Hydrodeoxygenation (HDO) of oleochemical waste oil into paraffins using iron molybdate (Fe-Mo-O) catalyst

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Abstract. The hydrodeoxygenation (HDO) of 1-dodecanol (C₁₂ fatty alcohol) in oleochemical waste oil was investigated in a continuous fixed-bed reactor using Fe-Mo-O catalyst between 200-300°C, 10-20 bars, and at fixed GHSV of 5121 hr⁻¹. The characterization of the product components was analyzed by GC-MS and further quantified by GC-FID to evaluate the effect of temperature and pressure on the HDO of 1-dodecanol to paraffin such as dodecane and lower carbon number of hydrocarbons. The reaction temperature is the most critical operating parameter that affects the performance of the HDO reaction. Conversion of 1-dodecanol increased up to 98.5% with increasing reaction temperature, while at 250°C, the dodecane selectivity was the highest. Two distinct HDO pathways were distinguished: dehydration-hydrogenation (Path 1) and dehydrogenation-decarbonylation/decarboxylation (Path 2). The high temperature and low pressure of the HDO promoted Path 2 route to produce paraffin with a lower carbon number from the reactant. The selectivity of dodecane was low, probably due to the cracking process that occurred at 300°C. The conversion of 1-dodecanol decreased with the increasing pressure, while dodecane's production rate follows the reverse trend of the conversion. High pressure of HDO promoted Path 1 route due to the higher selectivity of dodecane. In conclusion, the optimal temperature and pressure for HDO of oleochemical waste oil over Fe-Mo-O catalyst are 250°C and 20 bars, which gave the highest conversion towards dodecane and C₁₂ paraffin.

1. Introduction

Oleochemical waste oil comes from the residue of fatty alcohol production in the oleochemical industry. The reaction and chemical processes involved are transesterifications, hydrogenation, and fractionation and distillation. These processes produced products and by-products, commonly categorized into few groups such as fatty acids, fatty alcohols, fatty methyl esters, fatty amines, glycerol, and other oleochemicals derivatives. This oil is discharged to the wastewater treatment plant to ensure that effluent standards are satisfied by the regulation authorities. Nevertheless, the production of industrial fuels and chemicals from vegetable waste oils has resulted in a significant enhancement in oleochemical processes’ economics aside from decreases the environmental concerns of the production processes substantially [1]. Vegetable waste oil typically contains 50-60 wt.% of organic components, including acids, aldehydes, ketones, furans, phenolics, guaiacols, syringols, and sugars, 15-30 wt.% of moisture, and 20 wt.% of colloidal fractions [2]. Despite the fact, the high amount of oxygen in oleochemical waste oil induces its undesirable properties such as chemical instability due to unsaturated hydrocarbon chain and a strong re-polymerization tendency. It also generates high corrosiveness due to acidity, low
heating value, high viscosity, and water content, which are not conducive for direct usage as a fuel [2]. A catalytic hydrodeoxygenation (HDO), a process of removal of oxygen atoms and saturation of unsaturated bond, has been investigated in this paper to overcome these disadvantages of oleochemical waste oil.

HDO is a suitable technology for removing oxygen from bio-oils resulting in increasing volatility and thermal stability and reducing the viscosity [3]. A key role in developing a suitable catalyst for cost-effective HDO of bio-oils is the knowledge of the reaction pathway and mechanism. Nonetheless, understanding the HDO system of the whole bio-oils is highly challenging due to its different functionalities (phenolics, aldehydes, ketones, alcohols, organic acids, etc.) [3]. Therefore, this study was introduced to examine the fundamental understanding of the HDO of 1-dodecanol as a model oil to produce hydrocarbon-like biofuel. A systematic analysis was conducted under various process conditions over the Iron Molybdate catalyst (Fe-Mo-O), which allowed in determining the effect on reaction activity and its influence on the pathways.

2. Methodology

2.1. Experimental setup

All HDO tests were carried out in a continuous flow fixed-bed reactor connected to a hydrogen gas cylinder, a high-pressure liquid chromatography (HPLC) pump, and a condenser, as illustrated in Figure 1. The reactant and reactor temperature were controlled by its thermocouple and monitored by a PID temperature controller attached to a Solid-State Relay (SSR) work as a control center to send a signal to the heater. The pressure of hydrogen was controlled by a regulator controller connected to the gas cylinder. HPLC pump was used to control the flow rate of the reactant entering the reactor. The catalyst was loaded in a stainless-steel tubular reactor before heated from room temperature to the reaction temperature. The hydrogen gas was pressurized at the flow rate of 67 ml/min under experimental pressure. The temperature of the reactor was increased to the setpoint temperature. After the desired reaction temperature was reached, the reactant was continuously pumped at 0.1 ml/min into the reactor using an HPLC pump. The reactant was pre-heated to a temperature of 380°C before entering the reactor. The hydrogen gas and raw material liquid went parallel-down flow the reactor where the reaction occurs and passed through a vertical condenser. The samples were withdrawn every 15 minutes in the first hour until it reached steady-state conditions and 30 minutes for the next five hours intervals afterward. The HDO reactions were conducted at different temperatures varying from 250°C to 300°C, pressures from 10 bar to 20 bar, and a constant specified gas hourly space velocity (GHSV) of 5121 hr⁻¹.

2.2. Feed and product analysis

Components in liquid feed and product from HDO of oleochemical waste oil were identified using gas chromatography attached with mass spectroscopy (GC-MS). The products' occurrence was confirmed by comparing standard mass fragment data available with data acquisition software (Wiley and NIST standard libraries). The liquid feed and products were analyzed by gas chromatography (Shimadzu GC-17A) equipped with a flame ionization detector (FID). The capillary column consisted of a polar ZB-1 (30.0m × 0.25mm ID × 0.25 µm). The injection and detector temperatures were set to 200°C and 300°C, respectively. The column oven temperature was programmed from 50°C to 275°C and ramping at 8°C/min to obtain a well-resolved chromatogram. The column was kept at 50°C for 3 min, and the temperature was increased to 275°C and retained at this temperature for 5 minutes. The carrier gas was helium gas with a split ratio of 50:1.
3. Results and Discussion

3.1. Characterization of feed and product liquid

The components in oleochemical waste oil and liquid sample products produced from HDO were characterized using GCMS. As shown in Figure 2, the raw feed is mainly composed of hydrocarbon ranging from C8-C13. The identified components are 1) octanal, 2) nonane, 3) octanol, 4) decane, 5) octanoic acid methyl ester, 6) nonanol, 7) dodecane, 8) decanol, 9) dodecene, 10) dodecanal, 11) tridecane, 12) undecanol, 13) dodecanol, 14) nonene, 15) undecane, 16) decanal, 17) undecanoic acid, 18) dodecanoic acid. It was observed that the compounds remain the same after the HDO reaction. However, a few compounds were detected to form, which might be attributed to the different pathways of HDO reaction. The presence of these compounds could be due to the dehydrogenation-decarbonylation/ decarboxylation reaction, and the cracking process had occurred alongside the HDO reaction.
3.2. Catalytic screening

In the HDO of 1-dodecanol, dodecane was expected to be the main product based on the theoretical reaction of 1-dodecanol with hydrogen gas. Figure 3 showed the conversion of 1-dodecanol for HDO after 6h on stream. 1-dodecanol conversion reached the steady-state at 48.53% after 6h of reaction. The graph demonstrated an inconsistent trend of the conversion in the first two hours and began to exhibit stability after two hours. As shown in Figure 4, the HDO reaction formed a significant dodecane rate of 0.31 mmol/h and 54.5% yield. At 48.5% of 1-dodecanol conversion, Fe-Mo-O showed moderate activity, which gave selectivity=1.12 of dodecane after 6h reaction time, as presented in Figure 5. This result suggested that the molybdenum-based catalyst can be suitable to use as a HDO catalyst.

According to the HDO of 4-Methylphenol over unsupported MoP, MoS\textsubscript{2}, and MoO\textsubscript{3} catalysts [4], the MoO\textsubscript{3} catalyst in this study achieved a higher conversion, which resulted from the formation of anion vacancies that exposed the metal site of the catalyst. The anionic vacancies possess a net positive charge induced by the catalyst's strong acidic properties. This phenomenon increased the HDO of oxygenated compounds by dissociating hydrogen for hydrogenolysis or hydrogenation reactions. The distinctive characteristic of the active catalyst also depends on the oxidation state of the supported active metal. In a study of HDO of tricaprylin and caprylic acid over supported Ni-Mo oxide catalysts, Boda et al. [5] suggested that the active phase of a catalyst can be determined either oxide or metal. It also proposed that the oxide type catalyst produced mainly hydrocarbons with the identical carbon atom as the reactant. In contrast, the metal type catalyst produced hydrocarbons with shorter carbon number as the reactant. Therefore, in this case, the Fe-Mo-O catalyst used in this study is an oxide type catalyst since the same carbon number was mainly formed at the end of the reaction.
Figure 3. Conversion of 1-dodecanol after 6h on stream over Fe-Mo-O catalyst. Conditions: 200°C, 10 bar, 67 ml/min H₂ gas flow and GHSV of 5121 hr⁻¹.

Figure 4. Production rate of dodecane for HDO after 6h on stream over Fe-Mo-O catalyst. Conditions: 200°C, 10 bar, 67 ml/min H₂ gas flow and GHSV of 5121 hr⁻¹.

Figure 5. Selectivity of dodecane after 6h on stream over the Fe-Mo-O catalyst. Conditions: 200°C, 10 bars, 67 ml/min H₂ gas flow and GHSV of 5121 hr⁻¹.

3.3. HDO of fatty alcohol

3.3.1. Effect of reaction temperature. Figure 6 shows the conversion of 1-dodecanol in oleochemical waste oil after 6h on stream at different temperatures. The conversion of 1-dodecanol continuously reached the steady-state at 27.1%, 53.4%, 98.5% at 200°C, 250°C, and 300°C, respectively. The conversion of 1-dodecanol increased with the reaction temperature. Based on the results shown in Figure 7, the production rate of dodecane varies significantly with temperature. In the first 2 hours, the dodecane rate was inconsistent and started to reach the steady-state after 2 hours. The conversion showed an increase in the dodecane production rate from 200°C to 250°C and slightly decreased with the temperature increasing above 250°C. Assuming the steady-state was achieved after 6h on-stream time, the dodecane production rate was the highest at the temperature of 250°C with 3.13 mmol/h. The lowest rate of dodecane production was at 200°C, with 0.61 mmol/h. It can be concluded that the HDO process is favorable at 250°C. The reduction of dodecane production at 300°C might be due to the successive cracking reaction of the long-chain hydrocarbon and the pathway mechanism [6], which will further be discussed in Section 4.4. As declared in Sági et al. [7], the increasing temperature of 350°C and above became more significant for the cracking activity of the catalyst.
3.3.2. **Effect of reaction pressure.** The impact of different pressures on HDO reactions of oleochemical waste oil over the Fe-Mo-O catalyst was conducted at 10–20 bar, 250°C, H₂ gas flow of 67 ml/min, and GHSV of 5121 hr⁻¹. Figure 8 shows the conversion of 1-dodecanol in oleochemical waste oil after 6h on stream over Fe-Mo-O catalyst at different pressure. The hydrogen pressure exhibited a significant effect on the conversion of 1-dodecanol. At 250°C, the conversion is the highest at 10 bar (53.4%), followed by 15 bar (42.9%) and 20 bars (14.76%). It can be concluded that the conversion of 1-dodecanol decreased with increasing pressure, which indicates that higher pressures are unfavorable on the conversion of HDO reaction at 250°C. Figure 9 illustrated that the production rate of dodecane rises with increasing pressure. As the reaction pressures increased, dodecane production increased from 0.61 mmol/h to 3.54 mmol/h. It showed that higher pressures are favorable on the rate of dodecane production in the HDO process. The cracking of hydrocarbon chain products might be reduced with respect to the increasing hydrogen pressures, resulting in a positive reaction order. Therefore, this study suggested that the higher hydrogen pressure at 250°C would be the best condition for the production of C₁₂ paraffin.
3.4. Reaction mechanism

All product samples were measured at the same weight in the dilution step before analyzed by GC-FID. A few assumptions were made to determine the reaction pathway of the process to interpret the qualitative analysis of the product distribution of the HDO reaction. The first assumption suggested that the increment of the percentage of peak areas indicates the increase in the concentration of the components in weight percent. The second assumption suggested that the opposite statement from the first assumption, where the reduction of the percentage of peak areas indicates the decrease in the concentration (w.t.%) of the components. The analysis of the product distribution of reaction temperatures and pressures was illustrated in Figures 10 and 11.

According to [8], the production of alkanes leading to two different routes which are generally known as dehydrogenation-decarbonylation/ decarboxylation and dehydration-hydrogenation pathways. Figure 10 represents the concentration of odd-chained paraffin (C9 and C11) was the highest at the temperature of 300°C, while the lowest was at 250°C. Figure 11 revealed that the Fe-Mo-O catalyst yielded the odd-chained paraffin predominantly at 10 bars and produced the least at 20 bars. The formation of the odd-chained paraffin presented the loss in the liquid mass available, which is highly undesirable to be used as biofuel. These results indicate the presence of C11 paraffin (undecane) and other lower molecule paraffin in the liquid product, proven that the dehydrogenation-decarbonylation/ decarboxylation pathway has occurred during the HDO process. This pathway also can be explained by the existence of aldehyde (decanal) and carboxylic acid (undecanoic acid, dodecanoic acid), as discussed in Section 3.1.

Figure 12 showed the proposed reaction scheme of the HDO and cracking reaction for the 1-dodecanol. In the reaction sequence, the aldehyde and carboxylic acid appear as an intermediates product before forming the hydrocarbon with a lower carbon number as the reactant. As proposed in the figure, the dehydrogenation-decarbonylation/ decarboxylation pathway was expected to produce odd-chained alkanes as a product while the dehydration-hydrogenation path was expected to produce products with even-chained alkanes [10][11]. Typically, cracking activity was accounted to be into two conditions; thermal cracking and catalytic cracking (pyrolysis) of biomass, which is a simple process to produce bio-oils with a number of fuel-like products [13]. However, this reaction was highly unselective due to the production of undesirable compounds, which mostly oxygenates. Thermal cracking has occurred as
a result of high temperature supplied throughout the reaction, whereas catalytic cracking was believed to be dependent on the strength of the acid sites, type of active metal, porous structure of support, and reaction conditions [14]. Dodecane decomposed to lower molecular weight hydrocarbons such as n-undecane and n-nonane, besides n-decane literally can be formed as a result of n-undecane cracking. However, despite the presence of odd-chained alkanes, the concentration of even-chained alkane was significantly higher than odd-chained alkane in both effects of reaction temperature and pressure. Consequently, the HDO of 1-dodecanol over Fe-Mo-O catalyst mainly proceeded via a dehydration-hydrogenation pathway at the optimal temperature of 250°C and pressure of 20 bar.

Figure 10. C9-12 paraffin distribution in oleochemical waste oil after 6h over Fe-Mo-O catalyst at different temperatures. Conditions: 200–300°C, 10 bar, 67 ml/min H2 gas flow and GHSV of 5121 hr⁻¹

Figure 11. C9-12 paraffin distribution in oleochemical waste oil after 6h over Fe-Mo-O catalyst at different pressures. Conditions: 10–20 bar, 250°C, 67 ml/min H2 gas flow and GHSV of 5121 hr⁻¹

Figure 12. Proposed scheme of the reaction mechanism for HDO of 1-dodecanol improved from that reported in the literatures [3] and [4].
4. Conclusion

The dehydration-hydrogenation route (Path 1) becomes dominant over oxide type catalyst, promoting the formation of dodecane as a primary product, which has the same carbon number as the reactant. The second route follows the dehydrogenation-decarbonylation/ decarboxylation pathway (Path 2), resulting in the C11 paraffin with a lower carbon number than the reactant. High conversion of 1-dodecanol was observed at the highest temperature of 300°C. However, the dodecane production rate decreased at 300°C, which favors the dehydrogenation-decarbonylation/ decarboxylation pathway. A higher HDO temperature promotes cracking reactions and restraints the hydration-hydrogenation path, yielding higher hydrocarbons concentrations with lower molecular weight. In contrast, the HDO of 1-dodecanol resulted in the highest production rate of dodecane at a temperature of 250°C.

High pressure would favor the hydration-hydrogenation route in HDO reaction since it produced the highest rate of dodecane. It restraints the dehydrogenation-decarbonylation/ decarboxylation route due to the high ratio of adsorbed hydrogen to adsorbed 1-dodecanol molecules. However, the conversion of 1-dodecanol followed the reverse trend where the conversion decreased with the increasing pressure. Therefore, the optimal temperature and pressure for HDO of oleochemical waste oil over the Fe-Mo-O catalyst are 250°C and 20 bar, respectively, which gives 14.76% of 1-dodecanol conversion and the highest dodecane production rate with 3.54 mmol/ h without a sign of excessive cracking of dodecane.

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**Acknowledgment**
First and foremost, praise and thanks to the Almighty for His showers of blessings throughout my work to complete the project.