Hydrodeoxygenation of Linoleic Acid on Ni-Mo Catalyst

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Abstract

Bio-fuels have become an important alternative energy for many aspects due to increasing petroleum based fuel prices. One of the bio-fuels arises from the production of diesel-like-hydrocarbons from vegetable oils. In this contribution, the deoxygenation of linoleic acid was investigated in a continuous packed-bed reactor over a NiMo/Al_2O_3 catalyst under a high pressure of 3.5 MPa and a temperature range of 573-673 K. This study aimed to produce hydrocarbons in the diesel range from unsaturated fatty acid called linoleic acid as well as to elucidate the effects of temperature and hydrogen partial pressure on the product distributions. Products were mainly normal-alkanes, *n*-octadecane (C18) and *n*-heptadecane (C17). The distribution of desired-products (>C13 hydrocarbons) strongly depended on both the reaction temperature and the partial pressure of hydrogen. Under the studied reaction conditions, the ratio of C18 to C17 hydrocarbon was always greater than one. Surprisingly, as the partial pressure of hydrogen decreases, the C18/C17 ratio decreases to less than one. From this result, it was concluded that the oxygen atoms were mainly removed from fatty acid by hydrogenation reaction. Furthermore, at a high reaction temperature the yield of desired products decreased while the yield of cracking products increased.

Keywords: deoxygenation, hydrogenation, linoleic acid, NiMo catalyst

1. Introduction

In the past decade, the price of crude oil has continuously increased due to the limitation of oil production from refineries and high petroleum-fuel consumption. With strict environmental legislation, renewable energy has become an important energy source for many aspects, especially transportation section. Biofuel, nowadays, is a favorable alternative energy because it has less negative environmental impact on carbon dioxide emission and lower particulate matter [1,2].

Bio-diesel, produced from transesterification of vegetable oils, was recently introduced and used in diesel engines. However, biodiesel still has some adverse impacts on diesel engines due to oxygen atoms in the molecule. That can affect some physical properties e.g. high viscosity [3-5]. At the moment, bio-diesel needs to be mixed with a conventional diesel before being using in a modern diesel engine. However, the blending ratio between biodiesel and conventional diesel is limited. Therefore, the catalytic upgrading of vegetable oils to produce hydrocarbons in the diesel range becomes an alternative route. It is expected that its properties are similar to those of a conventional diesel so it can be used directly in a diesel engine [6-8].

Generally, the production of diesel-like hydrocarbons from vegetable oils can be achieved by various reactions such as pyrolysis or thermal cracking, catalytic cracking and deoxygenation. Both thermal and catalytic cracking yield high volume of hydrocarbons, but they cannot provide high yield of diesel range while deoxygenation can preserve hydrocarbons in the diesel range [9]. Dupain et al. [10] investigated the catalytic cracking of rapeseed vegetable oil under realistic FCC conditions. Hydrocarbon products were in both gasoline- and diesel-range. In addition, they obtained a large amount of aromatics in the gasoline fraction.

Triglyceride or fatty acids can be deoxygenated through decarbonylation, decarboxylation and hydrogenation [11]. Maki-Arvela et al. [12] and Kubičková et al. [13] studied the deoxygenation of stearic acid, ethyl stearate, and tristearine over a Pd/C catalyst in a semi-batch reactor under helium and low hydrogen partial pressure. They found that the main product obtained from those reactants was *n*-heptadecane, which mainly occurred via decarboxylation of stearic acid and via decarbonylation of its derivatives.

In this paper, deoxygenation of unsaturated fatty acid was investigated on a commercial NiMo/γ-Al_2O_3 catalyst in a flow reactor under a flow of hydrogen. The aims of this study are to evaluate the catalyst performance and products obtained from deoxygenation reaction.

2. Experimental

2.1 Chemicals

Linoleic acid, mainly found in soybean and sunflower oils, was used as an unsaturated fatty acid feed. Linoleic acid (>99%) was purchased from Acros. Dodecane (>99% from Acros) was used as a solvent. A model compound for the hydrodeoxygenation was a 5-10%wt. of linoleic acid in dodecane, which was used as a feed. A commercial NiMo/γ-Al_2O_3 in a reduced form was used as catalyst.

2.2 Catalytic Testing

The apparatus used for deoxygenation is illustrated schematically in Fig. 1.

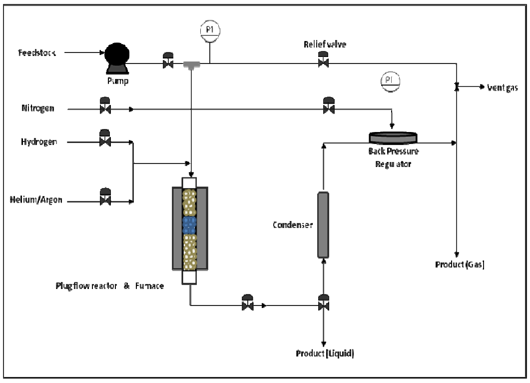


Fig. 1 A schematic experimental setup for deoxygenation.

The reaction was performed in a continuous fixed bed stainless steel ½" I.D. reactor equipped with an electric heating furnace and a thermocouple was placed in the center of the catalyst bed. A liquid condenser was placed on the outlet of the reactor. The pressure inside the reactor was controlled by a back pressure regulator with a flow of N_2. In each experiment, a specified amount of catalyst was placed in the center of the reactor. To ensure an effective preheating and minimize heat losses, the top and the bottom of the catalyst bed were filled with glass beads of 1 mm in a diameter. Before starting the feed, the catalyst was reduced in situ at 633 K for 4 h in a H_2 flow. The catalytic activity was evaluated at a constant total pressure of 3.5 MPa at a temperature range of 573-653 K under the H_2 flow and at W/F ratio of 0.7 h. To elucidate the influence of hydrogen partial pressure on the deoxygenation, different ratios of hydrogen to helium were applied. In all runs, reactant and product mixtures were analyzed using a HP6890 and Fisons 8000 series gas chromatographs equipped with a flame ionization detector.

3. Results and Discussions

3.1 Catalyst Deactivation

The deoxygenation of linoleic acid was evaluated on a NiMo catalyst at a constant pressure of 3.5 MPa and a temperature of 613 K under a H_2 flow for 13 h. This study aims to produce diesel-like-hydrocarbon so only desired products, which contain more than 12 carbon atoms in their molecule, were reported. The profile of total amount of desired products was shown in Fig. 2.

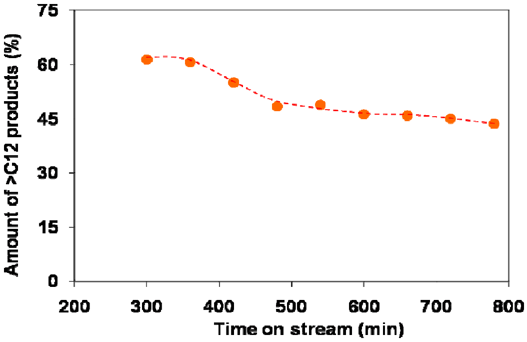
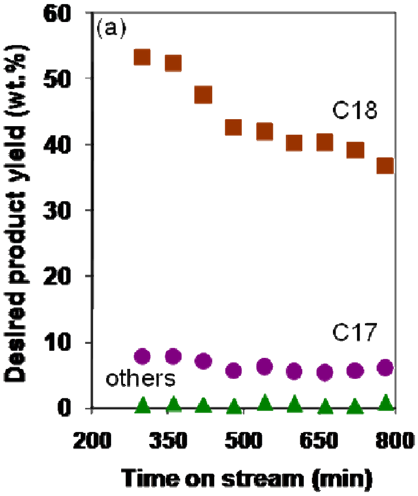


Fig. 2 Total amount of desired products obtained from the deoxygenation of linoleic acid as a function of time on stream.

As seen from fig. 2, the amount of desired products decreases from 60.7% to 43.6% after 13 h. This indicates the deactivation of the catalyst.



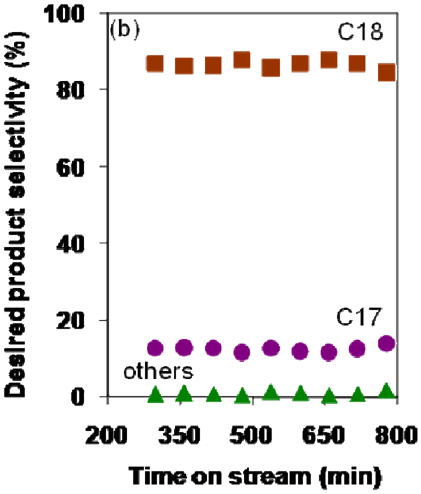


Fig. 3 (a) Desired products distribution and (b) desired products selectivity obtained from the hydrodeoxygenation of linoleic acid as a function of time on stream.

For clarification, the desired products are classified into C18, C17 and C13-C16 products. The distribution of desired products and their selectivities obtained from the deoxygenation of linoleic acid are shown in Fig. 3(a) and (b). In this study, the terms of product yield and product selectivity are defined as the following equations:

$$Yield\ A,\% = \%wt.of\ \ product\ \ A\ \ obtained$$

$$Selectivity\ A,\% = \frac{\%wt.of\ \ product\ A\ \ obtained}{\%wt.of\ \ total\ \ products\ obtained} \times 100\%$$

The main products are *n*-paraffins, which are *n*-octadecane (C18) and n-heptadecane (C17). The *n*-octadecane corresponded to hydrogenation of linoleic acid resulting from high H_2/fatty acid ratio [10]. In contrast, *n*-heptadecane corresponded to (hydro) decarbonylation/ decarboxylation of linoleic acid resulting from the formation of carbon monoxide/ carbon dioxide. These main reactions are shown below:

$$2C_{18}H_{32}O_2 + 5H_2 \longrightarrow 2C_{17}H_{36}+CO_2+CO+H_2O$$

$$C_{18}H_{32}O_2 + 2H_2 \longrightarrow C_{18}H_{38} + 2H_2O$$

3.2 Effect of the reaction temperature

The linoleic acid reaction was performed under different reaction temperatures. The variation of effluent is presented in Fig. 4. At low temperature the total amount of desired product increases as the reaction temperature increases. Beyond a certain temperature (623 K), the cracking reaction is dominant and leads to decrease of desired products.

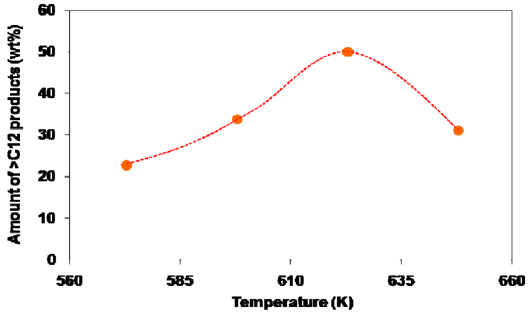


Fig. 4 The total desired products yield as a function of the reaction temperature.

Figs. 5(a) and 5(b) represent the yields and selectivities of C18, C17 and other desired products, respectively. As discussed above, the main reactions for the deoxygenation of fatty acid are hydrogenation and decarbonylation/decarboxylation. From the results, under the studied reaction conditions, hydrogenation is dominant. Therefore, the C18 hydrocarbon is found with higher selectivity than the C17 hydrocarbon. However, at high temperature, the selectivity of C18 is reduced resulting from thermodynamics. Whereas the hydrogenation reaction is an exothermic reaction, the decarbonylation/decarboxyla-tion is an endothermic reaction. So, the reaction temperature highly affects the product distribution.

3.3 Effect of hydrogen partial pressure

To elucidate the effect of hydrogen concentration, the deoxygenation of linoleic acid under different hydrogen partial pressures was performed.

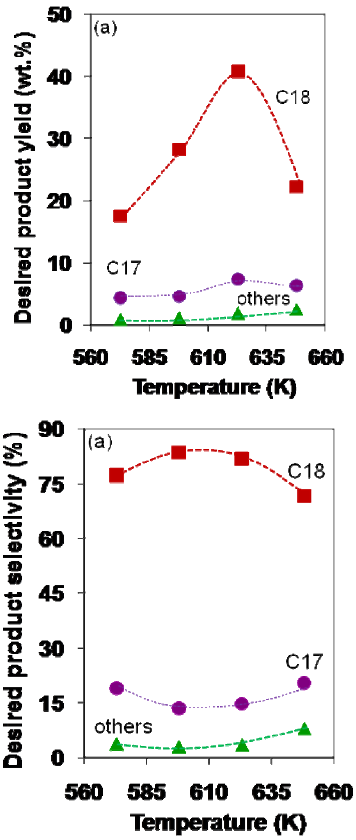


Fig. 5 (a) Desired products distribution and (b) Desired products selectivity as a function of the reaction temperature.

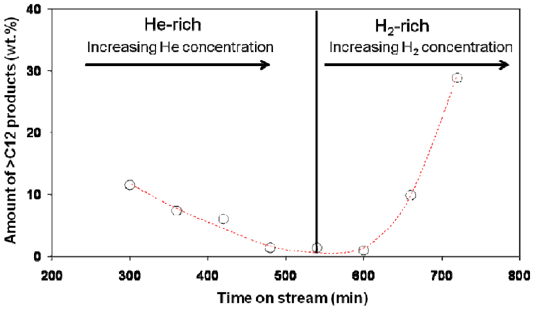


Fig. 6 The yield of total desired products as a function of time on stream under different environments.

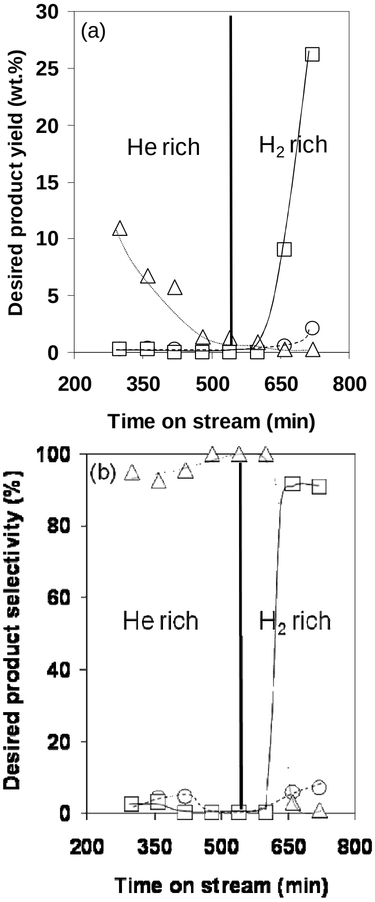


Fig. 7 (a) Desired product distribution and (b) desired product selectivity as a function of time on stream under different H_2/He ratio. Square: C18; Circle: C17; Triangle: other desired products)

After the reduction of catalyst, the reactor was pressurized to 3.5 MPa by increasing the H_2 flow, and then switched to a He flow. After feeding the linoleic acid for 9 h, H_2 was allowed to flow until the experiment was terminated. The amount of desired products is presented in Fig. 6. Surprisingly, as the concentration of He increases, the catalyst activity decreases; however, the catalyst activity increases as the concentration of H_2 increases.

Figs. 7(a) and 7(b) depict the distribution and the selectivity of desired products as a function of time on stream. An interesting change in the desired product distribution was observed under the He-rich environment compared to that under the H_2-rich environment. The amount of C17 and C18 products was hardly found under a helium flow. Opposite to a He-rich environment, the amount of both products formed was high under a H_2-rich environment. It is clear that under these reaction conditions linoleic acid was converted into C18 product via the hydrogenation, whereas C17 product was formed via decarbonylation/decarboxylation. Furthermore, other desired products were diminished under a high hydrogen partial pressure.

4. Conclusion

The main conclusions of this work can be summarized as follows:

The main products obtained from the catalytic (hydro)deoxygenation of linoleic acid over a commercial NiMo catalyst are linear long chain hydrocarbons in a diesel range.

Hydrocarbon products for the (hydro)deoxygenation of linoleic acid are mainly *n*-octadecane (C18) and *n*-heptadecane (C17).

Hydrogenation reaction plays an important role for the deoxygenation of fatty acids.

The product distribution depends on both the reaction temperature and the hydrogen partial pressure.

5. Acknowledgement

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