Hydroprocessing of kemiri sunan oil (*reutealis trisperma* *blanco* airy shaw) over NiMoCe/\(\gamma\)-Al,O, catalyst to produce green diesel

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Abstract. Kemiri Sunan is an alternative energy source that has a considerable amount of oil and does not compete for food source. Hydroprocessing of kemiri sunan oil has a big potential for renewable fuels. In this paper, NiMoCe/\(\gamma\)-AlO, catalyst is used for hydroprocessing of saturated kemiri sunan oil to produce renewable hydrocarbons. The catalyst was prepared by using wet impregnation method with variations of Ce 1\%, 5\% and 15\%. The characterization of catalyst was used by means of Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF). Hydroprocessing was performed using an autoclave batch reactor under operating conditions of 400\(^\circ\) C and 35 bar pressure for 5 hours. GC characterization showed that the product of renewable hydrocarbons is dominated by the C--C alkane chain.

Keywords: renewable oil, hydroprocessing, catalyst, Kemiri Sunan oil

1. Introduction

Fossil energy is the dominant primary energy supply in Indonesia. Fossil fuels hold responsible for 95.3\% of consumption, such as oil (46.1\%), coal (30.9\%) and natural gas (18.3\%) as the main fuels source [1]. Worldwide energy consumption reaches the highest ever presently, due to the growth of population and social development. One of the main energy consumers is the transportation sector which responsible for around one-fifth from the worldwide energy consumption. Due to the growth of population and more accessible transportation, the fuel requirement, particularly liquid fuels, will become higher in the years to come. Unfortunately, the progressive depletion of petroleum-based fuels created a global crisis of energy. The decreasing availability of petroleum resources takes place simultaneously with an emission increase due to greenhouse gases accountable for global warming. Therefore, methods that can offer greenhouse effect reduction are urgently required, which attracts a great attention to biofuels. Important experiments have been conducted to discover an alternative fuel to substitute gasoline and diesel. The preferable resolution is to discover an alternative fuel equals to the conventional one, namely, suitable with the available infrastructure, as well as sustainable, able to reduce CO emission and to reduce the environmental anthropogenic footprint. Renewable biomass sources can be transformed into an environmentally friendly fuels and a realogical option to generate fuel oil. Fuel oil obtained from biomass is clean as it contains insignificant amount of sulfur, nitrogen and ash content, generating fewer emissions of SO, NO\textsubscript{x} and soot compared to conventional fossil fuels. Zero net emission of CO\textsubscript{2} could be acquired since the CO released from biomass is able for photosynthetically recycling by plants [2].
Biofuels can be derived into four generations according to the nature of feedstock and corresponding production technology. Particularly, the previous biodiesel generation such as fatty acid methyl esters (FAME) is produced via transesterification mainly from vegetable oils and animal fats (complex mixture of triglycerides) by using a varied earth-abundant heterogeneous catalyst in the optimal process conditions. Even though the technology is perfect to be applied commercially, this biodiesel type contains a high amount of oxygenated compounds, suffering from considerable inherent, serious deficiency such as low heating value (or energy density), high viscosity, poor cold flow properties, oxidation instability and incompatibility toward fossil fuel due to its relatively high oxygen content and acidity, which render its practical application as transportation fuels. Therefore, great effort has been concentrated for the upgrading of biomass-derived bio-oils to a more stable and higher quality second-generation hydrocarbon-based biofuels via hydrodeoxygenation (HDO), decarboxylation or decarbonylation over specified catalysts. The produced biofuels obtained from deoxygenation methods comprises a high linear hydrocarbon amount and few oxygen, sulfur and nitrogen. The product carries remarkable physical and chemical characteristics (high cetane number, great cold flow properties, high heating value and excellent storage stability), which are fully compatible with fossil fuels, deemed promising for a large-scale application. Nevertheless, the commercial application of the second-generation biofuels is still under perfection, since some technical drawbacks are required to be resolved [3].

Vegetable oil hydro processing generates hydrocarbon product in the diesel boiling range, hence generally known as green diesel or renewable diesel. The products from hydroprocess method are alkanes in straight chains composed of 15–20 carbons, which shows a high similarity toward the current fossil diesel once it is isomerized. Hydroprocessing has been constructed to create alkanes with straight chain from fatty acid triglycerides of animal fat, and vegetable oils. Metal sulfide catalysts have been commonly applied for vegetable oil hydroprocessing, and other types of catalysts namely noble metal catalysts have also been reported. The transition metal catalysts require the sulfur-containing compounds (such as H.S) addition to maintain the active form of catalysts. One should note that sulfur might leach out from the catalysts over a long-term condition; therefore the quality of green diesel could be affected should the products be contained of sulfur residuals. On the contrary, the toxic and corrosive properties of H.S might cause a great danger for the environment, human health and instruments. Although noble metal catalysts were non-sulfided, these substances are not more expensive and not applicable for a large-scale process. Generally, the catalysts of transition metal are the sulfide form of NiMo, CoMo and NiW based catalysts containing P, B, and Cu. Nevertheless, lower emphasis has been placed on catalysts containing rare earth metal. Lanthanide or actinide metals incorporated with some metals (namely Ni, Co, Cu or Fe) were reflected as new type of supported catalysts precursors, which can be more active. Reports showed that cerium supports the activity of nickel/alumina catalysts in CO hydrogenation. Metallic catalysts supported by cerium are attractive since the properties of cerium can enhance their thermal stability, metallic dispersion, catalytic activity and decrease the carbon deposition. Thus, the ultimate purpose of this experiment is to promote the non-sulfide NiMo/γ-Al2O3 catalyst consists of Cerium (Ce) for the green diesel production. Hydroprocessing of kemiri sunan over NiMoCe/γ-Al2O3 catalyst [4] and hydrotreating of Kemiri Sunan oil over NiMo/γ-Al2O3 and CoMo/γ-Al2O3 catalysts have been reported [5–6]. By taking the biofuels competition problem with food sources into account, the option relies on the non-edible plant oil as the feedstock to generate green diesel for the transportation fuel. This work studies the hydroprocessing of Kemiri Sunan oil over NiMoCe/Al2O3 catalyst.

2. Experiments

2.1. Catalysts preparation and characterization

The NiMo catalyst (5wt.%Ni, 10wt.%Mo) was created using wet coimpregnation of aqueous solutions of (NH4)2MoO2, and Ni(NO3)2 with the aid of Al2O3 grain. Next, the NiMo/Al2O3 catalysts were dried overnight at 105 °C and calcined at 400 °C for 4 h. The NiMoOx/Al2O3 catalysts (where x indicates Ce content from 1 to 15wt.%) were produced by impregnation of NiMo/Al2O3 catalyst with a Ce(NO3)3 solution. Impregnated samples were dried overnight at 105 °C and calcined at 400 °C for 4 h. BET specific surface areas and pore size distributions were determined by N2 adsorption-desorption using Quantachrome Surface Area and Pore Distribution Analyzer instrument. The morphology images of samples were taken by Scanning Electron Microscope (SEM) equipped analyzer (OXFORD). X-Ray Diffraction (XRD Empyrian PANanalytical) was applied to specify the structural properties of the catalysts. Gas Chromatography with Flame Ionisation Detector (GC-FID) Agilent 6890 was used to measure quantitatively the hydrocarbon product. Helium was used as the carrier gas.
Table 1. Specific surface areas and pore size distributions of Catalysts

| Catalyst                        | Specific Surface Area (m²/g) | Total Pore Volume (Cc/g) | Pore Diameter (Å) | Decrease of Specific Surface Area (%) |
|---------------------------------|------------------------------|--------------------------|-------------------|---------------------------------------|
| γ-Al₂O₃                         | 306.44                       | 0.6846                   | 89.37             | 100                                   |
| NiMo/γ-Al₂O₃ sulfided           | 250.05                       | 0.6577                   | 105.2             | 18                                    |
| NiMoCe/γ-Al₂O₃, 1%              | 209.68                       | 0.5292                   | 100.9             | 31                                    |
| NiMoCe/γ-Al₂O₃, 5%              | 194.10                       | 0.5006                   | 103.2             | 36                                    |
| NiMoCe/γ-Al₂O₃, 15%             | 159.22                       | 0.3588                   | 90.15             | 48                                    |

![SEM Images](image-url)

Figure 1. SEM Images of (a) Al₂O₃, (b) NiMo/γ-Al₂O₃ sulfided, (c) NiMo/γ-Al₂O₃ Ce 1%, (d) NiMo/γ-Al₂O₃ Ce 5% and (e) NiMo/γ-Al₂O₃ 15%

2.2. Catalytic activity measurements
Kemiri Sunan oil was purchased from Ciawi Bandung. (NH₄)₆Mo₇O₂₄, Ni(NO₃)₂, Ce(NO₃)₃ and Al₂O₃ were purchased from Sigma-Aldrich. The experiments were conducted in an autoclave batch reactor completed with electrically heating system. The sulfided NiMo catalysts were activated in situ prior to the experiments with 5 % (v/v) dimethyl disulfide (DMDS) in gas oil at 400 °C and 3.5 MPa for 5 h. The catalytic hydroprocessing reaction conditions were fixed at 400 °C and 3.5 MPa. The liquid products were analyzed using a GC-FID.

3. Results and discussion

3.1. Catalyst characterization
Specific surface areas and pore size distributions of the support and catalysts are shown in Table 1. Al₂O₃ has considerably high surface area (306.44 m²/g) and large pore diameter (89.37 Å). This characteristic enabled the diffusion of bulky triglyceride molecules. Impregnation of Ni, Mo and Ce on
Al2O3 generated a decrease in the specific surface area. The impregnation of NiMoCe 15 % on Al2O3 can create more decrease in the specific surface area than the impregnation of NiMoCe 1 % and NiMoCe 5 % on Al2O3. The decrease of the particular surface area and total pore volume proposes the blocking of some pores in Al2O3 by the addition of Ni, Mo and Ce [7]. Figure 1 shows the metal distribution of Al, Ni, Mo, and Ce on the surface of the catalyst.

XRD analysis of catalysts is shown in figure 2. Typically, all catalysts have a uniform peak pattern for γ-Al2O3 at 2θ: 37º, 46º and 67º similar to figure 2a [8]. However, these peaks experience a diffraction decline in intensity. This occurrence showed that γ-Al2O3 support experienced a decline in specific surface area due to the metal impregnation of Ni, Mo and Ce [9]. In figure 2b, crystalline peak of MoO3 at around 2θ: 27º [9] was not observed, while in figure 2c, figure 2d and figure 2e the impregnation peak of Ce, which speculated as CeO2 in γ-Al2O3 support after calcination was expected. However, CeO2 peaks at 2θ: 28.6º, 33.1º, 47.5º and 56.4º [4] can be observed in figure 2d and figure 2e, while it was not obtained in figure 2c, indicating existence of CeO2 was with the impregnation of Ce 5 % and for Ce 15 % only.

Further measurement of elemental analysis by mean of X-Ray Fluorescence for γ-Al2O3 showed the γ-Al2O3 content in the support was 99.71 %, while in NiMo/γ-Al2O3 catalyst an amount of 4.90 % Ni and 9.94 % of Mo were observed. In the case of NiMoCe/γ-Al2O3 (1 %) catalyst, XRF analysis was 0.84 % Ce, for NiMoCe/γ-Al2O3 (5 %) was of 3.38 % Ce and for NiMoCe/γ-Al2O3 (15 %) catalyst was 15.6 % Ce.

3.2. GC analysis

Table 2 shows that the hydroprocessing of Kemiri Sunan oil using Ce 1% produce the highest conversion percentage of diesel fraction (C15-C18) about 57.79%. It indicates that Ce as a promotor can increase a catalytic activity in hydrogenation. This is because cerium oxide metal is well known as lewis base and most probably would donate its electron to NiO therefore enhancing the electron density to metal oxide and forming a complex structure with Ni. However, the low yield of hydroprocessing using Ce 1% is the amount of hydrocarbon C18 compared to yield of hydroprocessing using NiMo/γ-Al2O3 sulfided catalyst.
4. Conclusions
Renewable \( C_{15}-C_{18} \) alkanes as the main content of the diesel fraction have been successfully produced from hydroprocessing of Kemiri Sunan oil over NiMoCe/\( \gamma \)-AlO. 1 \% catalysts with conversion percentage of 57.79 \% at 400 °C, 3.5 MPa and 5h. NiMoCe/\( \gamma \)-AlO (1 \%) has the highest conversion percentage of Kemiri Sunan oil. The impregnation of Ce to NiMo/\( \gamma \)-AlO is proven to increase the conversion percentage of Kemiri Sunan oil. The NiMoCe/\( \gamma \)-AlO has the potential to replace the sulfided NiMo/\( \gamma \)-AlO in hydroprocessing of Kemiri Sunan oil and is expected to convert it to the renewable hydrocarbons.

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