



## Production of renewable diesel by hydrotreatment of soybean oil: Effect of reaction parameters



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### HIGHLIGHTS

- Hydrotreatment of oil in batch and continuous reactors, to produce green diesel.
- Finding the optimum operating conditions for using the Ni and CoMoS<sub>x</sub> catalysts.
- Comparisons of reaction and product, between batch and continuous systems.
- The Ni catalyst showed higher activity in decarboxylation/decarbonylation.
- The CoMoS<sub>x</sub> catalyst showed higher activity in hydrodeoxygenation.

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### ABSTRACT

The effects of varying reaction parameters on the hydrotreatment of soybean oil using Ni and CoMoS<sub>x</sub> catalysts were investigated. The reactions were carried out in both batch and continuous reactors, at reaction temperatures of 300–440 °C, and hydrogen pressures of 2.5–15.0 MPa. The effects on hydrotreating conversion, gasoline/jet/diesel selectivity, and the degree of oxygen removal were investigated, to find optimum hydrotreatment conditions using both types of catalysts. Analyses of liquid composition, using comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC-TOF-MS) and GC-flame ionization detection (FID), revealed that decarboxylation, decarbonylation, and hydrodeoxygenation reactions occurred competitively, and that each reaction pathway had different optimal conditions, as expected from the thermodynamic characteristics. The differences in the hydrotreatment reaction, liquid product compositions, and dominant reaction pathways between the batch and continuous reactions are also discussed.

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## 1. Introduction

The development of fuel production techniques from renewable resources is in great demand, as petroleum reserves are further depleted, and concerns about global climate change increase. One current industrial process is the transesterification of natural triglycerides present in vegetable oils with methanol to produce fatty acid methyl esters (FAMES), which can partially replace fossil-derived diesel fuels. However, production of FAMES by transesterification requires the addition of alkaline or acidic catalysts, producing impurities in the final product, such as residual

catalysts, free fatty acids, and unreacted or partially-reacted triglycerides. These can damage petroleum diesel engines, through clogging fuel filters, depositing on fuel pumps, corroding metal parts, and causing swelling of rubber components [1,2]. In addition, the energy density and oxidation stability of FAMES are significantly poorer than those of fossil-derived diesel, because of the presence of oxygen atoms in the FAME molecules [3–5].

In recent years, hydrocarbons produced by heterogeneous catalytic hydrotreatment of natural fats or oils have received considerable attention as a promising alternative to FAME-based biodiesel, because of their similar fuel properties to their petroleum counterpart; paraffin-rich hydrocarbons can be produced without metallic or acidic compounds, using the existing infrastructure of petroleum refineries [6,7]. However, liquid hydrocarbons obtained from catalytic deoxygenation of triglycerides can exhibit significant variations in chemical composition, depending on the reaction conditions and catalysts employed. To eliminate this inconsistency,

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and achieve better product control, we must develop a comprehensive understanding of the reaction mechanism, and the factors that determine the resulting liquid products.

As discussed in previous studies on the production of hydrocarbons from vegetable oils, fatty acids are formed in the initial stage of hydrotreatment, and oxygen atoms in fatty acids are removed by hydrotreating catalysts via three different reaction pathways: decarbonylation, decarboxylation, and hydrodeoxygenation [5]. Deoxygenation of fatty acids via decarbonylation or decarboxylation produces linear hydrocarbons that are shorter by one carbon atom, by releasing CO and water, or CO<sub>2</sub>, respectively. These two reactions are mildly endothermic. Decarbonylation requires one hydrogen molecule, while decarboxylation does not consume hydrogen. Oxygen atoms in fatty acids can also be removed by forming two water molecules via exothermic hydrodeoxygenation, which requires three moles of hydrogen per one fatty acid molecule. In addition to these liquid phase reactions, various gas phase reactions can also occur, e.g. methanation, and the water–gas shift reaction with CO, CO<sub>2</sub>, and hydrogen. Since gas- and liquid-phase reactions have different thermodynamic characteristics involving hydrogen as a reactant, as shown in Table 1 [8], the reaction temperature and hydrogen pressure can significantly affect the progression of the deoxygenation reaction with a given catalyst.

Typical catalysts for the hydrotreating of triglycerides can be categorized into two types: (1) noble metals and their alloyed catalysts, including Pd, Ni, Pt, and PtSn [9–14], as active materials, and (2) molybdenum-based sulfide catalysts, such as NiMoS<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and CoMoS<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> [15,16]. In our previous work, the effects of various heterogeneous catalysts on the synthesis of renewable hydrocarbons from soybean oil were investigated [17]. The metallic catalysts showed dominant decarboxylation and/or decarbonylation activity, whereas hydrodeoxygenation occurred competitively, using molybdenum-sulfide catalysts.

Once hydrotreatment liquid-phase reactions have occurred, subsequent reactions of hydrocarbon products can lead to the formation of other types of hydrocarbons, including olefins, isoparaffins, cycloparaffins, and aromatics. Since the fuel properties, such as the cloud point and cetane number, depend heavily on hydrocarbon composition [18], understanding and control of dehydrogenation, isomerization, cyclization, and aromatization during the catalytic deoxygenation of triglycerides is crucial.

In the present study, using one metallic and one molybdenum-sulfide catalyst, we investigated the effects of reaction temperature and initial hydrogen pressure as the predominant operating parameters, in the synthesis of renewable hydrocarbons from soybean oil. The reaction was conducted using both batch and continuous reactors, at reaction temperatures of 300–440 °C, and hydrogen pressures of 2.5–15 MPa. We varied these parameters widely, instead of using small processing windows, in order to fully comprehend deoxygenation using the two catalysts; not only optimizing these parameters, but also discovering their functional lim-

its. Hydrotreatment conversion, diesel selectivity, and changes in oxygen and hydrogen contents of the liquid products were examined, using simulated gas chromatography (GC) and elemental analysis. The effects of varying the reaction parameters on the deoxygenation pathways were investigated, via analysis of the liquid hydrocarbons by comprehensive two-dimensional GC time-of-flight mass spectrometry (GC × GC–TOFMS), and GC-flame ionization detection (FID); and the gaseous product composition was determined using a refined gas analyzer (RGA)–GC.

## 2. Experimental

### 2.1. Hydrotreatment in a batch reactor

Renewable hydrocarbons were produced by hydrotreatment of commercially available soybean oil (CJ Cheiljedang Co., 99.9% purity, Seoul, Korea), in a custom-built autoclave (volume 109 mL). 57.6 wt% Ni/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> was purchased from Alfa-Aesar (MA, USA), and CoMo/Al<sub>2</sub>O<sub>3</sub> with 2.8 wt% of Co and 7.6 wt% of Mo was purchased from Strem Chemical (MA, USA). H<sub>2</sub> and N<sub>2</sub> used in the hydrotreatment reaction were purchased from Shinyang Sanso Co. (Seoul, Korea) with 99.99% purity. The metal contents of each catalyst were analyzed, using inductively coupled plasma-atomic emission spectroscopy. 2.5 g of the Ni catalyst was reduced, by subjecting it to 2 MPa of H<sub>2</sub> at 400 °C for 1 h, and 2.5 g of the CoMo catalyst was sulfurized under 2.9 MPa of 15% H<sub>2</sub>S/Ar gas mixture at 400 °C for 1 h, prior to the deoxygenation reaction. The reason we adopted different activation procedures for the Ni and CoMo catalysts was that the metallic and Mo-based sulfide catalysts have different catalytic active sites. After the preparation of metallic catalysts, such as Ni/Al<sub>2</sub>O<sub>3</sub>, the active material usually exists as a form of metal oxide (NiO<sub>x</sub>). For the use of the Ni catalyst, the metal oxide should be reduced to metallic phase (Ni) using hydrogen prior to the reaction, so that the reaction takes place on the metal surface. On the other hand, the Mo-based catalysts, such as CoMo/Al<sub>2</sub>O<sub>3</sub>, have a slab-like structure. After the sulfurization of the CoMo catalyst with H<sub>2</sub>S, sulfur can enter into the sites between the CoMo slabs, and modify its electronic properties, such that the catalyst can exhibit high activity for the hydrodeoxygenation or hydrodesulfurization [19]. For the Ni catalyst, however, sulfur is known to decrease the catalytic activity, by occupying the active site on the metallic surface, due to its strong adsorption strength on the transition metal surface [20].

After catalyst activation, the reactor was cooled to room temperature, and depressurized to atmospheric pressure. 28.1 g of soybean oil was then introduced into the reactor, which contained pre-activated catalyst in a N<sub>2</sub> atmosphere, followed by purging of the reactor with H<sub>2</sub>. The reactor was pressurized with H<sub>2</sub> at the desired pressure, and was heated to the desired temperature for a duration of 1 h. A schematic of the batch reactor is shown in Fig. S1, and detailed specifications of the feed material and catalysts have been described in a previous report [17].

#### 2.1.1. Hydrotreatment in a continuous reactor

Hydrotreating of soybean oil was also performed in a fixed bed reactor (150 mL), containing 20.0 g of catalyst. The Ni and CoMo catalysts were activated at 400 °C under a flow of H<sub>2</sub> and a 15% H<sub>2</sub>S/Ar gas mixture, respectively, for 2 h prior to the deoxygenation reaction. After catalyst activation, the reactor was cooled to room temperature, pressurized with H<sub>2</sub> to the desired pressure, using a back-pressure regulator located at the outlet of the reactor, and then heated to the desired temperature. After reaching the desired reaction conditions, soybean oil and hydrogen were introduced into the reactor at a liquid hourly space velocity (LHSV) of 0.5 h<sup>-1</sup>, at a fixed H<sub>2</sub>/oil molar ratio of either 30.1 or 46.3. Each

**Table 1**  
Plausible reactions during the hydrotreatment of triglycerides [8].

	Reaction	Equation	ΔH <sub>573</sub> (kJ/mol)
Liquid phase reactions	Decarboxylation	R-COOH → R-H + CO <sub>2</sub> (g)	9.2
	Decarbonylation	R-COOH + H <sub>2</sub> → R-H + CO (g) + H <sub>2</sub> O (g)	48.1
	Hydrodeoxygenation	R-COOH + 3H <sub>2</sub> → R-CH <sub>3</sub> + 2H <sub>2</sub> O (g)	-115.0
Gas phase reactions	Methanation	CO + 3H <sub>2</sub> ↔ CH <sub>4</sub> + H <sub>2</sub> O	-216.4
		CO <sub>2</sub> + 4H <sub>2</sub> ↔ CH <sub>4</sub> + 2H <sub>2</sub> O	-177.2
	Water gas shift	CO + H <sub>2</sub> O ↔ H <sub>2</sub> + CO <sub>2</sub>	-39.2

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