

Diesel-like hydrocarbon production from hydroprocessing of relevant refining palm oil



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ARTICLE INFO

Article history:

Received 10 May 2012

Received in revised form 11 April 2013

Accepted 13 April 2013

Available online xxx

Keywords:

Bio-hydrogenated diesel (BHD)
Hydrotreated vegetable oil (HVO)
Green diesel
Renewable liquid fuel
Deoxygenation
Phosphorous

ABSTRACT

This paper demonstrates the initiated use of relevant refining palm oil for bio-hydrogenated diesel production. The conversions of crude palm oil (CPO) and its physical refining including degummed palm oil (DPO) and palm fatty acid distillate (PFAD) to diesel fuel by hydroprocessing were studied. The effects of operating parameters (i.e. reaction time, operating temperature, and pressure) and catalyst (i.e. Pd/C and NiMo/ γ -Al₂O₃) were examined in order to determine suitable operating condition for each feedstock. It was found that the hydroprocessing of CPO with Pd/C catalyst at 400 °C, 40 bar, and reaction time of 3 h provides the highest diesel yield of 51%. When gum which contains phospholipid compounds is removed from CPO, namely DPO, the highest diesel yield of 70% can be obtained at a shorter reaction time (1 h). In the case of PFAD, which consists mainly of free fatty acids, a maximum diesel yield of 81% could be observed at milder conditions (375 °C with the reaction time of 0.5 h). The main liquid products are *n*-pentadecane and *n*-heptadecane, having one carbon atom shorter than the corresponding fatty acids according to decarboxylation/decarbonylation pathways. Pd/C catalyst shows good catalytic activity for fatty acid feedstocks but becomes less promising for triglyceride feedstocks when compared to NiMo/ γ -Al₂O₃.

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1. Introduction

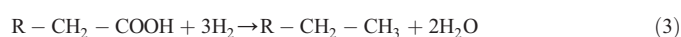
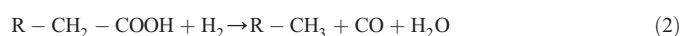
Due to an increase of the world's energy demand and petroleum-oil as well as the concern on global warming problem [1–3], the production of renewable fuels has therefore attracted much interest. Biodiesel is one of the promising alternative renewable fuels as it can reduce carbon dioxide (CO₂) in the carbon cycle as well as particulate matter (PM), un-burnt hydrocarbon and carbon monoxide (CO) emissions. Typically, triglycerides are converted via transesterification with methanol to produce fatty acid methyl esters (FAMES) which are commonly referred to as 1st generation biodiesel. However, the uses of FAMES still have some drawbacks such as limited compatibility with conventional diesel engines [4], increased NO_x emissions, low oxidative stability, gum formation, and possible engine problems due to their higher acid number than that of conventional diesel fuels [5]. In addition, glycerol, a by-product of this process, requires further usage or conversion to alleviate a glut of glycerol [6–11]. To overcome the disadvantageous of FAME, a hydroprocessing has been investigated as an alternative pathway of biodiesel production. In this process, triglycerides and fatty

acids are converted to straight chain alkane ranging from *n*-C₁₅ to *n*-C₁₈ known as middle distillates, which are suitable to use as diesel fuels. It was reported that the obtained straight chain alkanes have a high cetane number above 98 [12]. These processes are divided into two main types, which are hydrotreating of pure vegetable oil [4,5,13–16] and co-processing of vegetable oil with crude-oil-based refinery fractions [5,17,18]. Normally, hydroprocessing covers a large group of reactions such as hydrotreating (heteroatom removal e.g. sulfur and nitrogen as called hydrodesulfurization and hydrodenitrogenation respectively), hydrocracking, hydrogenation, isomerization and deoxygenation. Conventional hydroprocessing catalysts e.g. NiMo and CoMo have been used for many decades as hydrodesulfurization (HDS) catalysts for sulfur removal from petroleum products. Moreover, it has been found that conventional hydrotreating catalysts are suitable for deoxygenation of triglycerides. However, the deactivation of catalyst is a main problem because high oxygen content in triglyceride causes leaching of sulfur from the catalyst surface [19]. To conserve catalyst activity, sulfiding agents, such as H₂S [20] and dimethyl disulfide [17,21,22] are added in the reaction system but the amount of the sulfiding agent needs to be optimized for the desired activity of the catalyst and the targeted product quality. In addition, these compounds are very toxic and could easily poison many systems in humans, especially the nervous system. Therefore, non-sulfided catalysts, such as nitride

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catalysts, Pd and Pt, are of interest for the production of biofuels because they eliminate the need to add a sulfiding agent to a biomass-derived feedstock in order to prevent the deactivation of sulfided metal catalysts [23]. Previously, many metal catalysts such as Pd, Ni, Ru, Ir, Os, and Rh loaded on alumina or silica or activated carbon as well as some alloys and bimetallic catalysts have been studied in stearic acid deoxygenation. Among these catalysts, it was revealed that Pd/C shows the highest catalyst activity at 300 °C under 17 bar of helium in a semibatch reactor with a selectivity of 95% to heptadecane at complete conversion [24]. A wide range of oxygenated molecules were used as starting materials for hydroprocessing, such as fatty acids and their esters [25–28] or directly triglycerides [29,30]. Triglyceride of vegetable oil could be hydrogenated and broken down into various intermediates (i.e. monoglycerides, diglycerides and carboxylic acids) and the glycerol backbone of triglycerides is converted into propane. These intermediates are then converted into alkanes by three different pathways, decarboxylation, decarbonylation and hydrodeoxygenation, as shown in Eqs. (1)–(3), respectively.



As seen in Eqs. (1) and (2), the co-products from decarboxylation and decarbonylation are carbon dioxide (CO₂) and carbon monoxide (CO), respectively. Therefore, hydrocarbons resulting from decarboxylation and decarbonylation contain one carbon atom shorter than the total length of the fatty acid (C_(n-1)). The benefit of decarboxylation pathway is that no hydrogen is required to convert a carboxylic acid into a methyl group and CO₂ (as shown in Eq. (1)). For a decarbonylation pathway, the carboxylic group is reacted with hydrogen to produce a methyl group, CO, and water (as shown in Eq. (2)). On the other hand, hydrodeoxygenation (HDO) pathway yields generally 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. (3). It is noted that two additional reactions, water gas shift (Eq. (4)) and methanation (Eqs. (5)–(6)) are also needed to be considered due to the formation of CO₂ and CO [31].



The reaction performed in different atmospheric gases strongly affects the reaction performance. Comparison between the reactions performed under inert gas and hydrogen gas using Pd/C catalyst revealed that the reaction under reduced atmosphere was faster than under the case of inert atmosphere or lower concentration of H₂ [32]. In addition, the presence of hydrogen can reduce the aromatization reaction, which is undesirable because aromatics probably form coke, which leads to deactivation of catalyst [12]. Moreover, the aromatization reaction depends on reaction pressure and amount of unsaturated fatty acid [21]. The amount of aromatic compounds increased with an increase of unsaturated fatty acid, yet the opposite trend was observed when the reaction pressure was increased. When comparing the amount of aromatic compounds in deoxygenated

product between the use of palm oil, maracuja, and soybean oil as starting materials, Guzman et al. found that in case of palm oil, aromatic compounds could not be found even at low pressure (25 bar) but very high amount of aromatic compounds were observed at high pressure (90 bar) in the case of maracuja and soybean oil. This is because palm oil consists of polyunsaturated fatty acid, i.e. linoleic (C18:2) and linolenic (C18:3), about 12 wt.% while in maracuja and soybean oil are 71 and 64 wt.%, respectively. However, hydroprocessing of palm oil has been scarcely studied and limited to the use only crude palm oil as starting material [21].

For edible oil production, crude palm oil (CPO) is physically refined by removing impurities to the acceptable levels. Fig. 1 shows the refinery process of palm oil. Firstly, an impurity called gum (phospholipids, phosphotides) in CPO was removed by precipitation process. This process usually occurs at 90–130 °C and use phosphoric acid as a precipitant. At this state, degummed palm oil (DPO) is obtained. The DPO is then bleached to remove any undesirable impurities such as pigments and trace metals, giving a bleached palm oil (BPO). Next, the BPO is deodorized to eliminate free fatty acid content. This step gives refined, bleached, deodorized palm oil (RBDPO) and palm fatty acid distillate (PFAD) as a by-product. Finally, the RBDPO is fractionated to yield refined palm olein and refined palm stearin. It should be noted that PFAD was successfully employed as a starting material for the production of H₂ via steam reforming [33] and methyl ester in near-critical methanol condition [33].

Typically, uses of inedible oil and waste cooking oil are focused for biodiesel production to alleviate food vs. fuel debate. However, palm oil shows the advantage of the efficient planting, harvesting and collecting. In this study, the suitable operating conditions for the hydroprocessing of different palm oil feedstocks i.e. crude palm oil (CPO), degummed crude palm oil (DPO) and palm fatty acid distillate (PFAD) over commercial 5 wt.% Pd/C and synthesized NiMo/γ-Al₂O₃ were investigated.

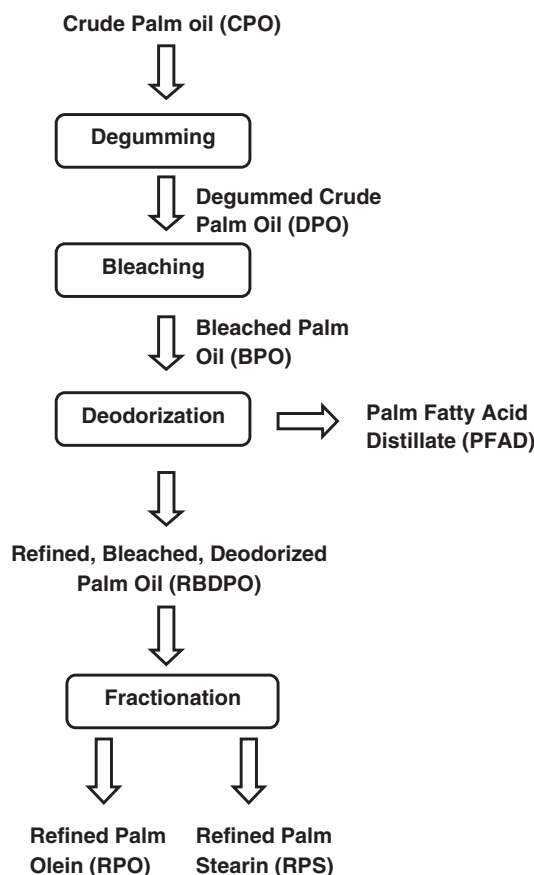


Fig. 1. Physical refining process of crude palm oil.

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