energy Research [22]. Ethanol (99.9%) for use as a supercritical solvent was supplied by OCI Company Ltd. Nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.999%), ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 5\text{H}_2\text{O}$ , 81.0–83.0%), and magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99%) were purchased from Sigma-Aldrich. Activated charcoal (AC) (BET surface area: 688  $\text{m}^2/\text{g}$ ) was also supplied by Sigma-Aldrich. The AC was washed several times with distilled water to remove contaminants; after cleaning, it was dried and sieved to between 0.50 and 0.85 mm. MCM-41 (BET surface area: > 800  $\text{m}^2/\text{g}$ ) was supplied by ACS Material.

### 2.2. Preparation and Characterization of Catalysts

Preparatory to the supercritical reaction, AC-supported catalysts were prepared by an incipient wetness impregnation method, which involved 25 wt% Ni, 10 wt% Mo and 2 wt% Mg being impregnated consecutively on AC. The AC-supported catalysts were dried at 100 °C for 12 h, calcined at 500 °C for 3 h in a  $\text{N}_2$  flow of 100 mL/min, and reduced at 400 °C for 8 h in a  $\text{H}_2$  flow of 100 mL/min [23]. For catalytic cracking, MCM-41-supported catalysts also were prepared by the incipient wetness impregnation method, 25 wt% Ni being impregnated on MCM-41. The MCM-41-supported catalysts were dried at 100 °C for 12 h, calcined at 500 °C for 3 h in a  $\text{N}_2$  flow of 100 mL/min, and reduced at 400 °C for 8 h in a  $\text{H}_2$  flow of 100 mL/min. The BET-specific surface area, pore volume, and pore diameter of the prepared catalysts were determined by  $\text{N}_2$  adsorption/desorption isotherms at  $-196$  °C in ASAP 2420 (Micromeritics Ltd). The specific surface was calculated using the BET equation, and the pore size distributions were analyzed by the BJH method.

### 2.3. Supercritical Ethanol Reaction and Catalytic Cracking Procedures

To perform a supercritical reaction, an autoclave reactor of 200 mL capacity was used. The reactor was heated with an electric heating system, and the temperature was measured with a thermocouple. A total amount of 100 g biocrude oil/ethanol mixture was fed into the reactor. The ratio of biocrude oil to ethanol was 2:8 (*w/w*). First, to enhance the efficiency of deoxygenation, the catalysts AC and MgNiMo/AC were used with 4 wt% mixture. Secondly, to reduce the oxygen content, 10, 20, and 40 g of plastic pyrolysis oils were additionally added to 100 g biocrude oil/ethanol mixture. The weight ratios of coffee biocrude oil to plastic pyrolysis oil were 1:0.5, 1:1, and 1:2, respectively. In a blending experiment with plastic pyrolysis oil, there was no need for a catalyst. After sealing, the reactor was purged with nitrogen gas to remove the air in the reactor. The purging process was repeated three times, and then the reactor was pressurized, with  $\text{N}_2$  to 30 bar as an initial pressure. The reaction was performed at 340 °C, the mixture being stirred at a rate of 500 rpm for 2 h and then cooled to room temperature by water circulation. All of the gas, liquid, and solid products were collected from the reactor for analysis. The gas product sample was first collected with a tedlar gas-tight bag at room temperature for compositional analysis and then the remaining gas was vented outside. The reactor was opened by removing its head cover, and all the products and catalyst present in the reactor were collected. The reactor was rinsed with acetone if necessary. The collected mixture was first filtered using 1.2  $\mu\text{m}$  glass fiber filter papers to separate the liquid and the solid phases. The solid phase, including the solid product and catalyst, was dried at 105 °C for 12 h, and the dried mass was measured to determine the solid product yield by deducting the weight of the catalyst used. Vacuum evaporation (60 °C, 1 h) and consecutive vacuum dry (50 °C, 5 h) were conducted to remove any reaction medium and washing solvent,

such as ethanol and acetone present in the collected liquid phase. The yields of liquid, solid and gas products were calculated according to the following formula:

Liquid product yield (wt%)

$$= \text{Weight of upgraded biocrude oil} / \text{Weight of biocrude oil} \times 100$$

Solid product yield (wt%)

$$= \text{Weight of produced solid product} / \text{Weight of biocrude oil} \times 100$$

Gas product yield (wt%) = Weight of produced gas / Weight of biocrude oil × 100

In preparation for catalytic cracking, 54 g of biocrude oil and 6 g of Ni/MCM-41 catalyst (9:1, *w/w*) were fed into the autoclave reactor. Prior to the reaction, the reactor pressure was increased to 30 bar to test for any N<sub>2</sub> leakage. After a satisfactory test result was obtained, the reactor pressure was decreased back to 0 bar. The reactor was heated with an electric heating system at a rate of 10 °C/min to 400 °C under a constant stirring rate of 400 rpm. When the temperature reached 400 °C, the reaction was stopped and then cooled to room temperature by water circulation. All of the gas, liquid, and solid products were collected from the reactor for analysis. The subsequent procedure was the same as detailed above.

#### 2.4. Analyses

The fatty acid contents of the spent coffee grounds and coffee biocrude oil were analyzed using the modified direct esterification method. To that end, samples totaling approximately 10 mg were first put into a vial. Two milliliters of chloroform–methanol mixture (2:1, *v/v*) was added to the samples, and the solution was then vigorously agitated for 10 min. With one milliliter of chloroform solution containing heptadecanoic acid (Sigma-Aldrich) as an internal standard (500 µg/L), 1 mL of methanol, and 300 µL of H<sub>2</sub>SO<sub>4</sub> were sequentially added to the vial, and the solution was vortex-mixed for 5 min. The vial was then submerged in a 100 °C water bath for 10 min, after which it was cooled to room temperature, supplemented with 1 mL distilled water, and intensely mixed for 5 min. After centrifugation, the lower layer (the organic phase) was injected into a gas chromatograph (Agilent 7890, Santa Clara, CA, USA.) for fatty acid methyl ester (FAME) analysis using the INNOWAX column (30 m × 0.32 mm × 0.5 µm; Agilent, Santa Clara, CA, USA). The initial oven temperature was 50 °C for 1 min, which was thereafter increased to 200 °C at a rate of 15 °C/min, then maintained for 9 min, which was subsequently increased again to 250 °C at a rate of 2 °C/min, and finally maintained for 2 min. Mix RM3 (C14:0 C24:0), Mix RM5 (C8:0 C18:2), and GLC50 (C16:1 C22:1) (Supelco) were utilized as the fatty acid standards. The weight of each of the fatty acids was calculated quantitatively through standard calibration. The other reagents used were of analytical grade.

The composition analyses of the coffee biocrude oil, plastic pyrolysis oil, and upgraded biocrude oils were performed on an Agilent 7890A gas chromatograph (HP-5 column, 30 m × 0.32 mm × 0.2 µm) equipped with a mass spectrometer (5975C). The carrier gas was He of 99.999% purity. The oven temperature increased from 45 to 250 °C at a rate of 8 °C/min. The compounds were identified using the National Institute of Standards and Technology (NIST) Mass Spectral Library. The analyses of the gas products were performed using an Agilent GC with a TCD (Carboxen 1000 column) for H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>, and with a FID (Carboxen 1000 column) for C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>. The elemental analyses were performed with a FLASH 2000, and the higher heating value (HHV) was calculated according to the DIN 51900 standard.

### 3. Results and Discussion

#### 3.1. Characterization of Spent Coffee Grounds, Coffee Biocrude Oil, and Plastic Pyrolysis Oil

The fatty acid contents and the compositions of the spent coffee grounds and coffee biocrude oil are summarized in Table 1. The total fatty acid content of the spent coffee grounds was 173.5 mg/g, which means that they contained 17.4 wt% lipids, including

triglycerides and free fatty acids based on their dry weight. The palmitic acid (C16:0) composition was 35.2 wt% total fatty acids, and the linoleic acid (C18:2) composition was 44.0 wt% total fatty acids. Goh et al. [18] reported a lipid extraction yield from spent coffee grounds of 14.5 wt% based on ultrasonic extraction, and their two main fatty acids were palmitic acid (32.8 wt%) and linoleic acid (44.1 wt%). Somnuk et al. [24] obtained a 14.7 wt% lipid extraction yield from spent coffee grounds using hexane, and the contents of their palmitic and linoleic acids were 34.4 and 43.1 wt%, respectively.

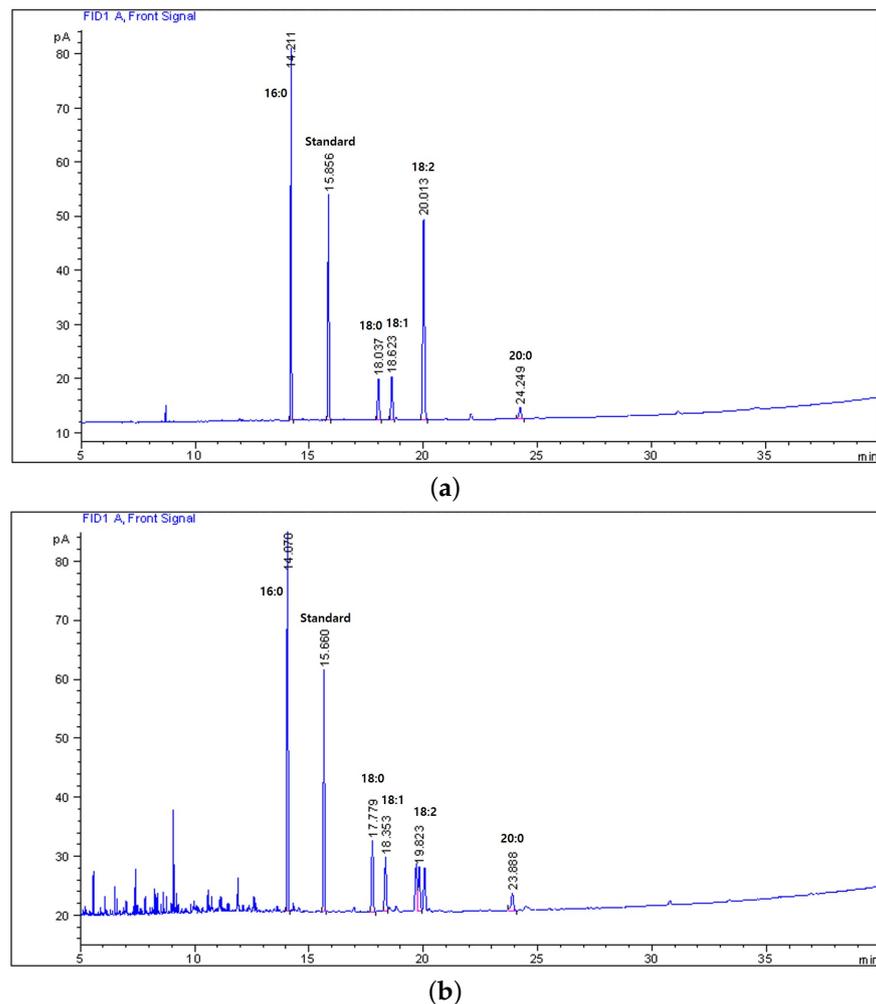
**Table 1.** Fatty acid contents and composition of spent coffee grounds and coffee biocrude oil by GC analysis.

Fatty Acids	Spent Coffee Grounds		Coffee Biocrude Oil	
	Content (mg/g)	Composition (wt%)	Content (mg/g)	Composition (wt%)
Palmitic acid (C16:0)	61.1	35.2	99.7	59.4
Stearic acid (C18:0)	12.2	7.0	19.3	11.5
Oleic acid (C18:1)	13.8	8.0	17.5	10.4
Linoleic acid (C18:2)	76.3	44.0	17.8	10.6
Linolenic acid (C18:3)	3.5	2.0	1.2	0.7
Arachidic acid (C20:0)	4.9	2.8	7.6	4.5
Eicosenoic acid (C20:1)	0.5	0.3	3.0	1.8
Behenic acid (C22:0)	1.2	0.7	1.8	1.1
Total	173.5	100.0	167.9	100.0

In the present study, the total fatty acid content of the coffee biocrude oil was 167.9 mg/g, which means that the oil contained 16.8 wt% lipids, including triglycerides and free fatty acids based on its dry weight. The palmitic acid (C16:0) composition was 59.4 wt% of total fatty acids. The stearic acid (C18:0), oleic acid (C18:1), and linoleic acid (C18:2) compositions were 11.5, 10.4, and 10.6 wt% total fatty acids, respectively. While the major fatty acids of the spent coffee grounds were C16:0 and C18:2, that of the coffee biocrude oil was only C16:0. The [C16:0]:[C18:0]:[C18:1]:[C18:2] weight ratios of the spent coffee grounds and coffee biocrude oil were 100:20:23:125 and 100:19:18:18, respectively. After fast pyrolysis, linoleic acid (C18:2) containing two double bonds was noticeably depleted. Although C18:1, with one double bond at position 9, was stable during high-temperature pyrolysis (500–600 °C), C18:2 with two double bonds at positions 9 and 12 is thought to have been converted to other molecules during pyrolysis. Primaz et al. [16] analyzed coffee biocrude oil under the optimal condition (500 °C) using two-dimensional GC. The major compounds were, similar to in the present study, palmitic acid (19.2 area%), oleic acid (11.1 area%), and stearic acid (9.9 area%). In the present study, the content of linoleic acid was decreased by the pyrolysis of coffee grounds. In Primaz's study, no linoleic acid was observed. The present GC graphs of the spent coffee grounds and coffee biocrude oil indicated peaks of C16:0, C18:0, C18:1, C18:2, and C20:0, among others (Figure 1). On the GC graph of the coffee biocrude oil, many small peaks before the C16:0 peak, representing hydrocarbons, aromatics, and phenols, were also observed.

The contents of the C, H, N, and O elements and higher heating values (HHVs) of the spent coffee grounds, coffee biocrude oil, and plastic pyrolysis oil are summarized in Table 2. The carbon content was the highest for plastic pyrolysis oil (80.5 wt%) and the oxygen content was the highest for spent coffee grounds (34.8 wt%). Due to the fact that high oxygen contents, affected by oxygenated compounds, make pyrolysis oil reactive and unstable, they need to be lowered in the process of pyrolysis oil upgrading. The N compounds of spent coffee grounds and coffee biocrude oil originate from the caffeine, protein, and trigonelline compounds [25]. In the present study, the HHVs were 24.4, 33.3, and 40.6 MJ/kg for the spent coffee grounds, coffee biocrude oil, and plastic pyrolysis oil, respectively. The coffee biocrude oil containing lipids of triglycerides and free fatty acids showed a larger HHV than a previous study's sawdust pyrolysis oil, which showed a 33.9 wt% oxygen content and a 25.2 MJ/kg HHV [23]. In the study of Somnuk et al. [24],

the contents of C, H, N, and O for spent coffee grounds were 53.0, 6.8, 2.1, and 38.1%, respectively. This composition was similar to that of our current study. Their HHV, meanwhile, was 23.1 MJ/kg. Bok et al. [26] reported that the contents of C, H, N, and O for coffee biocrude oil were 54.3, 7.4, 3.1, and 35.3%, respectively, and that the HHV was 23.2 MJ/kg. After fast pyrolysis, the O content was still high and the heating value was low, as the moisture content of the biocrude oil was 24.0 wt%. In the present study, biocrude oil was upgraded after evaporation in order to enhance its efficiency, resulting in the oxygen content decreasing to 16.9 wt%. Zhang et al. [20] produced pyrolysis oil with a HHV of 39.1 MJ/kg from a plastic mixture, and the contents of C, H, N, and O for plastic pyrolysis oil were 88.0, 8.1, 0.9, and 3.0%, respectively. Because plastic pyrolysis oil shows very high HHVs with low oxygen contents, the properties of coffee biocrude oil are expected to be further improved through the process of blending with plastic pyrolysis oil.



**Figure 1.** Fatty acid distributions of (a) spent coffee grounds and (b) coffee biocrude oil by GC analysis.

### 3.2. Upgrading Coffee Biocrude Oil by Supercritical Ethanol Reaction

The physical properties of catalysts are summarized in Table 3. The BET surface areas of AC and MCM-41 were 687.9 and 1010.2 m<sup>2</sup>/g, respectively. The BET surface area of MgNiMo/AC and Ni/MCM-41 decreased to 518.4 and 465.8 m<sup>2</sup>/g compared with the original catalysts, respectively.

**Table 2.** Elemental compositions of spent coffee grounds, coffee biocrude oil, and plastic pyrolysis oil.

	Spent Coffee Grounds	Coffee Biocrude Oil	Plastic Pyrolysis Oil
C (wt%)	55.3	70.0	80.5
H (wt%)	7.4	9.0	11.3
N (wt%)	34.8	3.8	0.6
O (wt%)	24.4	16.9	7.6
HHV (MJ/kg) <sup>a</sup>	24.4	33.3	40.6

<sup>a</sup> Calculated from Channiwala equation:  $HHV = 0.3491C + 1.1783H - 0.1034O - 0.0151N$ .

**Table 3.** Physical properties of catalysts.

	BET Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Avg. Pore Diameter (nm)
AC	687.9	0.56	3.25
MgNiMo/AC	518.4	0.45	3.51
MCM-41	1010.2	0.92	3.17
Ni/MCM-41	465.8	0.32	3.06

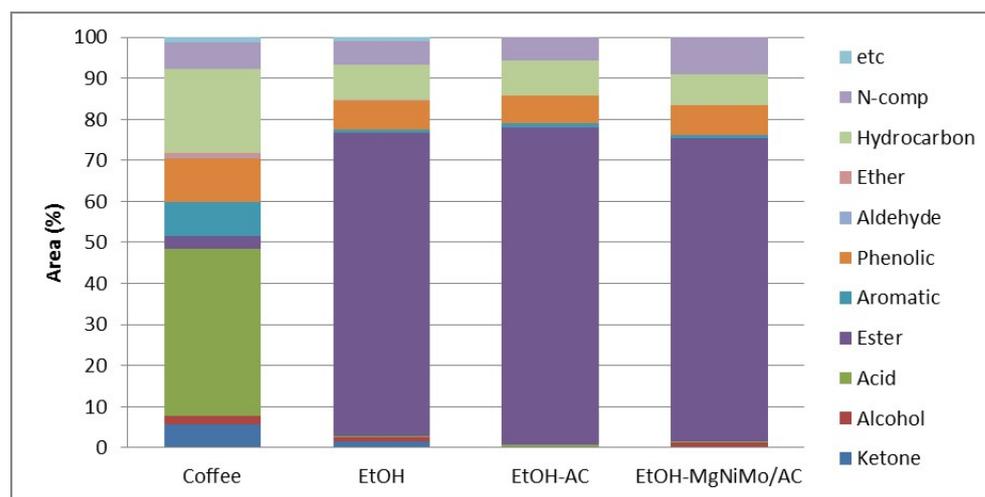
Coffee biocrude oil was upgraded using a supercritical ethanol reaction with and without a catalyst. The major components of the coffee biocrude oil were acids (40.9 area%), hydrocarbons (20.3 area%), phenols (10.6 area%), and aromatics (8.2 area%) (Figure 2). The major acids included palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), and linoleic acid (C18:2). Primaz et al. [16] reported that coffee biocrude oil contained acids (46.0 area%), esters (12.0 area%), hydrocarbons (13.0 area%), phenols (6.0 area%), and aromatics (5.0 area%). In the present study, the content of esters was lower (3.1 area%) than the corresponding result of Primaz et al. [16]. The major component was very different with sawdust pyrolysis oil, according to an earlier study: phenols (46.1 area%), with ester, aldehyde, and alcohol contents of 11.0, 10.3, and 9.4 area%, respectively, [23]. Among the phenols in that study, whereas the sawdust pyrolysis oil consisted of both methoxy phenol and alkyl phenol, the former having higher content, coffee biocrude oil mainly consisted of alkyl phenol.

**Table 4.** Compositions of fatty acid ethyl esters of upgraded coffee biocrude oils by GC-MS analysis.

	EtOH	EtOH-AC	EtOH-MgNiMo/AC
C16:0 ethyl ester (area%)	30.3	31.9	31.2
C18:0 ethyl ester (area%)	9.2	10.1	9.1
C18:1 ethyl ester (area%)	10.9	11.7	17.0
C18:2 ethyl ester (area%)	14.2	13.7	8.9
Total	64.6	67.4	66.2

During a supercritical ethanol reaction, the esterification of fatty acids with mainly ethanol occurs. Under the supercritical ethanol condition of 340 °C, the fatty acids of biocrude oil are converted to esters without any catalyst. Farobie et al. [27] reported that canola oil was converted to biodiesel of 100% fatty acid methyl ester under a reaction time of 10 min at 350 °C and an oil-to-methanol molar ratio of 1:40 without catalyst. Akkarawatkhosith et al. [28] produced biodiesel with 98.5% fatty acid ethyl ester from palm oil under a residence time of 5.2 min at 370 °C and an oil-to-ethanol molar ratio of 1:16 without catalyst. The ester content of coffee biocrude oil was 3.1 area%, but after a supercritical ethanol reaction without a catalyst, the ester content increased to 73.8 area% (Figure 2). The MgNiMo/AC catalyst was employed in the present experiment as it had shown good performance in the deoxygenation of bio-tar and biomass pyrolysis oil [10,23]; with MgNiMo/AC, the oxygen content of bio-tar decreased from 31.3 to 12.5% during a supercritical ethanol reaction at 350 °C for 1 h [10]; meanwhile, in the other study using the same catalyst, the oxygen content of sawdust pyrolysis oil decreased from 33.9 to 14.6% during a supercritical ethanol reaction at 340 °C for 2 h [23]. When AC and MgNiMo/AC catalysts were used in the present study, the compositions of the upgraded oils were

similar to those without catalyst. The reason was that the esterification of fatty acids occurred without any catalyst under the supercritical ethanol condition of 340 °C. After the supercritical reaction, the major component of the upgraded biocrude oil was C16:0 ethyl ester in all three cases because palmitic acid (C16:0), which was the major component of the coffee biocrude oil, was esterified with ethanol (Table 4). The contents of C18:0 ethyl ester, C18:1 ethyl ester, and C18:2 ethyl ester were roughly within a third to a half of that of C16:0 ethyl ester in area% (Table 4). The other components were hydrocarbons and phenols (Figure 2).



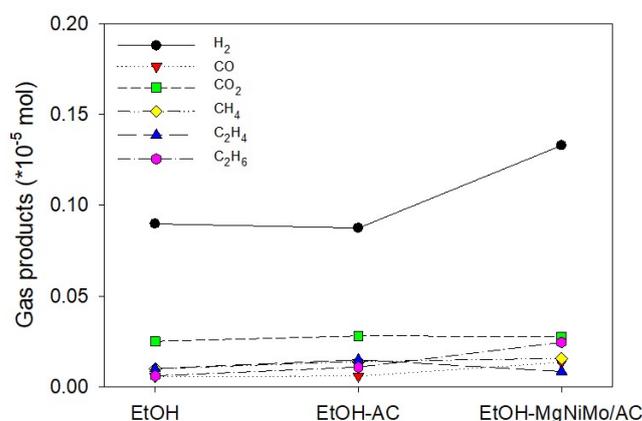
**Figure 2.** Compositions of coffee biocrude oil and upgraded coffee biocrude oils by GC-MS analysis (reaction conditions: biocrude oil = 20 g, ethanol = 80 g, AC or MgNiMo/AC = 4 g, temperature = 340 °C, reaction time = 2 h, N<sub>2</sub> initial pressure = 30 bar).

As a result of the upgrading reaction, the oxygen contents decreased from 16.9 wt% of coffee biocrude oil to less than 10 wt% (9.9, 9.1, and 8.5 wt% for oils upgraded by supercritical ethanol, supercritical ethanol with AC, and supercritical ethanol with MgNiMo/AC, respectively). Because the -COOH group of fatty acids had been converted to the -COOC<sub>2</sub>H<sub>5</sub> ester with -C<sub>2</sub>H<sub>5</sub> ethanol (Equation (1)), and -C<sub>2</sub>H<sub>5</sub> ethanol was bound to several compounds, such as phenols, the overall oxygen content decreased. Prajitno et al. [7] reported that the oxygen content of pyrolysis bio-oil derived from empty palm fruit bunch decreased from 26.8 to 12.6% during a supercritical ethanol reaction at 400 °C for 30 min without catalyst. In the present study, when MgNiMo/AC was used as a catalyst, the oxygen content of coffee crude oil additionally decreased to 8.5 wt%. As shown in Figure 3, the hydrogen content with MgNiMo/AC after the reaction was higher than in the cases without catalyst or with AC. Hydrogen can be efficiently produced from ethanol under the MgNiMo/AC catalyst condition (Equation (2)) [23]. CO and CH<sub>4</sub> were also produced from ethanol.



Therefore, MgNiMo/AC enhanced the production of hydrogen, which reacted with the biocrude oil, resulting in the oxygen content decreasing through deoxygenation. Some hydrogen was consumed in the reaction with biocrude oil, the rest remaining after the reaction. However, for upgrading coffee biocrude oil containing high fatty acids, MgNiMo/AC was not noticeably effective as the main reaction was esterification. The HHVs were 33.3, 37.0, 37.5, and 38.0 MJ/kg for coffee biocrude oil, oil upgraded by supercritical ethanol, oil upgraded by supercritical ethanol with AC, and oil upgraded by supercritical ethanol with MgNiMo/AC, respectively. After oil upgrading, the heating values were not significantly different. According to the report of Prajitno et al. [7], the heating value of pyrolysis

bio-oil from empty palm fruit bunch increased to 34.1 MJ/kg at 400 °C supercritical ethanol without a catalyst.

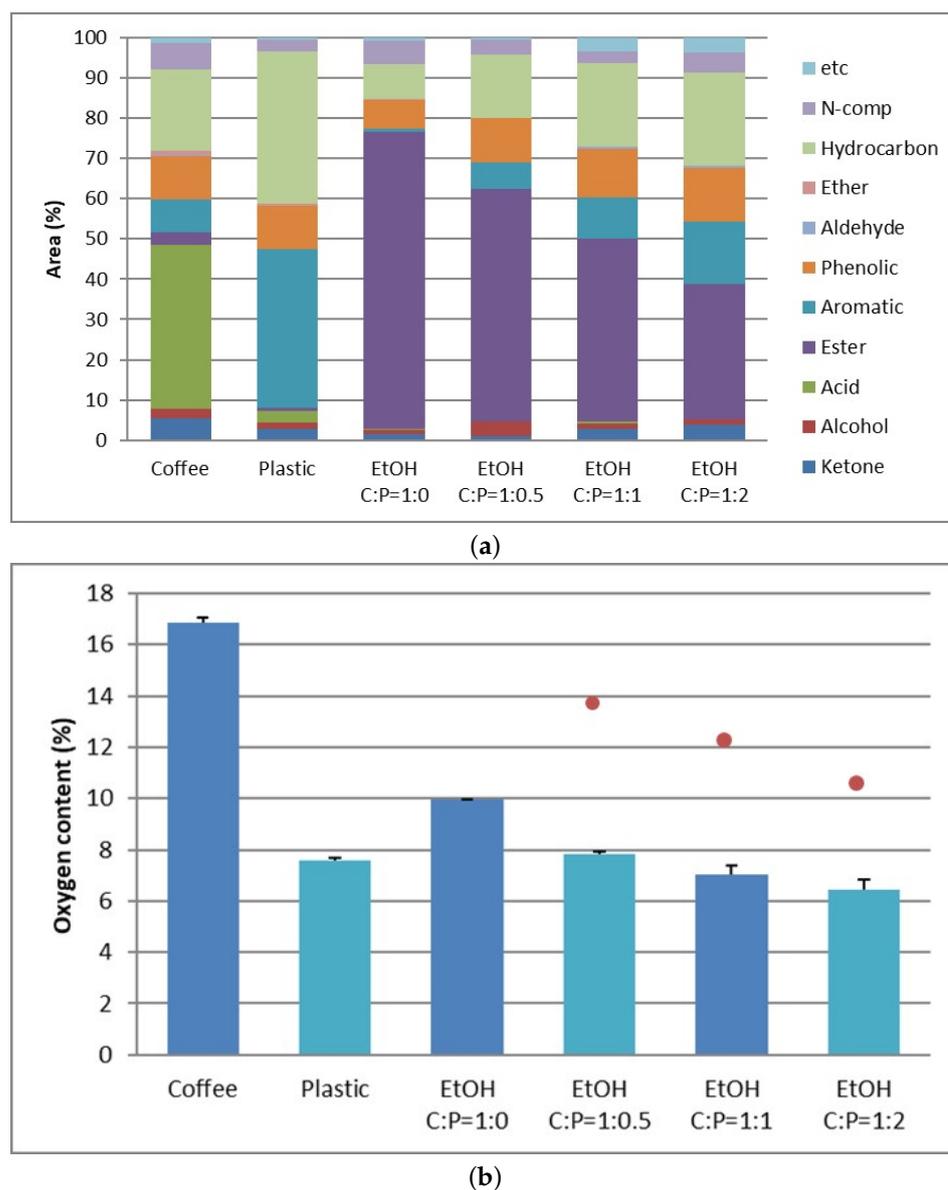


**Figure 3.** Gas production after supercritical reaction (reaction conditions: biocrude oil = 20 g, ethanol = 80 g, AC or MgNiMo/AC = 4 g, temperature = 340 °C, reaction time = 2 h, N<sub>2</sub> initial pressure = 30 bar).

### 3.3. Upgrading Coffee Biocrude Oil by Supercritical Ethanol Reaction with Plastic Pyrolysis Oil

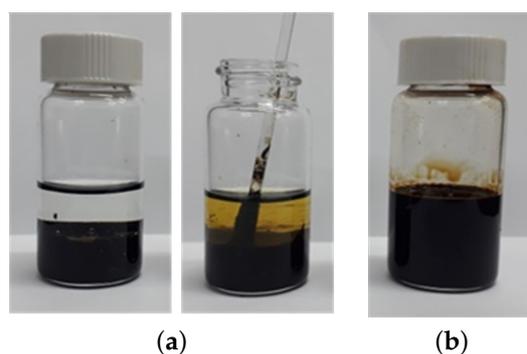
The plastic pyrolysis oil employed in the present experimentation mainly consisted of hydrocarbons and aromatics, unlike the acids and hydrocarbons in the coffee crude oil (Figure 4a). Because chlorinated compounds are hazardous, and poisonous to catalysts, and have acidic characteristics, polyvinyl chloride is not a desirable plastic. Pyrolysis oils produced from polyethylene and polystyrene are desirable for blending with biofuels. The mixture of coffee biocrude oil and plastic pyrolysis oil was reacted with supercritical ethanol without a catalyst to upgrade the properties of the former. The weight ratios of coffee biocrude oil to plastic pyrolysis oil were 1:0, 1:0.5, 1:1, and 1:2. As plastic pyrolysis oil is rich in hydrocarbons and aromatics, the low-grade properties of oxygen-rich coffee biocrude oil can be improved in combination with plastic pyrolysis oil [21]. After the supercritical ethanol reaction of coffee biocrude oil mixture, the major product was esters, produced by the esterification of fatty acids. When the blending ratios of plastic pyrolysis increased, the contents of hydrocarbons, phenols, and aromatics gradually increased with the decrease in the ester content.

Biocrude oil is typically immiscible with hydrocarbons due to the high oxygen content [29], which renders it immiscible with conventional fossil fuels as well [7]. When the hydrocarbon decene, instead of plastic pyrolysis oil with black color, was added to coffee biocrude oil to determine the miscibility of the two pyrolysis oils, the two phases were not completely miscible. As shown in Figure 5a, the top layer was decene and the bottom layer was coffee biocrude oil. However, after the supercritical ethanol reaction of the mixture of coffee biocrude oil and decene (1:1, *w/w*) under the same conditions (340 °C and 2 h), the product was miscible into one phase (Figure 5b). Therefore, upgraded coffee biocrude oil produced through a supercritical ethanol reaction with plastic pyrolysis oil is expected to have better properties than oil produced by the mechanical blending of plastic pyrolysis oil and coffee biocrude oil.



**Figure 4.** Characteristics of coffee biocrude oil, plastic pyrolysis oil, and upgraded coffee biocrude oils with plastic pyrolysis oil under supercritical ethanol. (a) Compositions by GC-MS analysis (C:P is the weight ratio of coffee biocrude oil to plastic pyrolysis oil). (b) Oxygen contents (reaction conditions: biocrude oil = 20 g; ethanol = 80 g; plastic pyrolysis oil = 10, 20, and 40 g; temperature = 340 °C; reaction time = 2 h; N<sub>2</sub> initial pressure = 30 bar).

The initial oxygen contents of the coffee biocrude oil and plastic pyrolysis oil were 16.9 and 7.6 wt%, respectively (Figure 4b). If the two pyrolysis oils were mechanically blended at the ratios of 1:0.5, 1:1, and 1:2, their oxygen contents would be 13.8, 12.2, and 10.7 wt%, respectively (calculated mathematically), although the complete one phase of oil could not be formed (red circles in Figure 4b). However, after the upgrading reaction under the ethanol condition, the oxygen contents were decreased through the supercritical ethanol reaction, yielding 7.8, 7.0, and 6.4 wt%, respectively. Hydrogen produced from ethanol reacted with the biocrude oil, and the oxygen content was decreased by deoxygenation. Because the -COOH group of fatty acids was converted to -COOC<sub>2</sub>H<sub>5</sub> ester, and -C<sub>2</sub>H<sub>5</sub> ethanol was bound to some of the compounds of both coffee and plastic oil, the overall oxygen content was further decreased.



**Figure 5.** Miscibility of (a) mixture of coffee crude oil and decene before/after stirring and (b) reaction product of coffee crude oil and decene under supercritical ethanol.

The heating values of the pyrolysis oils and upgraded coffee biocrude oils are summarized in Table 5. Plastic pyrolysis oil showed the highest heating value with a low oxygen content. When the blending ratio of plastic pyrolysis oil increased, the heating values of the upgraded oils also increased. The direct co-pyrolysis of biomass and waste plastic for high-grade biofuel production (an alternative to oil upgrading through the blending of two pyrolysis oils from biomass and waste plastic, as in the present study) has also been studied [30–32]. Elsewhere, when co-pyrolysis at the ratio of 1:1 of waste wood chip and polypropylene was performed at 500 °C, the oxygen content of the upgraded biocrude oil decreased from 42.3 to 10.9% and its HHV increased from 19.9 to 45.0 MJ/kg [33]. In another study, when co-pyrolysis at the ratios of 4:0, 3:1, 2:2, and 1:3 of waste newspaper and polyethylene was performed at 500–800 °C, the oxygen contents of upgraded biocrude oils decreased from 49.3 to 56.8 to 26.6–32.6, 14.9–20.6, and 2.4–5.4%, respectively, and the HHV increased from 14.2 to 16.8 to 21.2–24.8, 28.0–2–34.4, and 34.8–39.8 MJ/kg, respectively [34]. Zanella et al. [35] evaluated the co-pyrolysis of polypropylene and coffee waste at temperatures of 360–420 °C. When the fraction of polypropylene increased, the quantity of light liquid products decreased, while the fraction of heavy condensate products rose. Meanwhile, in the same study, when co-pyrolysis at the ratio of 1:1 polypropylene and coffee wastes was performed at 420 °C, the liquid yield was 71.7 wt%, whereas at 360 °C, the liquid yield was just 25.6 wt%. As all of these comparative results reveal, the present upgrading process has two advantages over the earlier processes: the effective utilization of waste plastic, and property improvement of biocrude oil.

**Table 5.** Heating values of coffee biocrude oil, plastic pyrolysis oil, and upgraded coffee biocrude oils.

	Coffee Biocrude Oil	Plastic Pyrolysis Oil	Upgraded Coffee Biocrude Oils (Supercritical EtOH)			
			C:P * = 1:0	C:P = 1:0.5	C:P = 1:1	C:P = 1:2
HHV (MJ/kg) <sup>a</sup>	33.3	40.6	37.0	38.8	39.6	40.1

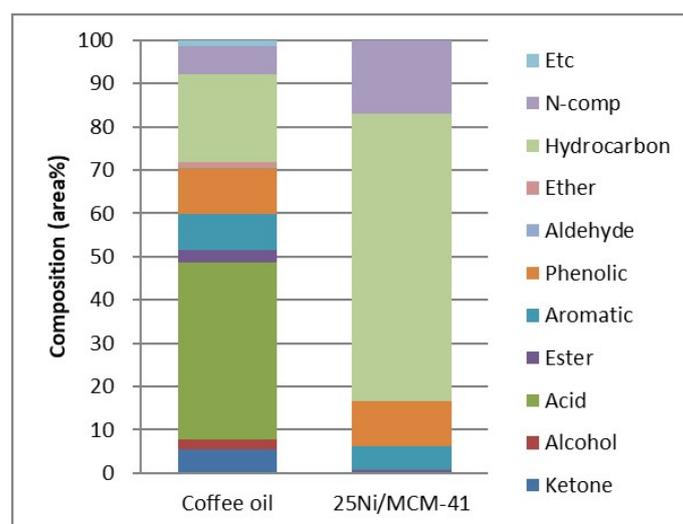
\* C:P is the weight ratio of coffee biocrude oil to plastic pyrolysis oil. <sup>a</sup> Calculated from Channiwala equation:  $HHV = 0.3491C + 1.1783H - 0.1034O - 0.0151N$ .

### 3.4. Catalytic Cracking of Coffee Crude Oil by Ni/MCM-41 Catalyst without Supercritical Ethanol

The Ni/MCM-41 catalyst has been employed for catalytic cracking of coffee crude oil using a batch reactor. Hu et al. [36] reported that a char-supported Ni catalyst showed good performance for the catalytic cracking of biomass tar: the content of single-ring aromatics increased and that of O-containing compounds decreased relative to the char catalyst without Ni; the oxygen content of biomass tar also decreased from 31.9 to 30.1 and 7.8 wt% for char and Ni/char, respectively. The MCM-41 catalyst has been used for the catalytic cracking of oleic acid, with the result being that the content of aromatic compounds increased with the increase in reaction temperature and reaction time. In addition, at 400 °C, large amounts of hydrocarbons with low aromatics content were produced from oleic acids by MCM-41 [37]. In the study of Twaiq et al. [38], the MCM-41 catalyst showed weak

Bronsted and Lewis acidity. This weak acidity led to the cracking of the linear chains (fatty acids) in palm oil, linear paraffin and olefins without further isomerization to naphthenes or aromatics. In the present study, the pressure was increased to 50.6 bar during the catalytic cracking of coffee biocrude oil at 400 °C. The initial hydrocarbons content was 20.3 area%. The acids (40.9 area%) with -COOH were converted to hydrocarbons (66.4 area%). The amount of aromatics was moderately decreased from 8.2 to 5.5 area%, and the ketones, alcohols, and acids disappeared (Figure 6). The hydrocarbons consisted of C9 to C21, including alkanes, alkenes, and cycloalkanes. During the catalytic cracking of fatty acids, deoxygenation occurred by reactions of dehydration, decarboxylation, decarbonylation, and others [39]. The content of pentadecane (C15) and heptadecane (C17) in hydrocarbons were high at 19.9 and 8.0 area%, respectively. The major components of the coffee biocrude oil were palmitic acid, stearic acid, oleic acid, and linoleic acid. Note that, when carbon dioxide is removed from palmitic acid, pentadecane can be produced, and when carbon dioxide is removed from stearic acid, heptadecane can be produced [38]. The contents of the alkanes of C13, C14, and C16 were 4.7, 6.4, and 4.1 area%, respectively. After catalytic cracking, the contents of the nitrogen compounds were increased. The content of pentadecanenitrile was the highest, with 9.4 area%. Octadecanenitrile, hexadecanamide, and octadecanamine, among others, were observed in the liquid product. Fischer et al. [25] also found nitrogen compounds after catalytic pyrolysis involving spent coffee grounds using ZSM-5 as a catalyst. They suggested that the amide had been produced from the amidization of acid with ammonia produced from proteinaceous compound and that the nitrile had been produced from amide pyrolysis [25].

After the present study's reaction, the product yields were 37.7, 36.5, and 25.8 wt% for liquid, coke, and gas, respectively. The heating value of liquid was 41.9 MJ/kg and the oxygen content was very low, 2.8 wt%. In the study of Mancio et al. [40], the catalytic cracking of crude palm oil at 450 °C was performed using a Na<sub>2</sub>CO<sub>3</sub> catalyst. When the catalyst dosage was increased, the concentration of hydrocarbons increased, whereas the concentration of oxygenates decreased. With a 15 wt% catalyst, the yields of liquid, coke, and gas were 58.0, 16.0, and 12.0 wt%, respectively. Twaiq et al. [41] performed the catalytic cracking of palm oil at 350–450 °C using HZSM-5, zeolite beta, and ultrastable Y catalysts. At 350 °C for the HZSM-5 catalyst, the yields of liquid, coke, and gas were 43.6, 6.1, and 41.8 wt%, respectively.



**Figure 6.** Compositions of coffee biocrude oil and upgraded coffee biocrude oil by catalytic cracking according to GC-MS analysis (reaction conditions: biocrude oil = 54 g, Ni/MCM-41 = 6 g, temperature = 400 °C).

### 3.5. Comparison of Methods for Upgrading Coffee Biocrude Oil

Coffee biocrude oil was upgraded by supercritical ethanol reaction, supercritical ethanol reaction with MgNiMo/AC catalyst, supercritical ethanol reaction with plastic pyrolysis oil, and catalytic cracking with Ni/MCM-41. The oxygen contents, HHVs, and liquid yields of the upgraded coffee biocrude oil are summarized in Table 6. The oxygen content of coffee biocrude oil decreased to 9.9 wt% after the supercritical ethanol reaction. After the catalytic supercritical reaction with MgNiMo/AC, the oxygen content also decreased (8.5 wt%). When the supercritical ethanol reaction was performed after coffee crude oil was blended with plastic pyrolysis oil (1:2, *w/w*), the oxygen content was further decreased (6.4 wt%). In the supercritical ethanol reaction, the liquid yields slightly increased as the  $-C_2H_5$  group originated from ethanol bound to oil compounds, which increased the molecular weights of the products. After the catalytic cracking of coffee pyrolysis oil, the oxygen content was very low, at 2.8 wt%, but the liquid yield was roughly half that of the other reactions. A significant amount of coke was generated after catalytic cracking in the present study. Therefore, the optimal condition for the catalytic cracking of coffee biocrude oil is required. Overall, a supercritical ethanol reaction with plastic pyrolysis oil can improve the properties of coffee biocrude oil and effectively make use of waste plastics. To obtain the full hydrocarbon product, instead of a mixture of hydrocarbon and ester products, catalytic cracking is necessary. Because coffee crude oil contains large amounts of fatty acids, hydrocarbon conversion by catalytic cracking is easier than employing biomass pyrolysis oil. Considering both HHV and liquid yield, supercritical EtOH with MgNiMo/AC had the best performance. MgNiMo/AC had no significant effect on oxygen removal compared to without catalyst, but the liquid yield increased by 5.0 wt% under the catalyst.

**Table 6.** Oxygen contents, heating values, and liquid yields of upgraded coffee biocrude oils.

Upgrading Methods	O (wt%)	HHV (MJ/kg) <sup>a</sup>	Liquid Yield (wt%)
Coffee biocrude oil	16.9	33.3	100.0
Supercritical EtOH	9.9	37.0	79.7
Supercritical EtOH with MgNiMo/AC	8.5	38.0	84.7
Supercritical EtOH with plastic pyrolysis oil	6.4	40.1	65.2
Catalytic cracking with Ni/MCM-41	2.8	41.9	37.7

<sup>a</sup> Calculated from Channiwala equation:  $HHV = 0.3491C + 1.1783H - 0.1034O - 0.0151N$ .

## 4. Conclusions

Coffee biocrude oil with high contents of fatty acids (40.9 area%) was upgraded by means of non-catalytic or catalytic supercritical ethanol reaction, supercritical reaction with plastic pyrolysis oil, and catalytic cracking. Because the fatty acids of the coffee biocrude oil were esterified with supercritical ethanol, the major product was esters. In the supercritical ethanol reaction of coffee biocrude oil with plastic pyrolysis oil (1:2 (*w/w*)), the oxygen content was decreased to 6.4 wt% and the heating value was increased to 40.1 MJ/kg. Therefore, a supercritical ethanol reaction with plastic pyrolysis oil can be one means of accomplishing two key objectives: improving biocrude oil's properties, and the utilization of abundant waste plastics. It is expected that low-oxygen-content and high-heating-value oil upgraded from coffee biocrude oil has the potential to be used as a biofuel. The use of bioethanol, produced from lignocellulosic biomass, as a supercritical fluid source in the upgrading process will improve the sustainability of the biofuel production process.

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