



Oil extracted from spent coffee grounds for bio-hydrotreated diesel production



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ABSTRACT

Oil extracted from spent coffee grounds is utilized as a renewable source for bio-hydrotreated fuel production. In the present work, oil yield up to 13% can be obtained by Soxhlet extraction with hexane as a solvent. As the extracted oil contained high content of free fatty acids (6.14%), therefore one step alkali-catalyzed for ester based biodiesel production is impractical. Hydrotreating of extracted oil was performed over two catalysts i.e. NiMo/ γ -Al₂O₃ and Pd/C with different operating parameters i.e. reaction time, operating temperature, and H₂/oil. It was found that the reaction time of 2 h and the reaction temperature of 400 °C are favorable operating conditions. The liquid products mostly consisted of *n*-pentadecane and *n*-heptadecane, which contain one carbon atom shorter than the corresponding fatty acid (C_{*n*-1}) i.e. palmitic and stearic acid, respectively. Unfavorable cracking of diesel product is pronounced at high temperature and prolonged reaction time. In addition, although increased H₂/oil promoted overall reaction and hydrodeoxygenation activity (C_{*n*-1}/C_{*n*} decreased) for both catalysts, hydrocracking is enhanced over Pd/C, leading to significant increase in gasoline yield. Moreover, Pd/C gave higher olefin content in liquid product (22.3 wt%) than NiMo/ γ -Al₂O₃ (4.8 wt%). However, NiMo/ γ -Al₂O₃ shows higher isomerization activity. The amount of isoparaffins catalyzed by NiMo/ γ -Al₂O₃ and Pd/C were 10.8 and 1.7 wt%, respectively. Physicochemical analysis of the diesel fraction exhibit satisfactory properties. The density and kinematic viscosity were consistent with the specification of commercial bio-hydrogenated diesel, NExBTL, while the cetane index was much higher than conventional diesel.

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1. Introduction

The use of fossil energy increases carbon dioxide concentration in the atmosphere, which directly affects the global warming problem [1–4]. To reducing dependence on fossil energy which is unsustainable, biofuels production has been expanding worldwide. Currently, commercialized biofuels are 1st generation biofuels based on food crops such as bio-ethanol (produced from coarse grains, especially corn, and sugarcane) and biodiesel [5].

Over 95% of the biodiesel were produced from edible oil [6,7]. The contributions of edible oil for biodiesel production in the world could be ordered as rapeseed oil, sunflower oil, palm oil and soybean oil. However, the use of edible oil for fuels purpose leads

to a global imbalance to the food supply [8]. In addition, the using of virgin edible oils as reactant can result in the increasing cost of feedstock [9]. To avoid the limitation, utilization of waste oil could serve a rapid implementation of biofuel without affecting food supplies or forcing changes in land use.

Nowadays, coffee is produced in a number of countries worldwide. The world coffee production was increasing from 7.2 to 8.6 million tonnes from 2007 to 2015 [10] and spent coffee ground (SCG) is generated in a large amount about 65 wt% of green coffee [11]. SCG is a solid residue available from production of coffee beverages by extraction of coffee powder with hot water. It contains high oil content about 11–20 wt% on a dry weight basis [12–14] and the dominant fatty acids of extracted oil from spent coffee ground were linoleic (C18:2), palmitic (C16:0) and oleic (C18:1) [15] whose carbon length suits for producing diesel fuel. Assuming 16 wt% oil content in SCG, the use of this oil as reactant

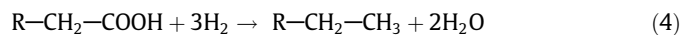
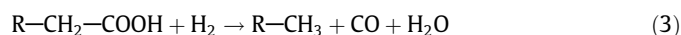
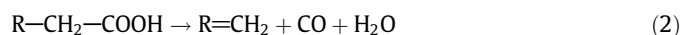
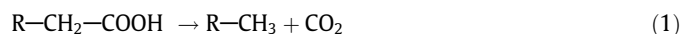
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for biodiesel production could produce about 0.9 million tonnes of biodiesel or ca. 3.5% of biodiesel market shared to the world's fuel supply (world biodiesel production 26 million tonnes based on the year 2014). Therefore, the coffee oil has a potential for biodiesel production and is considered as a low cost feedstock.

Coffee oil has been employed as a feedstock for production of fatty acid methyl ester (FAME) via transesterification (1st generation biodiesel) [12,16–19]. However, the ester-based biodiesel has many limitations, such as producing the excessive glycerol, low energy content, low oxidative stability [20] and plugging from the tank to the engine [21]. Moreover, FAME can be added into unmodified diesel engine just only ca. 7–10 wt% because of the molecular oxygen presence in the structure of FAME [22]. It is noted that the coffee oil also consists of high amount of free fatty acid ca. 16.3 wt% [16] therefore it is unsuitable for typical single step transesterification for FAME production catalyzed by basic catalyst [23]; otherwise other advanced techniques e.g. sub- and supercritical methanol [24] or superheated methanol technology is alternatively suggested [25,26].

To avoid the limitations of FAME, a hydrotreating process has been investigated as an alternative reaction for biofuel production. In this process, the triglycerides and free fatty acids are converted to straight chain alkanes as called “second generation biodiesel” or “diesel-like hydrocarbons” or “green diesel” or “bio-hydrotreating diesel (BHD)”. It has many advantages when compare to ester-based biodiesel such as high cetane number (55–90) [27] and feedstock flexibility (e.g. feedstocks with high FFA content and low quality) [20]. In addition, BHD can be fueled directly to current engines without modification and it is unnecessary to blend with fossil diesel if it is partially isomerized [20,28]. During hydrotreating process, several simultaneous deoxygenation reactions can occur including decarboxylation (DCO₂), decarbonylation (DCO), hydrodecarbonylation (HDCO) and hydrodeoxygenation (HDO), as shown in Eqs. (1)–(4), respectively.



Decarboxylation and decarbonylation produce CO₂ and CO, respectively so the obtained liquid product contains the hydrocarbons which one carbon atom shorter than the total length of the fatty acid (C_{n-1}). The benefit of decarboxylation, Eq. (1), is no hydrogen requirement for converting fatty acid to alkane. CO and water are produced accompanied with alkene via DCO (Eq. (2)) and alkane via HDCO (Eq. (3)). On the other hand, HDO pathway yields a hydrocarbon containing the same number of carbon atoms in the molecule as the corresponding fatty acid chain (C_n) and water as shown in Eq. (4). It is noted that two additional reactions, water gas shift (Eq. (5)) and methanation (Eqs. (6) and (7)) must be taken into account due to the formation of CO₂ and CO [29].



This research focuses on the hydrotreating of the extracted oil from SCG instead of virgin edible oil. The triglycerides (TG) and free fatty acids (FFA) in coffee oil was converted into straight chain hydrocarbons which have boiling point in a range of gasoline (50–220 °C) and diesel fuels (220–320 °C). The reactions were

carried out over two different catalysts i.e. 5 wt% Pd/C and NiMo/γ-Al₂O₃. The effect of operating parameters on catalysts activity was investigated.

2. Materials and methods

2.1. Chemical reagents

Calibration mixture for simulated distillation according to ASTM-2887 was purchased from Restex Co. *n*-Hexane was obtained from Fisher scientific Co. The spent coffee ground (*Coffea Arabica*) was obtained from Bon café Co. A commercial γ-Al₂O₃ was supplied by Fluka.

2.2. Catalysts preparation

5 wt% Pd/C catalyst was obtained from Aldrich Chemical Co. NiMo/γ-Al₂O₃ (2.45 wt% of Ni and 9.4 wt% of Mo) was prepared by an incipient wetness impregnation method. An aqueous solution of nickel nitrate, Ni(NO₃)₂·6H₂O (99.99%, Aldrich) and ammonium molybdate powder, (NH₄)₆ Mo₇O₂₄·4H₂O (99.99%, Merck) were used as a source of nickel and molybdenum, respectively. After impregnation, the sample was left at room temperature for 6 h and dried at 110 °C overnight. After that the sample was calcined by increasing the temperature from room temperature to 500 °C with a ramp rate of 3 °C min⁻¹ and held for 5 h. Both catalysts were activated before activity test. NiMo/γ-Al₂O₃ catalyst was presulfided under H₂S/H₂ mixture at 400 °C for 4 h while Pd/C was reduced under H₂ at 200 °C for 2 h.

2.3. Oil extraction

Before the extraction, SCGs were dried overnight at 110 °C in order to remove moisture. The dried SCGs were sieved for under a 60 mesh (125 μm) screen. They were loaded into the thimble of Soxhlet extractor and *n*-hexane was used as solvent. 3 L of *n*-hexane was used for 400 g of dried SCG and 12-h extraction time was required per batch. After extraction, the solvent was recovered in a rotary evaporator under high vacuum condition (IKA model: RV 10 digital). The % oil extraction can be calculated from the dried weight of SCG and the weight of the extracted oil after removing hexane follows Eq. (8).

$$\% \text{ oil extraction} = \frac{\text{weight of the extracted oil}}{\text{dry weight of SCG}} \times 100 \quad (8)$$

2.4. Catalyst characterization

The X-ray diffraction (XRD) patterns of Pd/C and NiMo/γ-Al₂O₃ were examined by the X-ray diffractometer (Rigaku, Miniflex II desktop X-ray diffraction). The experiments were performed with Cu K_α radiation and over the 2θ ranges from 20° to 80°. The crystallite sizes were estimated according to the Debye–Scherrer formula. The BET surface area, average pore size diameter and pore size distribution were measured by N₂ physisorption using BEL SORP mini II. To remove the moisture at the surface of catalysts, the catalysts were firstly pretreated at 150 °C for 3 h under 50 ml min⁻¹ of helium gas flow. The particle sizes of catalysts were determined by scanning electron microscope (SEM).

2.5. Reactor and operational details

The hydrotreating reactions were carried out in a shaking batch reactor. The activated catalysts and SCG oil were introduced into the reactor and then sealed the reactor. The reactor was purged

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