

# Hydroconversion of Triglycerides to Hydrocarbons Over Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst Under Low Hydrogen Pressure

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**Abstract** The hydroconversion of coconut oil to saturated hydrocarbons under low hydrogen pressure was demonstrated, using a sulfur-free Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst prepared by the co-impregnation of Ni and Mo species. The Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst exhibited remarkably high conversion of coconut oil as well as high selectivity for the generation of the hydrocarbon fraction associated with jet fuel. Examining variations in product distributions with contact time showed that hydrocarbons were produced primarily through the hydrogenolysis of triglycerides followed by hydrodecarboxylation of fatty acids. Increases in the contact time led to improvements in the proportion of hydrocarbons via the hydrodeoxygenation of fatty acids.

**Keywords** Coconut oil · Hydrodecarboxylation · Hydrodeoxygenation · Mo–Ni catalyst · Low hydrogen pressure

## 1 Introduction

The synthesis of renewable fuels has received considerable attention as a means of mitigating the environmental problems resulting from the current extensive use of fossil fuels [1]. In particular, there has been significant interest in

the use of two main biofuels: bioethanol and biodiesel. Bioethanol is commonly produced from edible biomass such as wheat, corn, and sugar cane, while biodiesel can be obtained from non-edible raw materials, including vegetable oils and fats, which consist primarily of triglycerides. Biodiesel, however, exhibits a 9–13 % lower heat capacity compared to conventional diesel fuels on a mass basis, due to the presence of excessive amounts of oxygen in the chemical components of the biodiesel [2]. For this reason, the conversion of triglycerides to hydrocarbons is seen as an alternative approach to producing biodiesel and an effective means of obtaining biofuels with suitably high heat capacity.

The catalytic cracking of triglycerides to allow the direct production of hydrocarbons has been investigated using both solid acid and base catalysts, such as ZSM-5 and MgO/SiO<sub>2</sub> [3–7]. Unfortunately, this process is generally unselective and tends to form a wide variety of undesirable products, including light hydrocarbons. In addition, subsequent hydrotreatment of the products is essential when producing saturated hydrocarbons for use as specialized fuels such as gasoline and jet fuel. Investigations of hydroprocessing of triglycerides over supported metal catalysts have revealed that saturated hydrocarbons with carbon numbers similar to those of the fatty acid portions of the original triglycerides are selectively formed through hydrodecarboxylation or hydrodeoxygenation [8–18]. In the former process, the oxygen atoms of triglycerides are removed as CO<sub>2</sub> to yield hydrocarbons with one carbon less than the parent fatty acid structure. In the latter process, hydrocarbons with the same carbon number as that of the fatty acid portion are formed as the result of the removal of the oxygen atoms as H<sub>2</sub>O. Which of the two reaction pathways dominates strongly depends on reaction conditions; in the hydroprocessing of vegetable oils, lower

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hydrogen pressure and higher temperatures and feeding rates favor hydrodecarboxylation over the hydrodeoxygenation [16, 19–21].

In the hydroconversion of triglycerides to hydrocarbons, conventional hydroprocessing catalysts such as sulfided Co–Mo, Ni–Mo and Ni–W exhibit high conversions and tend to generate hydrocarbons in the range of diesel and gasoline as a result of their high hydrogenation activities [11, 12, 22, 23]. The sulfided Ni–Mo catalysts in particular demonstrate high activities for the hydroconversion of vegetable oils to hydrocarbons as compared to either sulfided Co–Mo catalysts or monometallic catalysts such as Ni/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> [8, 16, 24]. The addition of sulfating agents such as CS<sub>2</sub> and dimethyl disulfide, however, is necessary to retain the activity of sulfided catalysts over long reaction periods, which leads to the undesirable contamination of the final products with sulfur compounds [25]. Furthermore, the hydroprocessing of triglycerides is generally performed under high hydrogen pressures (4–20 MPa). To allow for the more efficient utilization of hydrogen during the reaction process, as well as the production of sulfur-free biofuels, the hydroconversion of triglycerides to hydrocarbon should ideally be performed over sulfur-free catalysts which exhibit high hydrogenation activities under low hydrogen pressures.

Mesoporous materials such as MCM-41 and SBA-15 are well known as support materials capable of improving catalytic activities due to their high surface areas which allow very wide dispersions of the active phases of supported metal species [26]. In hydrodesulfurization processes, mesoporous alumina supports have been shown to assist in improving catalytic activity compared to that obtained with traditional alumina supports [27, 28]. The application of mesoporous alumina as a support has also improved the catalytic activity of a sulfided Co–Mo catalyst for the deoxygenation of triglycerides compared to the performance obtained with commercial alumina supports [20]. Nano-sized alumina has also been employed to produce highly dispersed metal species which exhibit improved catalytic activities and product distributions compared to conventional alumina during the isomerization and hydrocracking of paraffins [29, 30]. Based on the above, support materials that allow increased dispersion of metal species may be effective in the synthesis of catalysts with high hydrogenation activities for the hydroconversion of triglycerides to hydrocarbons.

In this study we investigated the catalytic activity of sulfur-free Ni–Mo supported on nano-sized Al<sub>2</sub>O<sub>3</sub> with fractal mesopores during the hydroconversion of coconut oil to hydrocarbons under low hydrogen pressure. The oil used in this work consisted primarily of triglycerides based on fatty acids with carbon numbers similar to those of the

hydrocarbons employed in jet fuel. During the experimental trials, contact time between the catalyst and the coconut oil was varied in an attempt to elucidate the reaction pathways under low hydrogen pressure.

## 2 Experimental

### 2.1 Catalyst Preparation

The Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, composed of both Ni and Mo supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, was prepared using the co-impregnation method. Extruded  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pellets with pores approximately 11 nm in diameter and surface areas of 225 m<sup>2</sup> g<sup>−1</sup> were produced in the laboratory and used as supports. The catalyst was prepared by first dissolving 5.1 g of nickel nitrate hexahydrate [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] in 2.5 mL of deionized water and 1.1 g of hexaammonium heptamolybdate tetrahydrate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] in 3.5 mL of deionized water at 60 °C. The two solutions were mixed and immediately combined with 10 g of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pellet extrudate in order to avoid forming metal complexes. The mixture was subsequently placed in a sealed container at room temperature overnight under an atmospheric pressure. The resulting material was initially dried at 120 °C for 3 h and then dried again at 200 °C for 3 h.

### 2.2 Hydroconversion of Coconut Oil

The hydroconversion of coconut oil was performed using a continuous-flow fixed bed reactor. The catalyst (1.0 mL) was placed into an 8 mm inner diameter stainless tube. Prior to the reaction, the catalyst was pretreated at 370 °C for 6 h under a hydrogen pressure of 0.4 MPa at a gaseous hourly space velocity (GHSV) of 5,000 h<sup>−1</sup>. Following pretreatment, the material was cooled to the reaction temperature of 350 °C and the hydrogen pressure was increased from 0.4 to 0.8 MPa. The reaction was performed by feeding coconut oil to the catalyst via a pump under a continuous flow of hydrogen, maintaining a molar ratio of H<sub>2</sub> to coconut oil (based on an estimated average molecular weight for the oil) of 15. In order to investigate reaction pathways, the liquid hourly space velocity (LHSV) of the coconut oil was varied between 1.0 and 20 h<sup>−1</sup>, such that the contact time (1/LHSV) varied from 0.05 to 1.0 h. The gaseous products were analyzed via gas chromatograph (Shimadzu GC-8A) using an TCD detector and a packed column having activated charcoal while liquid products were analyzed by gas chromatograph (Shimadzu GC-2014) incorporating an FID detector and a capillary column (SPB-1, 30 m × 0.25 mm, 0.25  $\mu$ m film thickness).

### 3 Results and Discussion

#### 3.1 Hydroconversion of Coconut Oil Over Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst

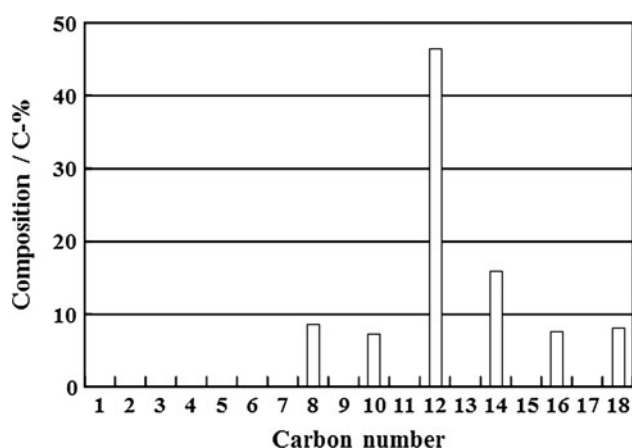
Figure 1 presents the fatty acid composition of the coconut oil employed as a feedstock in the present study. This composition was determined by transesterification of the oil with methanol followed by quantification of the resulting fatty acid methyl esters (FAMES) by gas chromatography. As shown in Fig. 1, the primary component of the oil is the saturated C<sub>12</sub> triglyceride, which accounts for more than 45 % of all triglycerides. The triglyceride fatty acids, however, exhibit a wide range of sizes, with carbon numbers ranging from 8 to 18.

The catalytic properties of sulfur-free Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Mo: 5.0 wt% and Ni: 9.1 wt%) were investigated during the hydroconversion of the coconut oil under a hydrogen pressure of 0.8 MPa, and with a contact time of 1.0 h, over a 4.5 h reaction period at 350 °C. Under these conditions, the catalyst demonstrated high conversion of the triglycerides (97 %) and high hydrocarbon yield (94 %), calculated as the molar ratio of the hydrocarbon products to the original fatty acid content of the triglycerides. The catalyst therefore performed well under a hydrogen pressure significantly below the pressures of 4–20 MPa typically applied in conventional hydroconversion of triglycerides. In cases where hydrogenolysis of the triglyceride molecule occurs at only one of the three ester bonds, the reaction may demonstrate complete conversion of the original triglycerides while still producing low hydrocarbon yield. This work, however, demonstrates a combination of high triglyceride conversion and high hydrocarbon yield, indicating that the triglycerides were selectively converted to hydrocarbons through the complete hydrogenolysis of all ester bonds over the Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, even under

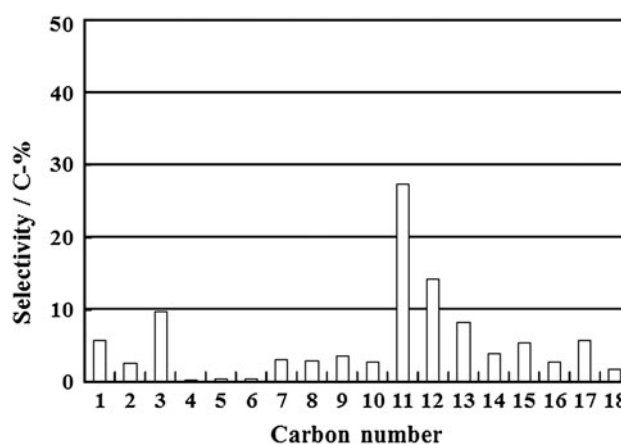
the low hydrogen pressure applied. Figure 2 shows the product distribution of hydrocarbons obtained following the hydroconversion of the coconut oil over the Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The major products were saturated C<sub>11</sub> hydrocarbons followed by saturated C<sub>12</sub> hydrocarbons, with an overall selectivity for the hydrocarbons in the jet fuel fraction (C<sub>8</sub>–C<sub>16</sub>) of 71 %. The relatively low amount of products in the C<sub>4</sub>–C<sub>6</sub> range suggests that there was minimal hydrocracking of the hydrocarbons initially formed to produce smaller molecules under the present conditions applied. We therefore conclude that sulfur-free Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is able to efficiently produce jet fuel hydrocarbons from coconut oil under low hydrogen pressure.

Considering the product distribution in more detail (C<sub>11</sub>: 27.3 % and C<sub>12</sub>: 14.3 %, C<sub>13</sub>: 8.2 % and C<sub>14</sub>: 3.9 %, C<sub>15</sub>: 5.4 % and C<sub>16</sub>: 2.7 %), it is evident that the reaction preferentially generates hydrocarbons with one carbon less than the parent fatty acid rather than with the same carbon number. The hydroconversion of triglycerides, fatty acids and fatty acid esters all proceeds through one of two main routes: hydrodecarboxylation, which produces hydrocarbons with one carbon less than the original fatty acid, and hydrodeoxygenation, which gives hydrocarbons with the same carbon number as the starting fatty acid structure [11, 20, 31]. The hydrocarbons in our product mixture having odd carbon number were therefore generated from the coconut oil triglycerides via the hydrodecarboxylation route, while those with even carbon number were obtained via the hydrodeoxygenation route. These results indicate that the Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, used under low hydrogen pressure, preferentially converts triglycerides via hydrodecarboxylation.

A significant C<sub>1</sub>–C<sub>3</sub> fraction was observed in the reaction products. In the hydroconversion of triglycerides, CO<sub>2</sub> and/or CO can be generated by decarboxylation and/or



**Fig. 1** Coconut oil fatty acid composition as determined by analysis of FAMES via GC



**Fig. 2** Hydrocarbon product distribution resulting from hydroconversion of coconut oil over Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> following a reaction time of 4.5 h with an LHSV of 1.0 h<sup>−1</sup>

decarbonylation of the fatty acid portions and, in the presence of metal catalysts, may be subsequently hydrogenated to form methane [11, 20, 24, 32]. In our study, no CO<sub>2</sub> was detected in the gaseous reaction products and only a very small amount of CO (1.2 C-% yield) was observed, indicating that all CO<sub>2</sub> and most CO formed was reduced. In addition, it has been shown that propane can be formed as a result of the hydrogenation of the triglyceride glycerol moiety [8, 16], and therefore, both methane and propane can be observed in relatively large quantities even under low hydrogen pressure conditions.

### 3.2 Effect of Contact Time on Product Distribution

In order to elucidate the reaction pathways during the hydroconversion of triglycerides over the Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst under low hydrogen pressure, the reaction was carried out employing various contact time values. The data are summarized in Fig. 3 and Table 1. Conversion of the triglycerides was increased from 64 to 97 % as the contact time was increased from 0.05 to 1.0 h, while the hydrocarbon yield was also improved from 48 to 94 mol %. At shorter contact times, the hydrocarbon selectivity exhibited dramatic improvement with contact time increases, although the improvement in selectivity plateaued at longer contact times above 0.5 h. It has been reported that the deoxygenation of triglycerides containing primarily C<sub>18</sub> fatty acid chains over Ni and/or Mo catalysts in the presence of hydrogen progresses via a  $\beta$ -elimination process to generate free fatty acids prior to the formation of hydrocarbons [11, 12, 16, 18]. Based on these studies, it is possible that, during the reaction in our study, the triglycerides were converted to the hydrocarbons through the

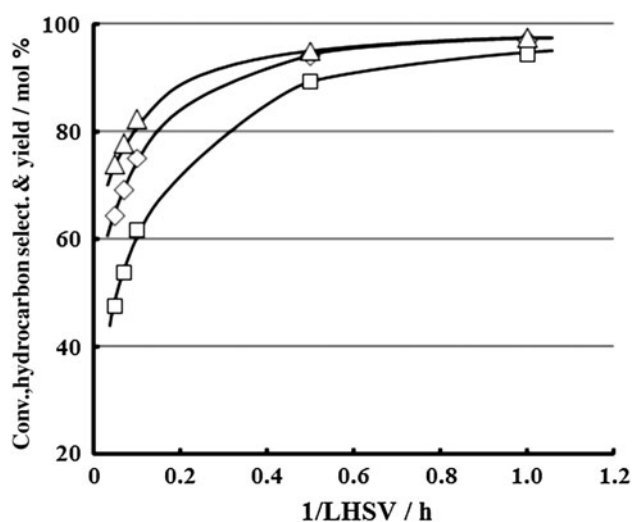
**Table 1** Product distributions following hydroconversion of coconut oil at varying values of contact time

Contact time (h):	0.05	0.07	0.1	0.5	1.0
Conversion (%):	64.2	69.0	75.0	94.1	96.9
Hydrocarbon yield (C-%)					
C <sub>1</sub>	0.2	0.5	0.4	2.4	5.4
C <sub>2</sub>	0.5	0.9	0.9	1.5	2.4
C <sub>3</sub>	2.3	4.5	4.3	7.6	9.2
C <sub>4</sub> –C <sub>6</sub>	1.2	0.7	0.7	0.7	0.9
C <sub>7</sub>	2.7	4.0	2.5	3.7	2.9
C <sub>8</sub>	2.0	1.8	1.2	3.1	2.7
C <sub>9</sub>	3.2	2.8	2.4	3.5	3.3
C <sub>10</sub>	1.3	1.1	1.2	2.8	2.5
C <sub>11</sub>	20.5	20.0	21.1	25.6	25.8
C <sub>12</sub>	3.3	2.4	6.8	15.4	13.5
C <sub>13</sub>	1.9	4.5	5.5	7.0	7.7
C <sub>14</sub>	0.8	1.3	4.3	3.7	3.7
C <sub>15</sub>	2.1	3.0	3.2	4.2	5.1
C <sub>16</sub>	1.1	1.7	2.9	2.4	2.5
C <sub>17</sub>	3.3	3.5	3.1	4.6	5.4
C <sub>18</sub>	1.0	1.0	1.2	1.3	1.6

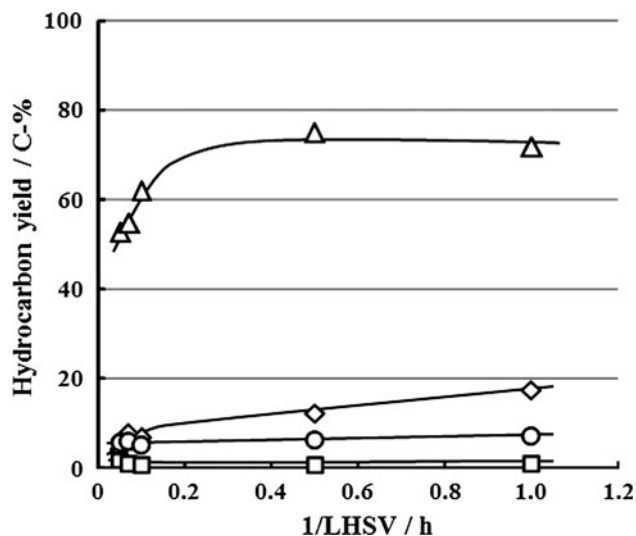
Reaction conditions: cat., Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Mo: 5 wt% and Ni: 9.1 wt%); temperature, 350 °C; hydrogen pressure, 0.8 MPa; molar ratio of H<sub>2</sub> to coconut oil, 15

formation of intermediate oxygenated compounds such as fatty acids and ketenes resulting from the hydrogenolysis of the ester bonds followed by removal of oxygen even under the low hydrogen pressure.

Figure 4 summarizes the observed changes in the yields of hydrocarbon products as the contact time was varied. The overall yield of the hydrocarbons corresponding to the



**Fig. 3** Conversion of triglycerides (diamond), hydrocarbon yield (square) and hydrocarbon selectivity (triangle) over Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a function of contact time (1/LHSV)



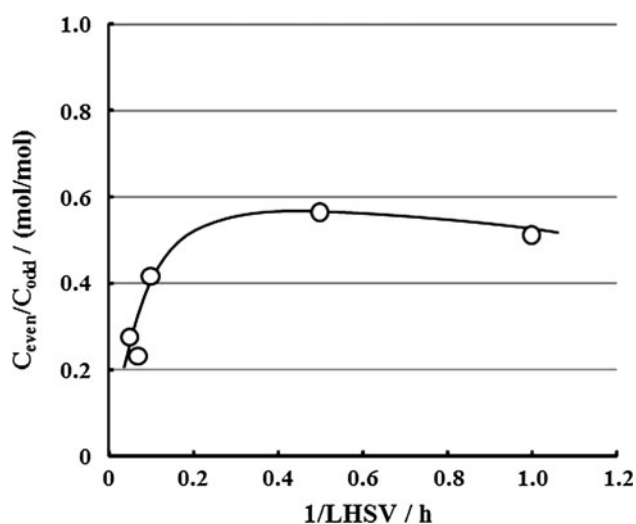
**Fig. 4** Product yield following coconut oil hydroconversion over Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a function of contact time (1/LHSV). C<sub>1</sub>–C<sub>3</sub> (diamond), C<sub>4</sub>–C<sub>6</sub> (square), C<sub>7</sub>–C<sub>16</sub> (triangle), C<sub>17</sub>–C<sub>18</sub> (circle)

kerosene fraction ( $C_8$ – $C_{16}$ ) as well as the  $C_7$  hydrocarbons was increased with increasing contact times when the contact time was below 0.3 h, while the yield was essentially independent of contact time at values above 0.4 h. By contrast, the yields of  $C_{17}$  and  $C_{18}$  hydrocarbons show no variation at all with contact time. There was essentially zero yield of  $C_4$ – $C_6$  hydrocarbons regardless of the contact time, suggesting that very little hydrocracking of the hydrocarbons generated during the reaction took place under the present conditions. The yield of  $C_1$ – $C_3$  hydrocarbons was increased as the contact time was increased over the range of 0.05–1.0 h, likely due to the hydrogenation of CO and  $CO_2$  to methane as well as the reduction of oxygenated  $C_3$  compounds derived from the glycerol backbone of the triglycerides to propane.

Table 1 presents a detailed summary of the product distribution resulting from the hydroconversion, from which it appears that the selectivity for hydrocarbons derived from the lauric acid moieties shows a significant dependence on the contact time. The generation of the  $C_{11}$  hydrocarbons, which are produced through the hydrodecarboxylation of lauric acid, was decreased with increases in the contact time. Conversely, the yield of the  $C_{12}$  hydrocarbons, which are obtained by removal of oxygen from lauric acid, was increased with increases in the contact time. In contrast to the yields of the  $C_{11}$ – $C_{12}$  hydrocarbons, the yields of other hydrocarbon fractions, such as  $C_7$ – $C_{10}$  and  $C_{13}$ – $C_{18}$ , were only slightly affected by variations in contact time. Furthermore, the molar ratio of the total yield of the  $C_8$ – $C_{18}$  hydrocarbons with even carbon numbers ( $C_{\text{even}}$ ) to the sum of the  $C_7$ – $C_{17}$  hydrocarbons with odd carbon numbers ( $C_{\text{odd}}$ ) was drastically increased with increases in the contact time at values of contact time

less than 0.2 h, as shown in Fig. 5. These observations indicate that increasing the contact time improves the hydrodeoxygenation rate, which is consistent with previous findings [21]. The decarboxylation of fatty acids to hydrocarbons can occur over metal catalysts even in the absence of hydrogen [24, 32–37], whereas the use of hydrogen is necessary for the hydrodeoxygenation of fatty acids to hydrocarbons through stepwise reduction via the formation of aldehydes and alcohols. Therefore, the changes in the  $C_{\text{even}}/C_{\text{odd}}$  molar ratio at short contact times demonstrate that increasing the contact time likely leads to increased activation of hydrogen on the metal species, resulting in enhanced stepwise reduction of the fatty acids. In contrast to the results observed at short contact times, the  $C_{\text{even}}/C_{\text{odd}}$  molar ratio underwent a slight decrease at the longer contact time of 1.0 h. Murzin and Co-workers [35] have reported bond scission between the ester carbonyl carbon and the  $\alpha$  carbon of the hydrocarbon chain during the deoxygenation of ethyl stearate to afford *n*-heptadecane, CO and ethanol. Thus, prolonged contact of the triglycerides with the metal species may also result in elevated rates of bond scission between the carbonyl carbon and the  $\alpha$  carbon of the fatty acid to generate the hydrocarbons with odd carbon numbers, resulting in a decrease in the  $C_{\text{even}}/C_{\text{odd}}$  molar ratio.

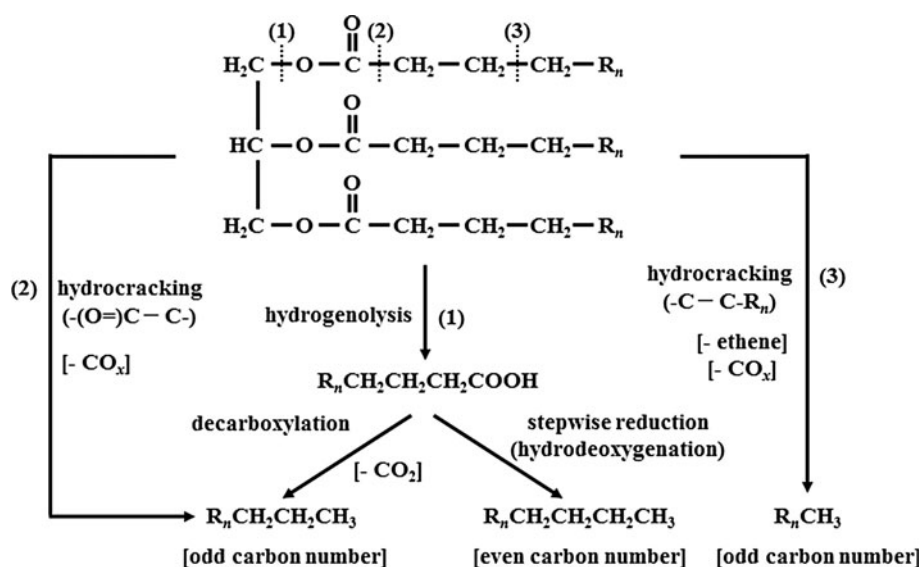
Drawing on the results described above, Fig. 6 summarizes the proposed reaction pathways associated with the hydroconversion of triglycerides composed of saturated fatty acid structures with even carbon numbers over sulfur-free Mo–Ni/ $\gamma$ - $Al_2O_3$  under low hydrogen pressure. In the initial stages, hydrogenolysis of the C–O bond between the fatty acid structure and the glycerol backbone yields fatty acids and the associated glycerol ester (1). The fatty acids thus formed are readily transformed into hydrocarbons with odd carbon numbers through subsequent hydrodecarboxylation. In addition, odd numbered hydrocarbons can also be produced through direct cracking of the bond between the ester carbonyl carbon and the  $\alpha$  carbon of the triglycerides, as in pathway (2), although this likely requires a prolonged residence time on the catalyst. By contrast, under conditions which enhance the reaction of fatty acids with activated hydrogen, hydrocarbons with even carbon numbers are generated by stepwise reduction (hydrodeoxygenation). Under low hydrogen pressure, the rate of fatty acid decarboxylation predominant relative to the rate of the stepwise reduction, leading to the selective formation of the odd numbered hydrocarbons. Morgan et al. [32] have proposed that the observed formation of significant amounts of ethene during the deoxygenation of tristearin in the absence of hydrogen involves bond scission between the  $\beta$  and  $\gamma$  carbons of the fatty acid structure. Since ethane was observed in the product mixture at higher yields than the  $C_4$ – $C_6$  hydrocarbons (as per Table 1), we also assume



**Fig. 5**  $C_{\text{even}}/C_{\text{odd}}$  molar ratio as a function of contact time (1/LHSV).  $C_{\text{even}}$  = sum of  $C_8$ – $C_{18}$  hydrocarbons with even carbon numbers,  $C_{\text{odd}}$  = sum of  $C_7$ – $C_{17}$  hydrocarbons with odd carbon numbers



**Fig. 6** Proposed pathways for the reaction of triglycerides over Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under low hydrogen pressure



that scission of the C–C bond between the  $\beta$  and  $\gamma$  carbon atoms of the fatty acid structure occurred to form hydrocarbons with three carbon number less than that of the parent fatty acid, together with ethene and CO<sub>2</sub>. These reactions are then followed by the hydrogenation of ethene and CO<sub>2</sub> to ethane and methane, respectively (3).

#### 4 Conclusions

High activity and enhanced selectivity for hydrocarbons in the jet fuel fraction (C<sub>8</sub>–C<sub>16</sub>) were successfully achieved during the hydroconversion of coconut oil over sulfur-free Mo–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared by the co-impregnation of Ni and Mo species followed by reduction at low temperatures. This reaction proceeded under a hydrogen pressure of 0.8 MPa, which is significantly lower than the pressures applied during conventional processes (4–20 MPa). The variations in product distribution with changes in contact time were ascertained. Although oxygenated compounds such as fatty acids and ketenes may have formed as a result of the hydrogenolysis of ester bonds following short contact times, yields of hydrocarbons generated from the original fatty acid moieties increased with increasing contact times. Hydrocarbons with odd carbon numbers were the majority product, even though the coconut oil was composed of triglycerides containing even numbered fatty acids, although the types of hydrocarbons resulting from the reaction varied with changes in contact time. An increase in the contact time at values below 0.2 h elevated the proportion of even numbered hydrocarbons as a consequence of improved reduction of the fatty acids and therefore increased rates of hydrodeoxygenation. By contrast, a long contact time of 1.0 h likely led to direct

cracking between the ester carbonyl and  $\alpha$  carbons or between the  $\beta$  and  $\gamma$  carbons of the fatty acid structure to yield the hydrocarbons with odd carbon numbers.

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