

# Diesel Precursors Via Catalytic Hydrothermal Deoxygenation of Aqueous Canola Oil Emulsion

Richard U. Ndubuisi<sup>1</sup> · Sayeh Sinichi<sup>1</sup> · Ya-Huei (Cathy) Chin<sup>1</sup> · Levente L. Diosady<sup>1</sup>

Received: 11 July 2018 / Revised: 14 January 2019 / Accepted: 6 February 2019  
© 2019 AOCS

**Abstract** Aqueous extraction for protein isolation from oilseeds is a promising alternative to the conventional hexane-based solvent extraction widely used in the industry. However, during aqueous extraction, a stable oil-in-water emulsion is produced that results in decreased oil yield. We demonstrated the conversion of this aqueous extract into renewable hydrocarbons on 20%w/w Ni/C at 315 °C and at an initial hydrogen headspace pressure of 1.95 MPa. Moderate yield (>50%) and selectivity (~70%) of hydrocarbons within the diesel range were obtained within 12 hours of reaction without additional external hydrogen input. It was also shown that a prolonged experimental run at 305 °C can result in near-complete conversion of triacylglycerol oil into diesel-range hydrocarbons (70%) and oxygenates (9%) with selectivity of ~80%. Although the study demonstrates for the first time the possibility of integrating aqueous extraction of protein with renewable diesel production in a hydrothermal medium, the limitations and challenges experienced during this initial study justify additional work that is presently underway.

**Keywords** Decarboxylation · Deoxygenation · Hydrocarbon · Catalyst · Renewable · Extraction

*J Am Oil Chem Soc* (2019).

✉ Sayeh Sinichi  
s.sinichi@mail.utoronto.ca

<sup>1</sup> Department of Chemical Engineering and Applied Chemistry,  
University of Toronto, 200 College Street, Toronto, Ontario, M5S  
3E5, Canada

## Introduction

The edible oil industry uses hexane for oil extraction from oilseeds. However, the toxicity and flammability of hexane prompt the search for safer and environmentally friendlier alternatives (Sinichi and Diosady, 2015). Consequently, in our group, IPA and aqueous extraction methods were developed for simultaneous oil and protein recovery from crops as a green alternative (Sinichi and Diosady, 2014; Tabatabaei and Diosady, 2012). Currently, biodiesel is the world's most important renewable fuel for compression-ignition (CI) engines. Biodiesel from mustard and canola oil has been tested in our group among others (Sinichi and Diosady, 2017; Tabatabaei et al., 2014).

“Green” diesel, which is a mixture of hydrocarbons produced via deoxygenation of vegetable oils, is an emerging alternative to conventional biodiesel that is made of fatty acid methyl esters (FAME). Renewable diesel could become more dominant in the future (Moser, 2010) given the close similarities between its fuel properties and those of conventional petro-diesel (Fu et al., 2011).

The major contributor to the cost of producing biofuels is the cost of feedstocks (International Renewable Energy Agency (IRENA), 2013). Inexpensive feedstocks usually have a high moisture content that adds to the processing cost due to the need for pretreatment prior to chemical transformation. A promising solution is the integration of protein extraction and inedible oil processing by direct hydrothermal conversion of the triacylglycerol (TAG) emulsions into hydrocarbon fuels. The goal of this study was to test the performance of a customized nickel catalyst in the production of diesel in a subcritical hydrothermal medium by decarboxylation of TAG, and to explore potential integration of fuel production with protein isolation.

While the development aims at full utilization of mustard and related seeds, due to canola's ready availability, high oil content, 40–45%, and its fatty acid profile (Przyblyski et al., 2005), canola oil was initially used as a starting material for the deoxygenation process. We are unaware of any reports on catalytic hydrothermal deoxygenation of TAG over nickel supported on carbon (Scheme 1). However, there have been related studies that involved nickel (Miao et al., 2016; Yang et al., 2018). For instance, Miao et al., reported the formation of renewable hydrocarbons over nickel supported on  $ZrO_2$  under low external  $H_2$  pressure (100 psi) in a hydrothermal medium (Miao et al., 2016). It was shown that the use of water improved conversion of palmitic acid to 64.7C % as opposed to just 17.2C % achieved in the absence of water. Moreover, the same authors in a different study have demonstrated the generation of in situ hydrogen via glycerol reforming and water-gas shift reactions in a study that involved Ni/ $ZrO_2$  catalysts using fatty acid and bio-oil feedstocks (Miao et al., 2018).

In a related work employing Pd as a catalyst, Savage et al. reported that RANEY Nickel was not active under the experimental conditions employed (Between 290–380 °C in a hydrothermal medium, i.e., (near or supercritical water) (Fu et al., 2011). In another closely related work, the catalytic deoxygenation of waste soybean oil over a Pd/C and NiO/ $\gamma$ - $Al_2O_3$  hybrid catalyst was carried out 300 °C using in situ  $H_2$  generated from the reforming reaction of glycerol obtained via the hydrolysis of TAG (Kordulis et al., 2016). However, it was reported that nickel did not exhibit deoxygenation activity under those conditions, but only increased the proportion of saturated hydrocarbons produced. Thus, Pd/C was the active deoxygenation catalyst (Kordulis et al., 2016). However, the hydrodeoxygenation of phenolic compounds and bio-oils in water using nickel has been reported (Sinichi and Diosady, 2017; Zhao et al., 2012). Such transformation usually requires bifunctional catalysts with both metal and acid sites, and so nickel in these catalysts is frequently supported on zeolites. Carbon is inexpensive and due to its large surface area promotes the deoxygenation reaction (Santillan-Jimenez and Crocker, 2012). Studying the catalytic hydrothermal conversion of TAG over Ni/C represents a cheaper alternative to precious metals and holds the potential for diesel production from cheap feedstocks. In line with this, Morgan et al. have reported the

activity of 20 wt.% Ni/C for deoxygenation in an organic medium (Morgan et al., 2010). In their study, the nickel catalyst was reportedly more active than the 5 wt.% Pd/C and 1 wt.% Pt/C catalysts due to a higher nickel content. However, the use of an organic solvent adds complexity and cost to processing, and defeats the purpose of aqueous extraction.

## Materials and Methods

### Materials

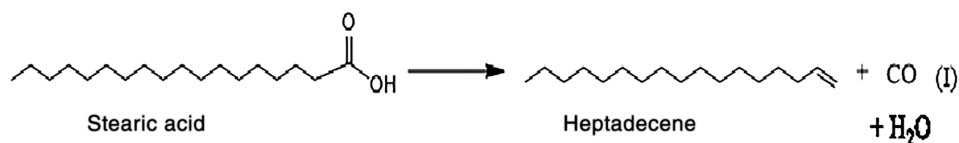
$Ni(NO_3)_2 \cdot 6H_2O$ ,  $C_8$ – $C_{20}$  alkane standard solution,  $C_{21}$ – $C_{40}$  alkane standard solution, glycerol (>99%), and activated carbon (Darco KB-G, surface area of  $1700 \text{ m}^2 \text{ g}^{-1}$ ) were obtained from Sigma Aldrich (St. Louis, MO, USA). ACS-grade hexane (min 99.5%) was purchased from Caledon Laboratories (Georgetown, Ontario, Canada). Fatty acid standards (GLC 402) were purchased from NU-CHEK PREP (Waterville, MN, USA). Canola oil distributed by Great Value Foods (Ontario, Canada) was purchased from a local supermarket.

### Canola Oil Characterization

Canola oil (~60 g) was hydrolyzed using a 1 L Parr reactor for 4.5 hours at 250–290 °C. After collecting and weighing the reactor contents, approximately 2 g of products was dissolved in hexane and diluted further for analysis using gas chromatography. A Clarus 580 Perkin Elmer GC (MA, USA) equipped with an auto sampler and a ZB-5HT column purchased from Phenomenex (CA, USA) was used. It should be noted that no derivatization was necessary because ZB-5HT is a high-temperature column specifically for high-boiling oxygenates including TAG. Response factors were obtained using standards from NU-CHEK PREP by dissolving a known amount of canola-free fatty acids (standard GLC reference 402) in hexane and testing on the GC.

### Decarboxylation of Canola Oil

For deoxygenation experiments, 1 L model 4521 and 300 mL model 4561 Parr reactors (IL, USA) were used. In



**Scheme 1** Decarboxylation reaction of canola oil

a typical experiment, ~200 g water, 100 g canola oil (to produce oil in water emulsion), and catalyst (~1.67 wt. % of incoming feed) were placed in the reactor. The reactor was then sealed and purged with N<sub>2</sub> for 4 min. Afterward, the pressure line was switched to the hydrogen supply and the reactor was purged for 2 min before pressurizing to the desired headspace pressure. The heater was switched on and the temperature controller was adjusted to the desired temperature. The impeller was switched on. The temperature was measured using a type J (Iron-constantan) thermocouple connected to the model 4831 TC. At the end of the run, the reaction was quenched using cold water passing through the internal cooling coils. At the end of the run, the reactor contents were collected and weighed. The aqueous phase was filtered off using WHATMAN<sup>®</sup> filter paper 934-AH on a porcelain Buchner funnel. The mushy organic products were further dried using molecular sieves of 3 Å with a contact ratio of 1:1 w/w for 24 hours and then extracted in hexane. After extraction, the mixture was vacuum filtered using surfactant-free cellulose acetate (SFCA) membranes, and the organic products were recovered using a rotavapor (Büchi Labortechnik AG, Flawil, Switzerland). To ensure no loss of important organic products in the aqueous phase, it was extracted with hexane and the extract was combined with the organic products. To ensure representativeness of the samples, the recovered organic products were gently warmed in a water bath. Samples were then taken and diluted in fresh hexane for analysis. The leftover organics retained on the catalyst were weighed.

To clarify calculations, oxygenated intermediates were treated as reactants because they retained the original oxygen present in the TAG. Equations 1–3 were used to compute the yield, selectivity, and conversion.

$$\text{Yield} = \frac{\text{Wt. of hydrocarbon product}}{\text{Wt. of canola oil charged}} \quad (1)$$

$$\text{Conversion} = \frac{\text{Initial wt. of oil} - \text{wt. of fatty acids left}}{\text{Wt. of canola oil charged}} \quad (2)$$

$$\text{Hydrocarbon selectivity} = \frac{\text{Yield}}{\text{Conversion}}. \quad (3)$$

### Ni/C Catalyst Preparation

An amount of 20 wt.% Ni/C was prepared by incipient wetness impregnation using an aqueous solution of nickel nitrate hexahydrate, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as the precursor, and activated carbon according to a published method (Moser, 2010). The impregnated catalyst was dried in fume hood for 24 hours and then oven dried at 140 °C for 12 hours. The dried catalyst was calcined and reduced in a tube

furnace (Waters, MA, USA) under flowing H<sub>2</sub>/He (60 mL min<sup>-1</sup>) using a ramp of 2 °C min<sup>-1</sup> until 350 °C was reached. This temperature was maintained for 5 hours.

### Analytical Methods

Organic products were analyzed by gas chromatography using a Clarus 580 Perkin Elmer GC equipped with a ZB-5HT column, 30 m × 25 mm × 0.25 μm. A single method for identification and quantification of both hydrocarbons and oxygenates was developed. A volume of 1 μL of sample was injected at 380 °C by the auto sampler using a split ratio of 20:1. The initial oven temperature was set at 130 °C, then increased to 190 °C using a ramp of 20 °C min<sup>-1</sup>, and then finally increased to 400 °C min<sup>-1</sup> using a ramp of 30 °C min<sup>-1</sup> then held at 400 °C for 4 min. The flame ionization detector was held at 400 °C.

The glycerol content in the aqueous phase was determined using the Dionex UltiMate 3000 UHPLC (Thermo Scientific, MA, USA) connected to a Q-Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Scientific) LC-MS system that was equipped with an Aminex HPX-87H 300 X 7.8 mm column. A volume of 20 μL of the sample was injected at a flow rate of 0.6 mL min<sup>-1</sup> using 0.1% formic acid in water as the mobile phase. The [M + Na]<sup>+</sup> = 115.0366 and [M + H]<sup>+</sup> = 93.0546 adducts were monitored. Sample concentrations ranged between 12.5 and 1250 ng mL<sup>-1</sup>.

A Varian 2100T mass spectrometer equipped with VF-5MS (30 m × 25 mm) by Agilent (CA, USA) was used for validation of products. A volume of 1 μL of the sample was injected by the auto sampler. The injector was held at 260 °C. The following temperature program was used on the oven: 60 °C for 1 min, ramp to 210 °C at 8 °C min<sup>-1</sup>, and finally ramp to 340 °C at 5 °C min<sup>-1</sup>.

## Results and Discussion

### Characterization of Canola Oil

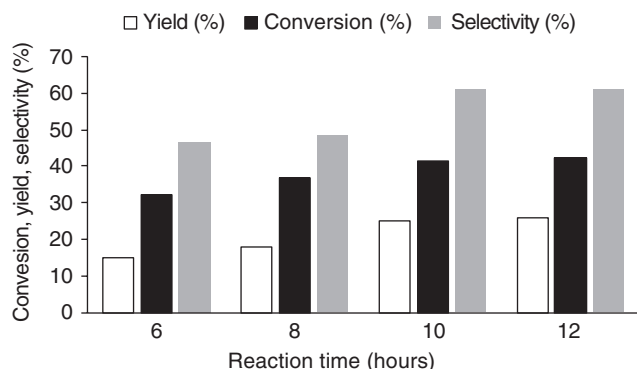
Canola oil is primarily composed of TAG. The composition of the canola oil fatty acids used for the decarboxylation test is presented in Table 1.

### Influence of Reaction Time on the Decarboxylation Reaction

Experiments were conducted between 6 and 12 hours at 2 hour intervals at 305 °C and 850 rpm under an initial H<sub>2</sub> headspace pressure of 2.76 MPa at 298 K at a fixed oil concentration of 33 wt.% (Fig. 1). The approximate amount

**Table 1** Composition of canola oil feedstock

Component	Wt. %
Palmitic acid (16:0)	4.5
Stearic acid (18:0)	1.4
Oleic acid (18:1)	62.1
Linoleic acid (18:2)	20.4
Linolenic acid (18:3)	10.3
Arachidic acid (20:0)	0.5
Behenic acid (22:0)	0.3
Erucic acid (22:1)	0.5

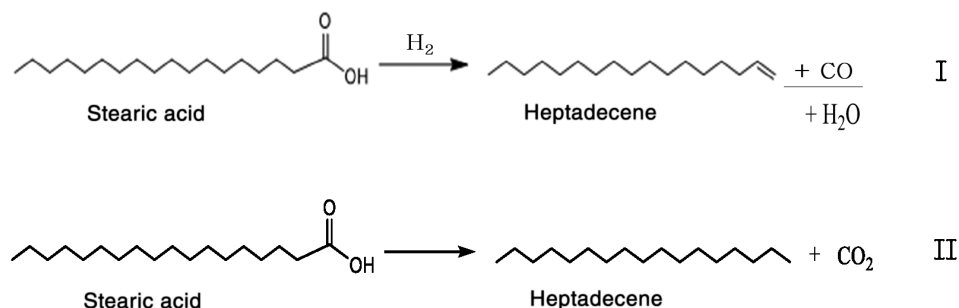


**Fig. 1** Effect of reaction time on conversion, yield, selectivity at 305 °C, Ni/C: oil ratio = 5%. Due to a long process time, only one round of experiments was performed

of hydrogen needed to saturate the olefinic bonds in the starting feedstock is approximately 0.48 mol.

At 6 hours, hydrolysis was already complete, therefore, no TAG was observed in the product mixture in agreement with Hollak et al. (Hollak et al., 2014). After hydrolysis and hydrogenation, two pathways become available (Scheme 2) for hydrocarbon formation; decarbonylation involving the removal of CO and decarboxylation involving the removal of CO<sub>2</sub>.

It should be noted that second reaction is thermodynamically favored, and does not require the presence of hydrogen. No evidence of hydrogen deprivation was discovered:



**Scheme 2** Decarbonylation and decarboxylation pathways

practically no unsaturated species were found at the completion of the runs. In fact, there were indications of hydrogen oversupply during the reaction. First, glycerol was not detected in the final product possibly due to its reforming into H<sub>2</sub>. Nickel catalysts are active in reforming of glycerol at temperatures and high pressures typical of those employed in this study, by the aqueous phase reforming (APR) process (Fu et al., 2011).

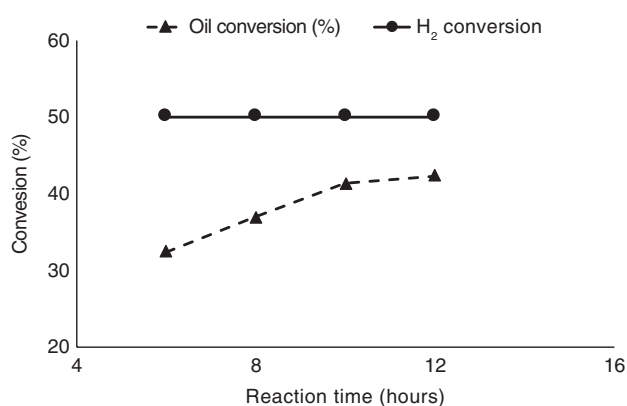
Conversion did not vary appreciably with hydrogen, as shown in Fig. 2, implying that the reaction was not limited by hydrogen availability.

APR of glycerol helps provide a reductive environment, which is needed to keep the catalyst active by preventing the formation of unsaturated species that are precursors for coke formation. In addition, it enhances the selectivity of the process and removes CO as CO<sub>2</sub> thereby preventing competitive adsorption. More importantly, in situ hydrogen production could reduce the dependence on external H<sub>2</sub> supply, and another benefit of the WGS reaction to the process is the conversion of CO to CO<sub>2</sub> (Fig. 2).

### Effect of Initial Hydrogen Input

In previous studies, it was noted that the yield of desired products did not increase continuously with hydrogen supply (Hollak et al., 2014). Immer et al. reported that different active sites are involved in the two pathways given above (Immer et al., 2010). Our results were consistent with this observation. Fig. 3 represents experiments at two different initial hydrogen headspace pressures.

Both experiments were conducted at 305 °C and 850 rpm, the catalyst: oil ratio was 4%, and the reaction pressure was the observed autogenous pressure. This effect theoretically should be more pronounced in a hydrothermal medium with inherently lower vapor pressure. This hydrogen effect might also explain the reason behind the poor yield of alkanes for reactions at 6 and 8 hours, because there was no indication of significant loss of catalytic activity (Table 2); alkane formation continued beyond 8–12 hours. The effect was also pronounced on ester

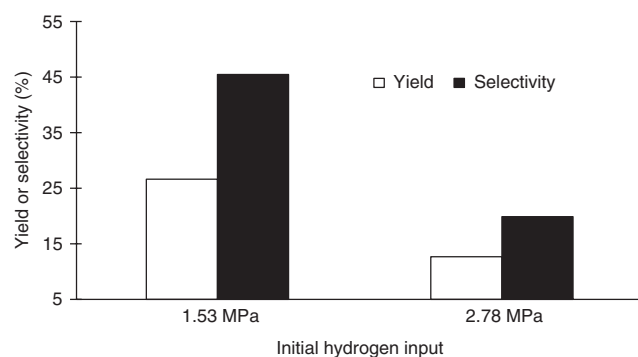


**Fig. 2** Conversion of reactants with reaction progress. Due to a long process time, only one set of experiments was performed

formation. Stearyl stearate was the dominant ester observed in the product mix and the concentration decreased by 77% when the initial H<sub>2</sub> pressure was decreased to 1.53 MPa from 2.78 MPa.

The presence of hydrogen has been known to promote the reaction although such an effect is not uniform, therefore, there is an optimum feed-to-H<sub>2</sub> pressure above which increasing the H<sub>2</sub> concentration can decrease alkane yields (International Renewable Energy Agency (IRENA), 2013; Przyblyski et al., 2005). In this study, employing a high-boiling solvent (water) resulted in H<sub>2</sub> partial pressure above the optimum needed to promote decarboxylation and favored the production of in situ H<sub>2</sub> via glycerol reforming. Furthermore, at high H<sub>2</sub> partial pressures, there is the possibility of competition for active sites on the catalyst surface. Increased H<sub>2</sub> pressure predisposes the reaction to follow the decarboxylation pathway (Tabtabaei and Diosady, 2012).

The pathway for stearyl stearate formation involves a reduction step. Once the fatty acids are formed by hydrolysis of the TAG, the reduction of an acid (stearic) into alcohol (steryl) could take place after which condensation with



**Fig. 3** Effect of hydrogen on yield and selectivity at 305 °C, after 8 hours of reaction. Due to a long process time, only one set of experiments was performed

**Table 2** Details of hydrogen consumption during deoxygenation

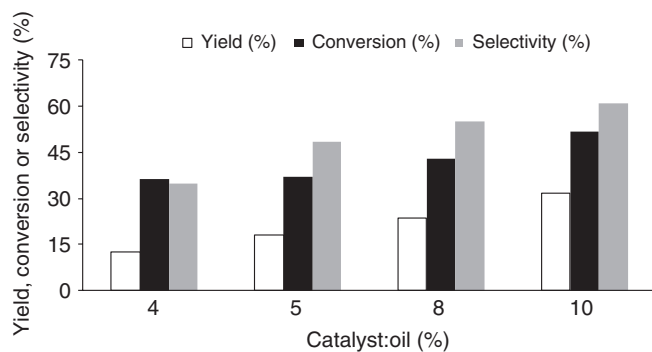
Sample/no.	Process conditions	Oil conversion (%)	Final pressure (kPa)
1	6 hours, 2760 kPa H <sub>2</sub> , 5 g Cat, 33.4 wt.% oil, 305 °C	32.4	1380
2	8 hours, 2760 kPa H <sub>2</sub> , 5 g cat, 33.3 wt.% oil, 305 °C	36.9	1380
3	10 hours, 2760 kPa H <sub>2</sub> , 5 g cat, 33.3 wt.% oil, 305 °C	41.3	1380
4	12 hours, 2760 kPa H <sub>2</sub> , 5 g cat, 33.3 wt.% oil, 305 °C	42.3	1380
5	8 hours, 2760 kPa H <sub>2</sub> , 5 g cat, 20.4 wt.% oil, 305 °C	42.9	1240
6	8 hours, 2760 kPa H <sub>2</sub> , 2.5 g cat, 20.0 wt.% oil, 305 °C	36.1	1650
7	8 hours, 2760 kPa H <sub>2</sub> , 6.1 g cat, 20.3 wt.% oil, 305 °C	51.8	965
8	8 hours, 1520 kPa H <sub>2</sub> , 2.5 g cat, 20.2 wt.% oil, 315 °C	64.2	830
9	8 hours, 1520 kPa H <sub>2</sub> , 2.5 g cat, 20.1 wt. % oil, 305 °C	49.9	830
10	8 hours, 1520 kPa H <sub>2</sub> , 2.5 g cat, 20.0 wt. % oil, 295 °C	12.7	830
11	12 hours, 1930 kPa H <sub>2</sub> , 6.1 g cat, 20.4 wt. % oil, 315 °C	79.7	830

an acid gives stearyl stearate. This reaction can take place without the aid of the catalyst.

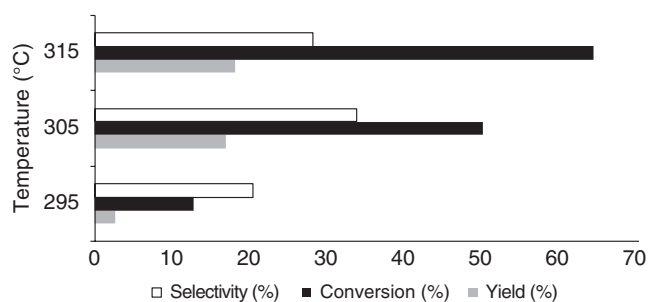
### Effect of Catalyst Loading on the Decarboxylation Reaction

Experiments were conducted at four different catalyst to oil ratios: 4, 5, 8, and 10% w/w (Fig. 4). All tests were conducted for 8 hours at 305 °C. The initial hydrogen headspace pressure was 2.76 MPa and the observed autogenous pressure at the reaction temperature was  $11.04 \pm 0.69$  MPa. As expected, the yield of alkanes increased with the catalyst to oil ratio. At a loading of 5 g Ni/C per 60 g of oil, i.e., a catalyst-to-oil ratio of 8%, the selectivity was 55%, and increased by only 9% at a catalyst: oil ratio of 10%. However, the yield increase was approximately 30% between the two ratios, suggesting that more by-products were also produced at higher ratios.





**Fig. 4** Effect of catalyst: oil ratio on alkane yield, conversion/selectivity; 8 hours, 305 °C. Due to a long process time, only one set of experiments was performed



**Fig. 5** Temperature effect on yield, selectivity, and conversion; 8 hours, Ni/C: oil ratio of 4%. Due to a long process time, only one set of experiments was performed

### Effect of Reaction Temperature

The influence of temperature on the reaction was investigated at three different temperatures; 295, 305, and 315 °C (Fig. 5). At a catalyst-to-oil ratio of 4% at an oil

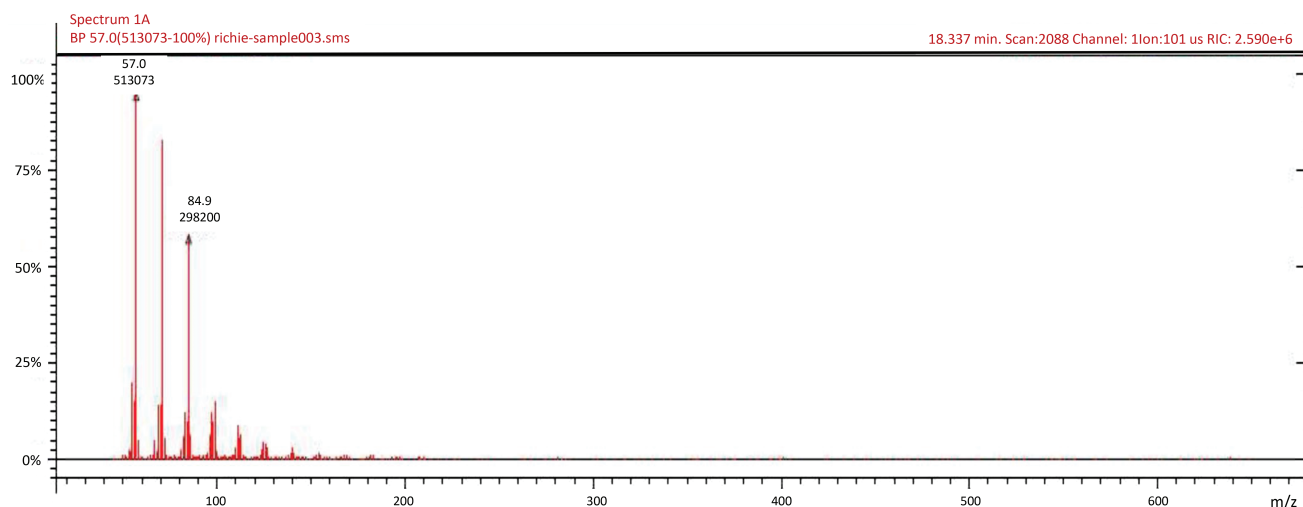
concentration in water of 20%w/w, the initial hydrogen headspace pressure was 2.78 MPa.

Conversion was strongly dependent on temperature. Notably, at higher temperatures, the propensity for side reactions and gas formation was higher. Side reactions involving cracking and other reactions can contribute to yield loss and formation of many compounds. Thus, the yield and selectivity did not vary as much with temperature as the conversion. This is more evident with unsaturated feedstocks as is typical in this work, especially considering that cracking can potentially take place below the set point temperature. At 315 °C, the loss of material to the gas phase was over 30% of the weight of starting feedstock. Indicative of extensive side reactions was the fact that only about 75% of the products was identified and quantified as hydrocarbons. The unidentified products were oxygenates, and had retention times within the alcohol and lower ester (C16 and C18) regions of the chromatogram. Despite the side reactions, the yield of hydrocarbons increased with temperature as expected.

Under the conditions used for the experimental studies, carbon alone was not active without catalyst, although such activity has been reported at much higher temperatures (350–400 °C) (Zhao et al., 2012).

### Production of Renewable Diesel with High Yield and Selectivity

Two test reactions were conducted incorporating the information from the parametric studies to select the best process conditions. The first test reaction was conducted for 12 hours at 315 °C at a catalyst to oil ratio of 10% and an initial hydrogen headspace pressure of 1.95 MPa. The oil concentration in water was 20%w/w. Conversion was 100%



**Fig. 6** Mass spectrum of heptadecane, the main product of canola oil decarboxylation

**Table 3** Mass balance for decarboxylation of canola oil at 315 °C, 12 hours, 10 wt.% Ni/C: oil

Input Canola oil = 61.5 g	Output liquid-phase = 44.5 g					
	Liquid alkanes (63.2 wt.%)		Oxygenates (36.8 wt.%)			
		<i>g</i>	%		<i>g</i>	%
	C17	23.2	82.4	Stearic acid	11.1	67.7
	C15	1.6	5.9	Palmitic acid	1.1	6.5
	Others	3.3	11.7	Stearyl stearate	0.2	1.1
				Other oxygenates	4.0	24.7
	Total	28.1	100		16.4	100

with respect to the loaded oil, but since the intermediate oxygenates were considered as precursors for hydrocarbon production, the calculation for conversion involved treating them as reactants as well. No glycerol or nickel was observed in the aqueous phase. Also, no unsaturated alkanes were formed. The products were validated using mass spectrometry as described above. The fragmentation pattern for the heptadecane major product was matched to the observed fragmentation pattern of the standard acquired from Sigma Aldrich. In total, 100% of the oil reacted, forming approx. 37% intermediate oxygenates and about 63% final hydrocarbon products.

The most prominent peaks at *m/z* 57, 71, and 85 correspond to the butyl, pentyl, and hexyl cations, respectively (Fig. 6). Fragmentation occurred at the C–C linkages, producing alkyl radicals and alkyl carbocations. Mass balance of the major components of interest is shown in Table 3. The gas phase was not analyzed as the focus of the work was liquid-phase hydrocarbons within the diesel boiling range, and the collection and analysis of the gas-phase products were very difficult with the available equipment.

In total, 72.4% of the starting oil was recovered and identified as useful organic products out of which about 63% comprised of diesel components. The remaining 37% were made up of fatty acid intermediates and oxygenates.

In the second test reaction, decarboxylation was carried out for 23 hours with occasional purging of gas phase and resupply of fresh hydrogen at room temperature (Fig. 7). Prior to decarboxylation, hydrogenation of the canola was done for 6 hours at 250 °C using a standard BASF (N-645 Engelhard Nickel Droplet Catalysts) hydrogenation catalyst at a hydrogen headspace at 2.1 MPa. For the decarboxylation reaction, an Ni/C: oil ratio of 7%, oil concentration of about 26%, and temperature of 305 °C were used. Conversion was greater than 90% while both yield and selectivity also remained high (>70%).

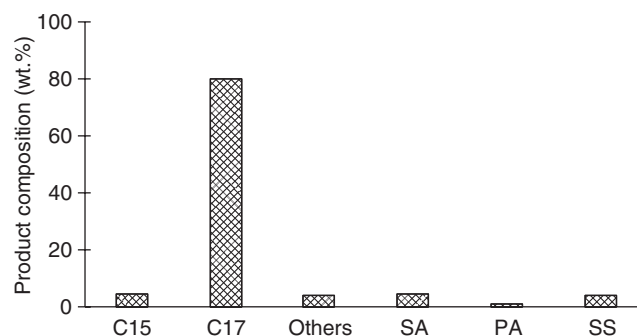
Over 75% of the weight of canola initially charged was recovered as liquid organic products. The rest of the oil was converted to low molecular weight components that were lost in the gas phase. The high selectivity of the

process is reflected in the chromatogram given below, which virtually contains only alkanes.

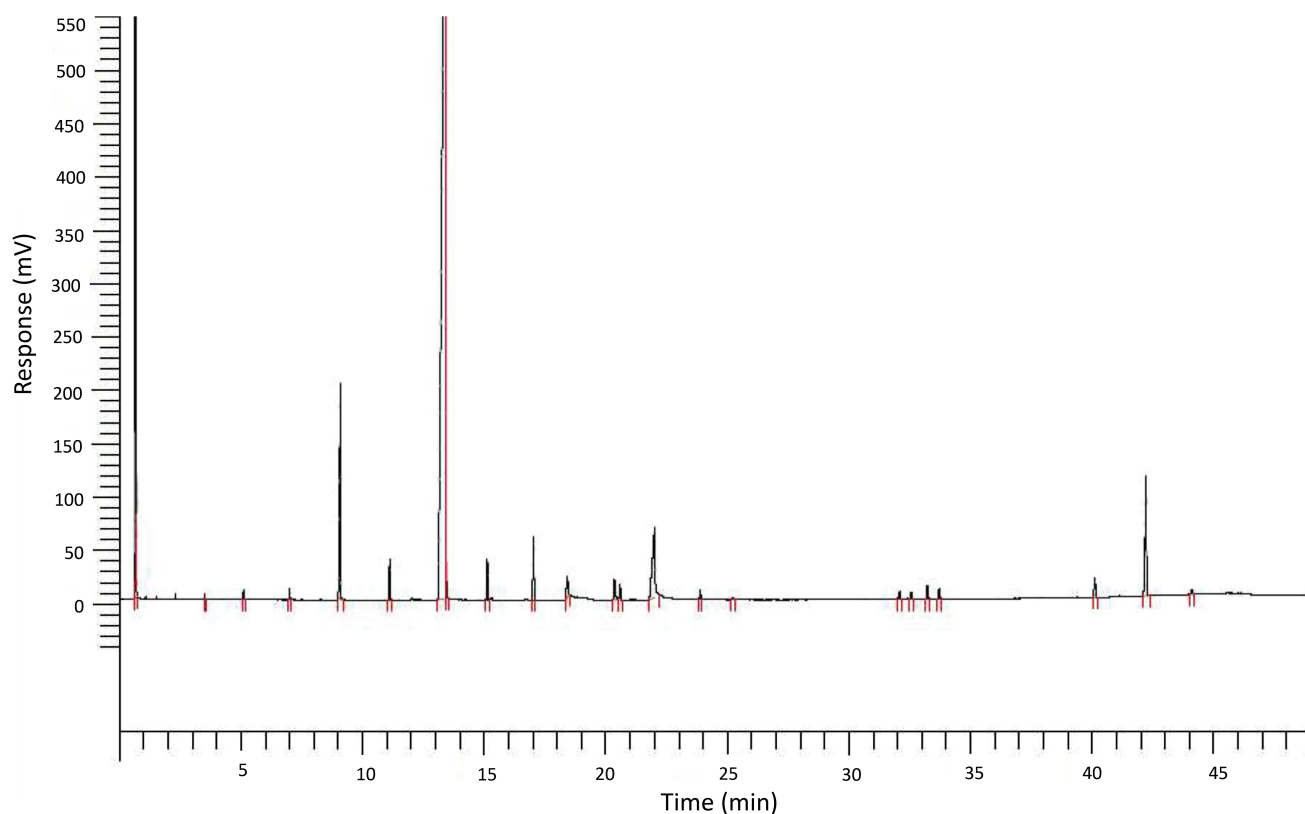
According to Fig. 8, the tallest peak (13.36 min) represents heptadecane, the major product. The second tallest peak is for pentadecane (9.21). The peaks around 25 min are the fatty acids, mostly stearic acid, whereas those on the far right of the chromatogram are esters, the tallest of the three being stearyl stearate. All products were identified using mass spectrometry as previously described.

The results obtained from this run indicate that purging the gas phase enhances very markedly the production of desired alkanes. Clearly, carrying out the process in continuous mode would provide better conversion and yields (Table 4).

To put the work in context, Fu et al. reported that Raney Nickel was not active toward the catalytic hydrothermal deoxygenation of palmitic acid (Fu et al., 2011). The low cost of the catalytic system and mild reaction conditions employed in our study make our work encouraging. For instance, to realize heptadecane formation of about 70% with 80% selectivity over activated carbon, Sergiy et al. had to employ temperatures over 350 °C and pressures >3500 psi (24.1 MPa) in a flow system, which typically facilitates reaction due to reduced deactivation (Popov and Kumar, 2015). Although Hollak et al. had reported alkane



**Fig. 7** Composition after 23 hours decarboxylation; 305 °C, Ni/C: oil = 7 wt.%. Other = alkanes excluding C12–C20, C15 and C17, SA = stearic acid, PA = palmitic acid, and SS = stearyl stearate



**Fig. 8** Chromatogram for decarboxylation of canola oil; 23 hours, 305 °C, Ni/C: oil = 7%

**Table 4** Mass balance for decarboxylation of canola oil at 305 °C, 23 hours, 7 wt.% Ni/C: oil

Input Canola oil = 100.2 g	Output liquid-phase = 74.6 g					
	Liquid alkanes (88 wt.%)			Oxygenates (12 wt.%)		
		g	wt.%		g	wt.%
	C17	59.7	90.8	Stearic acid	3.4	37.7
	C15	3.2	4.9	Palmitic acid	0.7	8.1
	Others	2.8	4.3	Stearyl stearate	2.8	31.7
				Other oxygenates	2.0	22.5
	Total	65.7	100		8.9	100

formation at just 250 °C using in situ hydrogen derived from glycerol reforming in a hydrothermal medium, the study used a Pd/C that is more expensive by about three orders of magnitude (Popov and Kumar, 2015). In a similar study, Vardon et al. achieved complete deoxygenation after hydrogenation of oleic acid within 2 hours; however, this was over a Pt-Re/C catalyst, again which is much more expensive than nickel (Vardon et al., 2014). Thus, the results obtained are promising especially in light of the simplicity and inexpensiveness of the system and justify the need for more experiments.

## Conclusions

Carbon-supported nickel catalysts are active in converting an aqueous TAG oil emulsion into renewable diesel. In a prolonged run, no significant irreversible deactivation of the catalyst occurred. A reasonably high conversion (~90%) was obtained with very good yields of desired hydrocarbons at high selectivity (~77%) at 305 °C. Alkane formation was strongly dependent on reaction time and temperature. Alkane yield was higher under lower initial hydrogen pressures. Although the study was constrained by the available



equipment, it clearly demonstrated the potential for developing an integrated solvent-free process for producing food-grade proteins by proven processes, followed by conversion of the stable oil/water emulsion to hydrocarbons by decarboxylation in the presence of water. This eliminates the need for the very expensive de-emulsification step that has been the stumbling block in attempts to develop aqueous oil extraction processes for oilseeds. The process has the further advantage of producing hydrocarbons, rather than methyl esters of fatty acids – and these are readily included in diesel fuel without the limitations of traditional biodiesel. It should be noted that due to equipment limitations, neither the fresh or spent catalysts were studied further. The authors believe that such work is necessary, and this should be addressed in future, collaborative work with the Multidisciplinary Laboratory for Innovative Catalytic Science. Notwithstanding, the benefits of the work are highly promising, and the individual trials indicate alkane formation under the test conditions. Thus, further research is justified.

**Acknowledgment** This project was funded by the Natural Sciences and Engineering Research Council of Canada.

## References

- Fu, J., Lu, X., & Savage, P. E. (2011) Hydrothermal decarboxylation and hydrogenation of fatty acids over Pt/C. *ChemSusChem*, **4**: 481–486.
- Hollak, S. A., Ariëns, M. A., de Jong, K. P., & van Es, D. S. (2014) Hydrothermal deoxygenation of triglycerides over Pd/C aided by in situ hydrogen production from glycerol reforming. *ChemSusChem*, **7**:1057–1062.
- Immer, J. G., Kelly, M. J., & Lamb, H. H. (2010) Catalytic reaction pathways in liquid-phase deoxygenation of C18 free fatty acids. *Applied Catalysis A: General*, **375**:134–139.
- International Renewable Energy Agency (IRENA). (2013) Production of liquid biofuels; Technology brief. 4. Production of International Renewable Energy Agency (IRENA). IEA-ETSAP and IRENA<sup>®</sup> technology Brief P10.
- Kordulis, C., Bourikas, K., Gousi, M., Kordouli, E., & Lycourghiotis, A. (2016) Development of nickel based catalysts for the transformation of natural triglycerides and related compounds into green diesel: A critical review. *Applied Catalysis B: Environmental*, **181**:156–196.
- Miao, C., Marin-Flores, O., Davidson, S. D., Li, T., Dong, T., Gao, D., ... Chen, S. (2016) Hydrothermal catalytic deoxygenation of palmitic acid over nickel catalyst. *Fuel*, **166**:302–308.
- Miao, C., Marin-Flores, O., Dong, T., Gao, D., Wang, Y., Garcia-Pérez, M., & Chen, S. (2018) Hydrothermal catalytic deoxygenation of fatty acid and bio-oil with in situ H<sub>2</sub>. *ACS Sustainable Chemistry & Engineering*, **6**:4521–4530.
- Morgan, T., Grubb, D., Santillan-Jimenez, E., & Crocker, M. (2010) Conversion of triglycerides to hydrocarbons over supported metal catalysts. *Topics in Catalysis*, **53**:820–829.
- Moser, B. R. (2010) Camelina (*Camelina sativa* L.) oil as a biofuels feedstock: Golden opportunity or false hope? *Lipid Technology*, **22**: 270–273.
- Popov, S., & Kumar, S. (2015) Rapid hydrothermal deoxygenation of oleic acid over activated carbon in a continuous flow process. *Energy & Fuels*, **29**:3377–3384.
- Przybylski, R., Eskin, M., Mag, T., & McDonald, B. E. (2005) *Canola oil. Bailey's industrial oil and fat products*. Hoboken, NJ: John Wiley & Sons Inc.
- Santillan-Jimenez, E., & Crocker, M. (2012) Catalytic deoxygenation of fatty acids and their derivatives to hydrocarbon fuels via decarboxylation/decarbonylation. *Journal of Chemical Technology and Biotechnology*, **87**:1041–1050.
- Sinichi, S., & Diosady, L. L. (2014) Isopropyl alcohol extraction of dehulled yellow mustard flour. *Journal of the American Oil Chemists' Society*, **91**:2143–2153.
- Sinichi, S., & Diosady, L. L. (2015) Isopropyl alcohol extraction of mustard oil. *International News on Fats, Oils, and Related Materials*, **26**:178–182.
- Sinichi, S., & Diosady, L. L. (2017) Production of isopropyl and methyl esters from yellow mustard oil-IPA miscella. *Journal of the American Oil Chemists' Society*, **94**:485–495.
- Tabatabaei, S., Boocock, D. G. B., & Diosady, L. L. (2014) Biodiesel feedstock from emulsions produced by aqueous processing of yellow mustard. *Journal of the American Oil Chemists' Society*, **91**: 1269–1282.
- Tabatabaei, S., & Diosady, L. L. (2012) The isolation of yellow mustard oil using water and cyclic ethers. *Journal of the American Oil Chemists' Society*, **89**:935–945.
- Vardon, D. R., Sharma, B. K., Jaramillo, H., Kim, D., Choe, J. K., Ciesielski, P. N., & Strathmann, T. J. (2014) Hydrothermal catalytic processing of saturated and unsaturated fatty acids to hydrocarbons with glycerol for in situ hydrogen production. *Green Chemistry*, **16**:1507–1520.
- Yang, O., Sohn, J., & Lee, D. (2018) Preface: International symposium on catalytic conversion of energy and resources. *Research on Chemical Intermediates*, **44**:3713–3722.
- Zhao, C., Kasakov, S., He, J., & Lercher, J. A. (2012) Comparison of kinetics, activity and stability of Ni/HZSM-5 and Ni/Al<sub>2</sub>O<sub>3</sub>-HZSM-5 for phenol hydrodeoxygenation. *Journal of Catalysis*, **296**:12–23.