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Nickel sulfide, nickel phosphide and nickel carbide catalysts for bio-hydrotreated fuel production

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ABSTRACT

A series of nickel catalysts i.e. nickel sulfide (NiS), nickel phosphide (NiP) and nickel carbide (NiC) was investigated for hydrotreating of spent coffee oil to produce bio-hydrotreated fuel (BHF). Catalytic tests were carried out at 375–425 °C and 20–40 bar of initial H_2 pressure (before heating) with reaction time of 0–3 h. The activity of the catalysts are in the order of NiC > NiP > NiS; however NiC tended to promote cracking reaction resulting in high gasoline and gaseous yields. On the other hand, although NiS gives the lowest oil conversion, it is favorable to diesel yield with lowest methanation and cracking activity. Compared with decarboxylation (DCO_2) and hydrodeoxygenation (HDO), decarbonylation (DCO) was the major route for deoxygenation of coffee oil for all the catalysts. The ratio of (DCO + DCO_2) to HDO (as represented by C_{n-1}/C_n) decreased in the order NiS > NiC > NiP. Ketones as intermediate products (ca. 3 wt%) were detected in case of NiP. They could be generated via rearrangement of alcohol and keto-enol tautomerism. Significant amount of aromatics (4 wt%) with some isomerization products (0.9 wt%) can also be observed in NiS catalyzed liquid products while trace amount of these compounds were detected for NiP and NiC catalysts. Physiochemical analysis of the diesel fraction exhibited satisfactory properties. The density and kinematic viscosity were consistent with the specification of commercial bio-hydrogenated diesel, NExBTL. Since main products are straight chain hydrocarbons, high cetane index (> 110) could be achieved.

1. Introduction

Bio-based feedstocks are greatly of interest for fuel production because of depletion of fossil-based feedstocks and fluctuation of oil price. Not only the economic point of view but also the environmental problems are realized, especially global warming problem. Among the bio-based feedstock, triglycerides i.e. vegetable oils and animal fats are the most promising raw material because they offer many great properties including ready availability and renewability as well as the number of carbon atoms is suitable for liquid fuel production. Biofuels produced from edible triglyceride are called as 1st generation biofuels. In fact, more than 95% of ester-based biodiesel was derived from edible-oils [1,2] and about 50% was came from soybean oil (based on data of 2015) [3]. However, there are several criticisms on using edible crops

for fuel purpose. This can lead to a global imbalance on the food supply and other environmental problems are caused by requiring much of arable land [2,4]. In addition, the use of virgin edible oils leads to increasing the cost of feedstock [5]. In case of biodiesel production, the cost of feedstock is 70–95% of the total production costs [6]. To overcome the limitations, the non-edible and/or waste oils have become more attractive. Spent coffee grounds (SCGs) are considered as a by-product in a coffee industry and contain high oil content about 16 wt% on a dry weight basis. This extracted oil could provide ca. 3.5% of biodiesel market share to the world's fuel supply (based on the year 2014) [7].

Coffee oil has been converted to ester-based biodiesel [6,8–11] and recently to bio-hydrotreated diesel in our previous work [7]. Although ester-based biodiesel has been used as diesel fuel, it has many
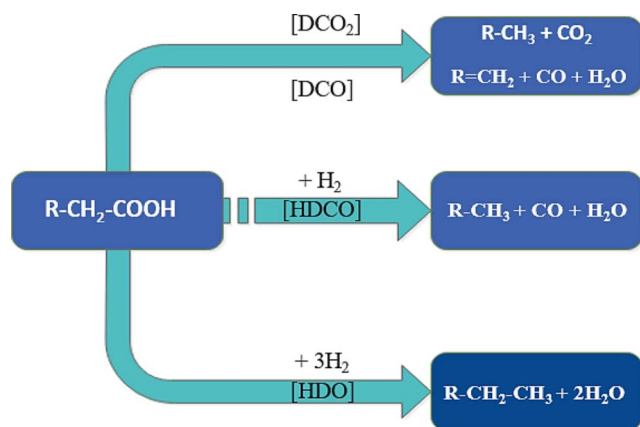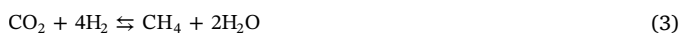
Fig. 1. General deoxygenation reaction pathways during hydrotreating.

drawbacks such as higher cloud point, higher viscosity [12] filter plugging, increasing of NO_x emissions [13], corrosion of metal parts [14] compared with petroleum derived diesel. Moreover, just only 7–10 wt% can be added to an unmodified diesel engine [15] because their oxygenated structure is different from fossil diesel fuel. In addition, the coffee oil contains high free fatty acids [7], therefore it commonly requires esterification step prior to the main transesterification step [16]. Alternatively, techniques such as sub- and supercritical methanol [17] or superheated methanol technology are alternatively suggested [18,19]. However, one-step hydrotreating process is desired for renewable fuel production from high impurity feedstocks. The obtained products from hydrotreating are the straight chain alkanes as called "bio-hydrotreated fuel (BHF)" which have a high cetane number and are considered as drop-in fuels.

During hydrotreating, four simultaneous reaction routes in liquid phase i.e. decarboxylation (DCO_2), decarbonylation (DCO), hydro-decarbonylation (HDCO) and hydrodeoxygenation (HDO) can occurred, as shown in Fig. 1. Both n-alkanes and alkenes can be generated, while CO_2 and CO are produced from DCO_2, DCO and HDCO so the obtained hydrocarbon is one carbon atom shorter than the corresponding fatty acid of coffee oil (C_{n-1}). The benefit of DCO_2 is no hydrogen requirement for producing n-alkanes. In case of DCO, the generated alkenes can be hydrogenated to form n-alkane (C_{n-1}). On the other hand, hydrodeoxygenation (HDO) pathway yields a hydrocarbon containing the same number of carbon atoms as parent fatty acid chain (C_n) and water. According to stoichiometry, hydrogen requirement of HDCO is less than HDO. Because the generated CO and CO_2 as well as the presence of H_2 in the reaction system, other possible reactions such as water gas shift (Eq. (1)), methanation (Eqs. (2) and (3)) and hydrogenation are also needed to be considered [20].

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad (1)$$

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O \qquad (2)$$

$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O \qquad (3)$$

In case of the generated CO_x gases are further reduced to CH_4, the H_2 consumptions are higher than in the case of HDO.

Nickel- and cobalt-molybdenum sulfides are the conventional hydrotreating catalysts which have been widely studied and industrialized. However, the sulfiding agents are very toxic for living organism and cause environmental problems. Moreover, they can react with the reactants and intermediates to form the undesirable S-containing products [21,22]. Therefore, catalysts without adding any sulfiding agents are currently explored. Noble metal catalysts such as Pd, Pt, Rh and Ru showed the high hydrotreating activities [23–25]. Nevertheless, the high price of noble metals is the main limitation in industrial application.

Other active form such as Ni phosphide (NiP) [26] and Ni carbide

(NiC) [27] has been employed for desulfurization. More recent NiP has been used for deoxygenation of several model compounds e.g. di-benzofuran [28], methyl laurate [29], methyl oleate [30]. Nickel phosphide offers the lower activities of cracking and methanation when compared with metallic Ni because of the effects of ligand and ensemble on metal site [31]. NiP show both metallic and acidic properties and this might lead to form the synergetic effect. Among transition metal phosphide catalysts including Ni, Co, Fe, Mo and W phosphides, MoP exhibits the highest conversion for hydrodeoxygenation of methyl laurate. Although NiP gave comparatively lower conversion (ca. 72%) than MoP (ca. 85%), methanation of NiP was much lower than that of MoP. In addition, NiP favored the deoxygenation process through decarboxylation/decarbonylation (DCO_x) (C_{n-1}/C_n = 4.17) while HDO was the main reaction pathway for MoP (C_{n-1}/C_n = 0.04). Therefore, NiP offered an advantage of lower H_2 consumption [32]. Recently, Zhang et al. [31] prepared NiP supported on γ-Al_2O_3 by temperature-programmed reduction method for hydrotreating of methyl laurate. They claimed that γ-Al_2O_3 support offers several benefits including large specific area, good thermal stability and intrinsic acidity, suitable to hydrotreating. High methyl laurate conversion (ca. 95%) with 95% of selectivity of C_{11-12} can be obtained with 10% Ni loading.

For NiC, there is very scarce research on an investigation of this catalyst for hydrotreating of triglyceride/fatty acid molecules or their derivatives. Some transition metal carbides such as Mo_2C [33] and W_2C [34] have been applied for hydrodeoxygenation of methyl stearate and stearic acid, respectively. They have been reported as promising catalysts because they showed great hydrotreating activity and have a benefit of an inexpensive catalyst over noble metals. However, Manoli et al. [27] reported that hydrodesulfurization activity over NiC/Al_2O_3 (initial conversion of 82%) outperformed Mo_2C/Al_2O_3 (3% initial conversion). NiC is expected to exhibit high catalytic activity for deoxygenation and thus it was investigated in our present study. Moreover, direct comparison among NiS, NiP and NiC for deoxygenation is studied in various operating conditions.

The aim of this research is to compare the catalytic activity of a series of Ni active forms including NiS, NiP and NiC for synthesis of hydrotreated fuels. Hydrotreating of oil extracted from spent coffee ground over these catalysts under suitable reaction conditions was conducted. Physicochemical properties of hydrotreated diesel fraction product i.e. distillation temperature, density, viscosity and cetane index were compared with specification of commercial standard.

2. Materials and methods

2.1. Chemical reagents

The catalyst precursors ($Ni(NO_3)_2\cdot6H_2O$ and $NH_4H_2PO_4$) and alumina support were purchased from Aldrich and Fluka, respectively. The calibration mixture for ASTM-2887 was supplied by Restec Co, while n-Hexane (solvent for Soxhlet extraction) was supplied from Merck & Co., Inc. The fresh coffee grain was obtained from Bon café Co (*Coffea arabica*). Hydrogen gas (99.99 vol%) was purchased from Linde (Thailand) Public Co.,Ltd.

2.2. Catalysts preparation

All catalysts were prepared by wet impregnation method on the commercial γ-Al_2O_3 support. The aqueous solution of $Ni(NO_3)_2\cdot6H_2O$ (99.99%, Aldrich) was used as nickel source. The nickel contents in all catalysts were 15 wt%. After impregnation, the samples were dried at 110 °C overnight and then calcined at 500 °C for 5 h with a ramp rate of 3 °C/min.

For nickel sulfide catalyst, the calcined catalyst was presulfided under 60 ml/min of 10 vol% of H_2S/H_2 mixture at 400 °C for 4 h. In case of nickel phosphide catalyst, $NH_4H_2PO_4$ was used as a phosphorus source for co-impregnation. The molar ratio of phosphorus to nickel