

Optimizing Reaction Conditions for the Isomerization of Fatty Acids and Fatty Acid Methyl Esters to Their Branch Chain Products

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Received: 29 March 2010/Revised: 11 November 2010/Accepted: 12 November 2010/Published online: 1 December 2010
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Abstract In order to improve the oxidative stability and cold flow properties of oleic acid or methyl oleate, branch chain isomerization was conducted using a beta zeolite catalyst. Reaction conditions of temperature (200–300 °C), pressure (0.1–3.0 MPa), and co-catalyst (0–2 wt%) were optimized based on branch chain conversion and the cloud point of the ester following the isomerization reaction of oleic acid or methyl oleate. Fourier transform infrared spectroscopy (FTIR) and Gas Chromatograph equipped with Mass Spectrometry (GC/MS) analyses were used to analyze and quantify the isomerization product samples, while the cloud point of each sample was tested. The lowest and therefore, best cloud point measured was –15.2 °C at conditions of 200 °C, 3 MPa, and 2% co-catalyst using methyl oleate as a starting material. The highest branch chain conversion achieved was 50% under conditions of 300 °C, 1.5 MPa and 0% co-catalyst using oleic acid as a starting material. The use of oleic acid and methyl oleate is based on whether it is optimal to carry out the skeletal isomerization before or after the esterification reaction. Performing the isomerization reaction on the ester was preferred over the fatty acid based on the *trans* isomerization and cloud point results. Reducing the unbranched *trans* isomers was desirable in obtaining a low cloud point.

Keywords Fatty acid methyl ester · Isomerization · Branch chain · FTIR · Cloud point

List of symbols

MO	Methyl oleate
OA	Oleic acid
CP	Cloud point
BC	Branch chain
FTIR	Fourier transform infrared spectroscopy
FFA	Free fatty acid(s)
FAME	Fatty acid methyl ester(s)
GC/MS	Gas chromatograph/mass spectrometry

Introduction

Branched chain fatty acids (FA) and fatty acid methyl esters (FAME) have various applications. Branched FA compounds have applications as detergents and surfactants as well as uses in the lubricant industry. Branched FAME could have uses as a biodiesel additive. Cold flow properties and oxidative stability are two important properties if the branched chain FA and FAME are to be used as surfactants and fuel additives, respectively. FA are derived from vegetable oils which are composed of both saturated and unsaturated fatty acids. Saturated FA are stable, whereas unsaturated FA with a C=C are unstable and subject to oxidation [1]. Cold flow properties (cloud point and viscosity) can be improved by the addition of a branch chain [2]. Therefore, if the unsaturated fatty acid can be branched then hydrogenated, it would have the stability of a saturated FA or FAME, and should possess good cold flow properties (low cloud point and viscosity). The improvement of cold flow properties may allow the FAME to be used as a biodiesel additive in order to improve the cold flow properties and oxidative stability which are the

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two major issues with biodiesel. If the addition of branched chain FAME can give biodiesel a wider market use, a large market is created for the reaction product since biodiesel has many advantages over conventional diesel. Most studies have shown a clear life-cycle reduction in CO₂ emissions (e.g. 78% reduction reported by Tyson [3]) taking into account all fossil fuel energy used in crop cultivation and production. There can also be economic advantages to the use of biodiesel [4, 5].

FA and FAME can be branched using zeolite-based solid acid catalysts which facilitate the skeletal isomerization of the hydrocarbon tail, to form a methyl or ethyl side chain [6]. This reaction takes place in the pore space of the zeolite material containing acid sites. The side chain created from branching can lower the cloud point of the fatty acid or fatty acid methyl ester. By lowering the cloud point of a substance, the cold flow properties are improved [7]. Alkyl branching of the hydrocarbon chain can be a viable way of improving the cloud point. The mechanism of the isomerization has been proposed by Martens and Jacobs [8]. Inside the zeolite pore space the carbon–carbon double bond forms a cyclic three or four carbon carbocation ring within the hydrocarbon chain. This ring, being unstable, loses a proton, opens up and the corresponding methyl or ethyl side chain is formed. This process of carbocation formation and destruction can also cause a migration of the double bond towards the carboxylic acid group. As well at high temperatures, there is increased cracking of the molecule, generating undesired products [9].

Ideal conditions as stated by Koivusalmi and Jakkula [10] for the isomerization of FA are temperatures of 220–300 °C, pressures of 0.1–2 MPa, and with water used only as a co-catalyst of 1–3 wt%. The reaction is ideally carried out in a batch process for approximately 5–6 h with a zeolite catalyst loading of 1–10% [10]. Results from Yori et al. [6], found two different optimal temperatures of 275 and 150 °C based on the reduction of the cloud point as criteria. These authors found that the lower optimal temperature of 150 °C was due to a reduced amount of coking on the catalyst as compared to samples run at higher temperatures. The optimal high temperature is due to the increased fluidity and reaction rates that increase with higher temperatures. The difference in the optimal temperatures could be due to the unstable nature of the carbon–carbon double bond. Ngo et al. [7], studied the effects of different co-catalysts (water and methanol). The researchers performed the isomerization reaction on oleic acid (C18:1) at 250 °C for 6 h and 2.5 wt% zeolite loading. A maximum conversion of 99% oleic acid to products was achieved in the presence of 2 wt% H₂O based on the amount of oleic acid used. Under the conditions utilized,

the desired product, methyl isostearate, was formed with a selectivity of 82%.

Branch chain isomerization can be performed on either the fatty acid or a fatty acid methyl ester. The key purpose for the isomerization is to improve the cold flow properties of the compound and the stability through hydrogenation. Therefore, the isomerization step could be incorporated either before or after the esterification reaction, according to Fig. 1. The purpose of testing the isomerization reaction on both the FA and FAME is to see which compound is better suited for the isomerization reaction. Then either the necessary esterification/de-esterification reaction can be performed to create the desired FA or FAME.

Quantifying the conversion of the isomerization reaction usually involves the use of gas chromatograph (GC) with a mass spectrometer (MS). This method is often time consuming; and, the equipment necessary is often expensive to acquire. Use of Fourier transform infrared spectroscopy (FTIR) can be a simple, quick and low cost method of quantifying conversion when GC/MS is not available. FTIR measures the absorbance of the different bonds in a compound or mixture of compounds. Using this feature, compounds can be quantified by choosing a unique bond specific to the compound [11–13]. A standard curve can be generated using the absorbance of a particular bond as the dependant variable and the concentration of the compound as the independent variable. This method is particularly useful for measuring the conversion of an isomerization reaction due to the fact that isomerization changes the bond structure of a compound. FTIR has been proven useful in determining free fatty acid (FFA) content of oils [14–16]. There are limited studies in the literature on the use of FTIR for quantifying conversion of reactions based on changes in bond structure. Using the similar methods of FFA quantification, determination of the change in bond structure of fatty acids or fatty acid methyl esters (FAME) can be accomplished.

The objective of this study was to find the optimal reaction conditions for the isomerization of methyl oleate or oleic acid to their branched chain isomers, as well as to investigate whether the isomerization step should occur on the acid or the ester. With limited studies done on optimizing reaction conditions for the zeolite catalyzed branch chain formation, a full range of different temperatures, pressures, amounts of co-catalysts and starting materials was examined. These conditions were evaluated and optimized based on cloud point and conversion to their respective branched chain isomers. Once these conditions are optimized for the ideal compounds, future studies can be applied to mixtures generated from vegetable oils.

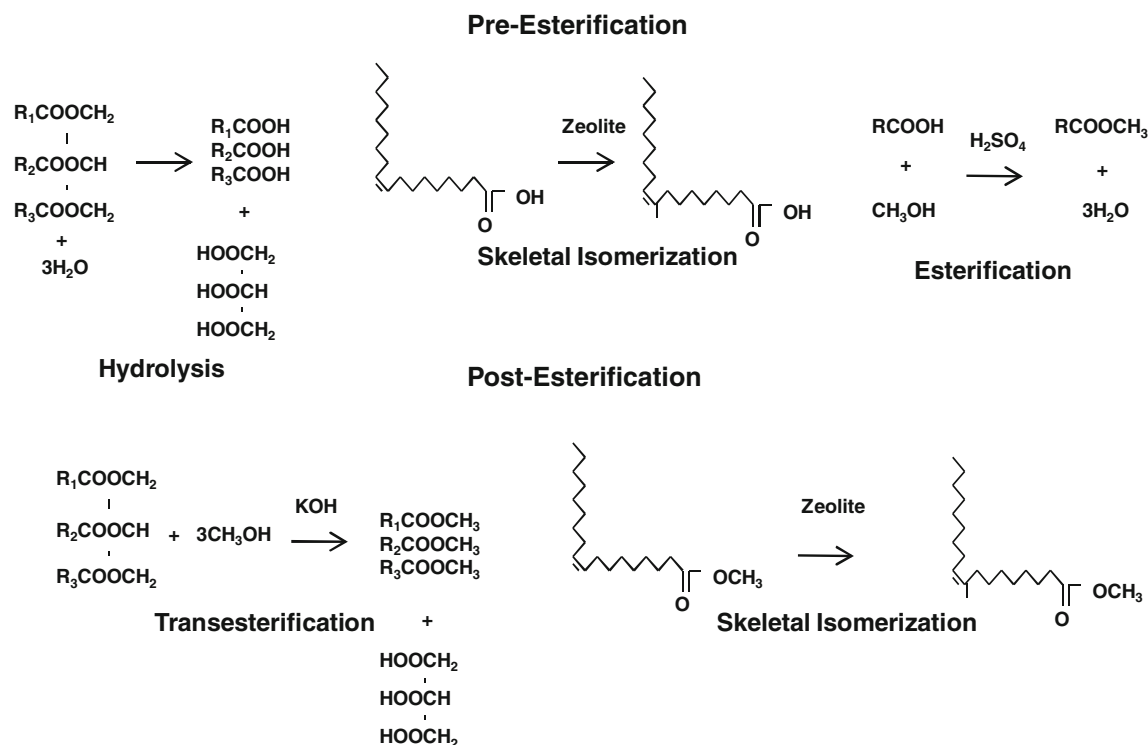


Fig. 1 Potential process for the combination of isomerization and esterification/de-esterification of fatty acids to branched chain fatty acids

Experimental Methods

Isomerization

The isomerization reactions were carried out in an Autoclave series mini-reactor purchased from Autoclave Engineers (Div. of Snap-Tite Inc.) (Erie, PA, USA) under the various reaction conditions described in Table 1. The mixture of methyl oleate (Acros Organics Fair Lawn, NJ, USA), methanol (Acros Organics Fair Lawn, NJ, USA) (if called for) and beta zeolite (Zeolyst International, Valley Forge, PA, USA) of 2 wt% were charged into the autoclave for the methyl oleate study. For the oleic acid (Fisher Scientific, Fair Lawn, NJ, USA) experiments, water was used in place of methanol as the co-catalyst. The beta zeolite catalyst had a pore size of $5.5 \times 5.5 \text{ \AA}$ and $7.6 \times 6.4 \text{ \AA}$, a Si/Al molar ratio of 360 and surface area of $620 \text{ m}^2/\text{g}$ (Zeolyst International). The catalyst was pre-calcined prior to experiments at $500 \text{ }^\circ\text{C}$ for 3 h and stored at room temperature until it was used for the experiments. The reaction mixture was mixed at a speed of approximately 600 rpm and purged with $>99\%$ N_2 for 15 min to remove all traces of oxygen prior to heating. The temperature was ramped up to the desired temperature within 10 min while purging with N_2 . Once the temperature was at the desired point the pressure was set to the desired pressure (Table 1). The reaction was carried out for 5 h

based on literature studies [9, 17]; and after which point, the reaction mixture was cooled to room temperature using cooling water, and lastly the pressure was released before the sample was removed from the autoclave. The sample and catalyst were transferred to a 50-mL centrifuge tube. The separation of catalyst from the sample was carried out in an Allegra 25R Centrifuge at 12,000 rpm for 20 min at room temperature. The ester samples were then transferred to a 20-mL glass container and analyzed for cloud point, FTIR absorbance and GC/MS analysis, while the fatty acid samples were esterified according to the esterification conditions. After analysis the samples were stored at $4 \text{ }^\circ\text{C}$ and shaded from direct light.

Esterification

Methanol and fatty acid were used at a molar ratio of 10:1. A catalyst of 2 wt% 95% sulfuric acid was mixed with the methanol in a 100-mL glass reaction chamber until fully dissolved. Next the fatty acid was added to the reaction mixture and stirred at 300 rpm while heated under reflux for 1.5 h. Once the reaction was complete the mixture was washed with distilled water 3 times to separate the ester from the methanol, acid and other impurities. Lastly, the ester was dried with a desiccant pack (calcium chloride) to remove any traces of water emulsified in the ester. The acid value of the ester was taken according to ASTM D974-08

Table 1 FTIR results of methyl oleate and oleic acid isomerization

Experimental conditions				Experimental results					
				MO study			OA study		
Run #	Temperature (°C)	Pressure (MPa)	H ₂ O or methanol (wt%)	Conversion (%)		CP (°C)	Conversion (%)		CP (°C)
				BC-isomer	<i>trans</i> -Isomer		BC-isomer	<i>trans</i> -Isomer	
C1	23	0	0	0	0	-15.6	0	0	-15.6
C2	250	1.5	0	0	0	-15.7	0	0	-15.6
1	200	0.1	0	14	1	-15.2	34	12	-15.1
2	225	0.1	2	0	3	-12.9	20	39	-13.4
3	250	0.1	1	21	8	-11.6	14	52	-8.5
4	275	0.1	0	11	28	-8.1	36	51	-6.7
5	300	0.1	2	12	40	16.2	42	54	-1.3
6	200	1.5	1	33	0	-14.9	25	57	-8.1
7	225	1.5	0	19	3	-14	31	57	-8.3
8	250	1.5	2	25	8	-13.3	20	57	-0.1
9	275	1.5	2	31	16	-12.2	12	57	2.9
10	300	1.5	0	22	30	-11.7	50	54	0.3
11	200	3	2	36	0	-15.2	33	35	-7.4
12	225	3	1	25	0	-14.7	31	39	-4.9
13	250	3	0	40	5	-14.9	40	42	-6.2
14	275	3	1	17	13	-13.3	27	65	-0.7
15	300	3	1	22	23	-11.8	5	64	0.7

C1 Control #1, C2 Control #2, BC Branch chain, MO Methyl oleate, OA Oleic acid, CP Cloud point

Table 2 Conversion to methyl oleate of isomerized oleic acid samples after esterification with 95% sulphuric acid in methanol

Run #	Acid value (mg KOH/g ester)	Conversion to methyl oleate ^a (%)
1	0.156	99.93
2	0.128	99.94
3	0.096	99.95
4	0.185	99.91
5	0.146	99.93
6	0.163	99.92
7	0.056	99.97
8	0.142	99.93
9	0.187	99.91
10	0.151	99.93
11	0.123	99.94
12	0.151	99.93
13	0.049	99.97
14	0.135	99.93
15	0.131	99.94

^a Remaining difference is oleic acid

method in order to ensure >99.9% conversion of fatty acid to fatty acid methyl esters (FAME). Table 2 shows that the esterification reaction achieved yields of no less than

99.91% and acid values between 0.049 and 0.185 mg KOH/g ester.

Instrumentation

The cloud point analysis was carried out on the Cloud, Pour and Freeze Point Analyzer, Model PSA-70X, acquired from Phase Technologies (Richmond, BC) with an accuracy of ± 1 °C. At the start of a run, a standard sample of known cloud point was tested to be within 1 °C of the known cloud point in order to ensure proper operation of the instrument. The sample cup was then cleaned with heptane and then flushed with 150 μ L of sample twice. Next the sample of unknown cloud point was tested, 150 μ L of sample was placed inside the analyzer and the temperature was lowered at a rate of 1.5 °C/min until crystals first appeared. The cloud point analyzer meets and complies with the ASTM D5773 method for the testing of the cloud point.

Infrared analysis was carried out on a Varian 3100 FTIR equipped with an Attenuated Total Reflectance (ATR) crystal. The absorbance of each sample was taken over the wavelength range 4,500–650 cm^{-1} . FTIR measures the absorbance of each chemical bond or specific group i.e., $-\text{CH}_3$ group of a compound. A 50- μ L amount of each sample was placed on a horizontal ZnSe crystal and

samples were scanned 64 times and co-added together at a resolution of 4 cm^{-1} . The signal was analyzed using Varian Resolutions Pro software which employed baseline and ATR correct features.

FTIR Quantification

The compound methyl 16-methyl heptadecanoate (Sigma–Aldrich, Oakville, ON, Canada) was used as a branched chain isomer for quantification. Standards were made in methyl oleate at concentrations of 75, 50, 25, 10 and 0%. Peaks of interest in the absorbance profile are $2,955$ and $2,864\text{ cm}^{-1}$ which corresponds to the $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively [11, 15]. The ratio of the $2,864/2,955\text{ cm}^{-1}$ peaks were calculated and plotted against the concentration of branched chain isomer and a standard curve was generated with an R^2 value of 0.99 in order to calculate the concentration of branched chain fatty acid methyl ester in the unknown samples. The ratio of peaks was linear to the wt% of branch chain fatty acid methyl ester in the sample analyzed. This allowed a linear equation to be generated and fast accurate analysis of the conversion to branch chain isomers.

The calibration of *trans* double bond formation was similar to the branched chain fatty except that the compound methyl elaidate (Sigma–Aldrich, Oakville, ON, Canada) was used as the standard. The absorbance of the *trans* double bond is at 968 cm^{-1} and a peak at $1,744$ ($\text{C}=\text{O}$) was used to stabilize the reading by taking the ratio of the two [11].

The heights of the peaks were utilized for all absorbencies due to poor peak resolution, especially useful between $3,100$ and $2,750\text{ cm}^{-1}$ where there was no full peak separation. Taking the heights simplifies the analysis and removes errors of area integration due to poor peak resolution [11]. The second safeguard against error was taking the ratio of two peaks, i.e., $2,864/2,955\text{ cm}^{-1}$ for branch chain isomers and $968/1,744\text{ cm}^{-1}$ for *trans* isomers. This removes the error due to variations from scan to scan.

GC/MS Method

GC/MS analysis and characterization was carried out on a Varian CP 3800 gas chromatograph (Varian, Mississauga, ON) equipped with a capillary WCOT fused silica $25\text{ m} \times 0.32\text{ mm}$ wax 52CP column with split ratio 10:1. A Varian 4000-8 mass spectrometer set to scan from 30 to 350 m/z at a rate of 1.5 scans/s. Helium was the carrier gas through the column at a rate of 2 mL/min . The injector temperature was set at $280\text{ }^\circ\text{C}$ and the column was initially set at $150\text{ }^\circ\text{C}$ for 0.5 min; ramped at $5\text{ }^\circ\text{C/min}$ to $200\text{ }^\circ\text{C}$ and held for 2 min; then ramped to $250\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C/min}$ and held for 5 min, for a total time of 27 min.

Optimization

The optimization was carried out with Minitab 15 software, by means of a full factorial design. The factors used were temperature, pressure and wt% co-catalyst. The responses that were optimized were the conversion and cloud point of the ester. The factorial design was a three-factor two-level design according to the reaction conditions stated in Table 1.

Results and Discussion

FTIR Analysis

Methyl oleate was taken as a baseline sample for absorbances and all samples after undergoing isomerization were compared for any change in absorbance peaks. The peaks of interest altered after the isomerization reactions were $2,955\text{ cm}^{-1}$ ($-\text{CH}_3$ group), $2,864\text{ cm}^{-1}$ ($-\text{CH}_2-$ group) and 968 cm^{-1} (*trans* $-\text{HC}=\text{CH}-$ group) as shown in Fig. 2. There was no other significant change to the absorbance spectrum of the samples after each run.

Methyl Oleate Study

As shown in Table 1, there is an increase in the cloud point as the reaction temperature increases, with the pressure having little effect on the cloud point, except for the $300\text{ }^\circ\text{C}$ and 0.1 MPa condition causing a sharp increase in the cloud point. The cloud points of the different experimental conditions range from $-15.2\text{ }^\circ\text{C}$ for $200\text{ }^\circ\text{C}$ and 3.0 MPa (Run 11) to $16.2\text{ }^\circ\text{C}$ for $300\text{ }^\circ\text{C}$ and 0.1 MPa (Run 5) as shown in Table 1. These results are consistent with the study by Yori et al. [6], where the low temperature of $150\text{ }^\circ\text{C}$ was the

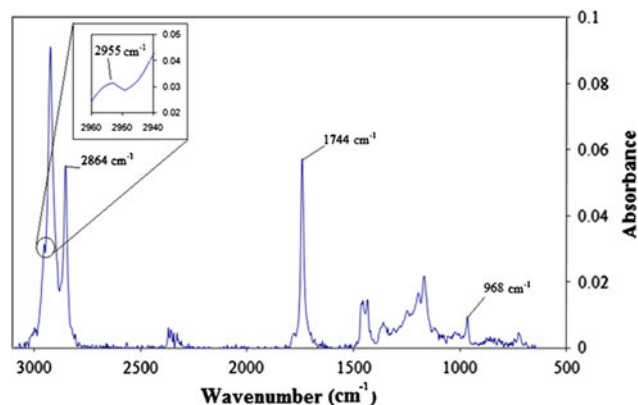


Fig. 2 FT-IR absorption spectra of isomerized methyl oleate under the reaction conditions of $250\text{ }^\circ\text{C}$ and 0.1 MPa

optimal reaction temperature for decreasing the cloud point of biodiesel, using a similar zeolite-based catalyst and a temperature range of 125–275 °C in nitrogen gas at atmospheric pressure. The conversion of methyl oleate to branched chain esters under the various reaction conditions has also been investigated. However, the conversion to branched chain isomers does not follow any specific temperature dependence, indicating reaction temperature is not a significant factor within the range studied. Increasing the pressure of the reaction increased the conversion, but only at low temperatures (200–250 °C). Branch chain conversion ranges from 0 to 40% for reaction conditions 225 °C and 0.1 MPa and 250 °C and 3.0 MPa (Runs 2 and 13 in Table 1), respectively.

Experimental reproducibility was tested by running triplicates of two experimental conditions chosen at random. The standard deviation of the results were calculated as 3.2 and 2.1% for Runs 1 (200 °C and 0.1 MPa), and 3 (250 °C and 0.1 MPa), respectively. Therefore, the difference in results had to be >4% for the difference to be significant. The cloud point analysis was also repeated and the deviation is within the ± 1 °C accuracy of the instrument which confirmed the reproducibility of the results.

The rise in cloud point with increasing reaction temperature is due to the undesired isomerization reaction which changes the *cis* double bond configuration to a *trans* double bond within the molecule. The change in bond configuration is also what explains the rise in cloud point. The melting point of a substance is an indicator of its cloud point, therefore, for example, methyl elaidate (*trans* double bond ester) has a much higher melting point of 9 °C [2] than that of *cis* double bond ester methyl oleate –20 °C [18]. This *trans/cis* isomerization ratio increases as reaction temperature increases, and decreases with increasing reaction pressure. The MO (methyl oleate) runs in Table 1 show a substantial increase in cloud point from –8.1 °C (275 °C and 0.1 MPa) to 16.2 °C (300 °C and 0.1 MPa) which was due to the sharp increase in *trans* bond formation of 28–41%, respectively, and negligible increase in branch chain formation. A comparison of the cloud point results versus the branch chain and *trans* isomer isomerization results shows that *trans* isomers have a much greater negative effect on the cloud point than the potential positive effect of branching the hydrocarbon. A case where the branch chain formation directly affects the cloud point is shown in Table 1 for the MO runs between Run 1 (200 °C and 0.1 MPa) and Run 2 (225 °C and 0.1 MPa). The cloud point increases from –15.2 to –12.9 °C, and the branch chain conversion decreases from 14 to 0%, respectively; while, there is negligible increase in the *trans* bond isomerization. The presence of the *trans* bond esters causes a rise in the cloud point of the mixture. This illustrates the

advantages that branching the hydrocarbon chain can have on the cloud point of the biodiesel.

Oleic Acid Study

Isomerization reactions were carried out on oleic acid under the reaction conditions of 200–300 °C and 0.1–3 MPa with 0–2 wt% co-catalyst. After the isomerization reaction was completed, the mixture was centrifuged and esterified to create an ester as previously stated. The OA (oleic acid) cloud point results, shown in Table 1, increased with increasing reaction temperature: ranging from –15.1 °C for Run 1 (200 °C and 0.1 MPa) to 2.9 °C for Run 9 (275 °C and 1.5 MPa). The increase in pressure from 0.1 to 1.5 MPa increased the cloud point in every case; whereas, an increase from 1.5 to 3.0 MPa did not consistently raise the cloud point. The rise in cloud point can be explained again by the unwanted side reaction of *cis* double bond configuration conversion to *trans* configuration.

The OA branch chain conversion results (Table 1) are very erratic, with no clear pattern that emerges. The values range from 4% for Run 15 (300 °C and 3.0 MPa) to 51% conversion for Run 10 (300 °C and 1.5 MPa), which correspond to a study by Zhang and Zhang [17] showing a branch chain conversion range of approximately 8–40% using a variety of different catalysts. Most of the results from this work show conversion to branch chain products to be in the 30–40% range. This is consistent with the results of Ha et al. [19], and Tolvanen et al. [20], who have reported conversions of 32 and 30% branch chain isomers, respectively, using a zeolite based catalyst and oleic acid and linoleic acid as a starting material.

An emerging pattern is the correlation between the *trans* isomer conversion, branch chain conversion and cloud point. There are two cases where cloud point decreases with increasing temperature for the OA study. First case, by increasing the temperature from 275 to 300 °C at 1.5 MPa, the cloud point of 2.9 °C decreases to 0.3 °C, while the branch chain conversion increases from 12 to 50% with negligible change in *trans* isomer conversion. Therefore the drastic increase in branch chain isomer could have had a positive effect on the cloud point. A second case is the decrease in cloud point from –4.9 °C (225 °C and 3.0 MPa) to –6.2 °C (250 °C and 3.0 MPa), while the *trans* isomer conversion is negligible and the branch chain conversion increases from 32 to 41% in the OA study, as shown in Table 1. The second case takes less of an increase in branch chain isomers to affect cloud point because the *trans* isomer conversion is lower: 57% compared to 40% in cases one and two, respectively. These two results indicate that branching has the potential to decrease the cloud point by at least 2.5 °C given the proper conditions.

GC/MS Analysis

A GC/MS analysis was performed on the products of the reaction conditions 1–15 for both starting material in order to identify the compounds and verify the FTIR results. The MS analysis of the results showed various compounds, some detected by the FTIR analysis and others that were not. Figure 3 shows a typical GC spectra obtained at reaction conditions 250 °C and 0.1 MPa. GC/MS analysis results are summarized in Tables 3 and 4 for the methyl oleate and oleic acid starting material, respectively. The MS analysis has identified four different *trans* methyl octadecenoates. These products are formed from carbocation formation, migration and reforming as a *trans* double bond at the various carbons without branching [21]. The concentration of the various *trans* bond esters decreases as the double bond position is shifted farther from the original 9 position, with the concentration of position 9 > position 11 > position 8 > position 6. The trend is held constant, with the overall amount increasing with temperature. The increase in temperature increases the degree of double bond migration with the high temperatures having the greatest amount of methyl 6-octadecenoate due to the higher reaction rates at higher temperatures.

The overall conversion of methyl oleate increases with increasing temperature and is the highest with the median pressure value of 1.5 MPa. As conversion increases so does the cloud point of the sample in all but one of the cases. The oleic acid starting material reaction at 275 °C and 1.5 MPa has a conversion of 75% with a cloud point of 2.9 °C; while, under 300 °C and 1.5 MPa reaction conditions, has a cloud point of 0.3 °C with a conversion of 80%. This decrease in cloud point is most likely due to the significant rise in methyl isooctadecenoates from 25 to 50%, respectively. The methyl isooctadecenoates are grouped together in the results due to the inability of the MS to differentiate between the limited branched fatty acids in the library.

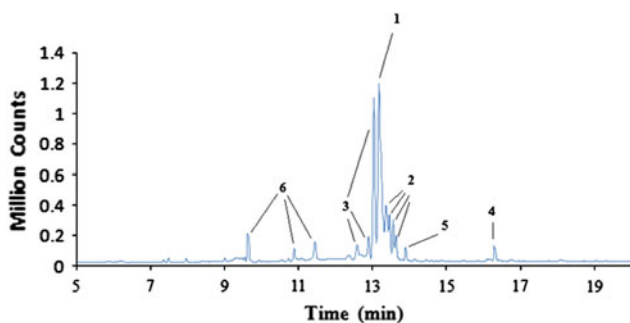


Fig. 3 GC analysis of reaction products of isomerized ester at reaction condition 250 °C and 0.1 MPa, **1** *cis*-methyl octadecenoate, **2** *trans*-methyl octadecenoate, **3** methyl isooctadecenoates, **4** methyl hydroxyoctadecenoate **5** γ -stearolactone and **6** Shorter chain methyl hexa-, penta- and tetradecenoates (cracked products)

The slight discrepancy between the GC/MS and FTIR results can be attributed to two factors. First the FTIR detects the *trans* configuration of the carbon–carbon double bond in both the branched and unbranched compounds, whereas the GC/MS separates the compounds and measures them individually (i.e. (3) and (2.1–2.4) in Tables 3 and 4); therefore, giving two different results. A second reason is the effect of the CH₃ group on the IR absorbance of the C=C bond. The peak used to quantify the *trans* double bond is the group R¹HC=CHR². The group frequency for the unbranched molecule (R¹HC=CHR²) is in the range of 980–960 cm⁻¹. When a methyl branch is added, this changes the group to R¹R³C=CHR², thus affecting the intensity and widening the peak [22]. However, overall results from the GC/MS analysis support the FTIR findings of bond rearrangement with respect to the reaction conditions.

Three products identified by the GC/MS analysis and not through FTIR analysis were methyl hydroxyoctadecenoates, stearolactones and cracked products. These products were not picked up by the FTIR because they do not differ significantly in bond structure and exist at small concentrations of <3% for the hydroxyl esters and the stearolactones and <5% for the cracked products. These compounds also only exist in samples run at high temperatures, i.e., >250 °C. Their effect on cloud point would be minimal, since C₁₄–C₁₆ and hydroxyl esters have a lower melting point and therefore, a lower cloud point than that of the methyl octadecenoates [2, 18]. Therefore, using melting points as indicators of cloud points, these three species would not have a significant effect on increasing cloud point of the samples.

Optimization Study

An optimization study was conducted to examine the effects of the co-catalyst on the cloud point and branch chain conversion of the various reaction products. There is evidence in the literature that supports the idea of using water or methanol to improve the conversion of the isomerization reaction by facilitating the transfer of the protons [7, 10, 20]. Beta zeolite being an acid catalyst, it will catalyze the esterification/de-esterification reactions. Therefore, this study uses water for the oleic acid experiments and methanol for the methyl oleate experiments in order to prevent these reactions from taking place. The use of a factorial design allows for the user to get the maximum amount of data from a reasonable amount of experiments [23]. A secondary purpose to the optimizations study is to find an optimal set of reaction conditions. The conditions studied were temperature, pressure and wt% co-catalyst. The responses that were optimized were the branch chain conversion (BC) and cloud point (CP) of methyl oleate

Table 3 GC/MS analyzed isomerization products of methyl oleate

Run #	Temperature (°C)	Pressure (MPa)	Water (wt%)	Conversion ^a (%)	Area (wt%) ^b								Cloud point (°C)	
					3	2.1	2.2	2.3	2.4	5	6	4		
C1	23	0	0	0	0	0	0	0	0	0	0	0	0	–15.6
C2	250	1.5	0	3	0	0	0	0	0	0	0	2	0	–15.7
1	200	0.1	0	24	15	2	0	0	0	0	0	0	0	–14.6
2	225	0.1	2	15	8	3	0	0	0	0	0	0	0	–12.9
3	250	0.1	1	30	19	4	1	0	0	0	0	1	0	–11.6
4	275	0.1	0	35	11	8	2	2	1	2	1	1	1	–8.1
5	300	0.1	2	37	10	10	3	3	2	2	3	2	2	16.2
6	200	1.5	1	28	23	1	0	0	0	0	0	0	0	–14.9
7	225	1.5	0	23	9	2	0	0	0	0	0	0	0	–14
8	250	1.5	2	35	25	3	1	0	0	1	0	0	0	–13.3
9	275	1.5	2	42	23	4	3	0	0	2	2	0	0	–12.2
10	300	1.5	0	47	22	5	3	2	0	2	3	1	1	–11.7
11	200	3.0	2	19	16	1	0	0	0	0	0	0	0	–15.2
12	225	3.0	1	15	10	1	0	0	0	1	1	0	0	–14.7
13	250	3.0	0	24	18	3	2	0	0	1	1	1	1	–14.9
14	275	3.0	1	29	17	4	1	0	0	2	1	0	0	–13.3
15	300	3.0	1	33	22	4	2	1	0	1	2	1	1	–11.8

3 Methyl Isooctadecenoates, 2.1 *trans*-methyl 9-octadecenoate, 2.2 *trans*-methyl 11-octadecenoate, 2.3 *trans*-methyl 8-octadecenoate, 2.4 *trans*-methyl 6-octadecenoate, 5 stearolactone, 6 Shorter chain methyl esters (cracked products), 4 methyl hydroxyoctadecenoate, C1 control #1 no reaction pure product, C2 control #2 exposed to median reaction conditions for 5 h with no catalyst

^a Conversion is defined as $(100 - \text{unreacted methyl oleate}) \times 100\%$

^b GC separated area curves using dodecane as internal standard

(MO) and esterified oleic acid (OA), as summarized in Table 5. The optimal predicted conditions were experimentally verified to check the accuracy of the model as shown in Table 5. The results are organized to show the optimal conditions of each of the responses separately, and in various combinations. The optimal response for the combination of all four factors is 200 °C, 1.25 MPa and 0 wt% co-catalyst.

The two highest predicted values for branch chain conversion and cloud point were 53% and –17.5 °C, respectively. The highest branch chain conversion was for when oleic acid was isomerized; while, the lowest cloud point was when methyl oleate was isomerized. Therefore two contour plots of isomerized methyl oleate and oleic acid branch chain conversion, Figs. 4 and 5, respectively, were created to show the combined effect of the reaction conditions. From these plots it is clear that the optimal conditions do reflect the conditions predicted by the optimization study.

Melting Point and Mechanism

Melting points of a substance are accurate indicators of cloud points; therefore, melting point data from the

literature is used where cloud point data is lacking. The melting point of methyl stearate is 38 °C and the branched chain isomer methyl 16-methylheptadecanoate is 27 °C [2]; therefore, branching the chain provides advantages in lowering the melting point of a substance and subsequently the cloud point. The undesired side reaction of *cis* to *trans* double bond isomerization eliminates any reduction caused by the branching of the molecule. Methyl oleate (*cis* configuration) has a melting point of –20 °C and methyl elaidate (*trans* configuration) has a melting point of 9 °C [2]. Thus the potential 11 °C reduction from branching is negated by the possible 29 °C increase from the *cis* to *trans* double bond isomerization.

The results of the study all showed an increase in cloud point from the control values (–15.6 and –15.7 °C), which was not the intended goal of the study. However, an examination of the reaction products and research into the isomerization mechanism provides an understanding as to why the cloud points have increased. The mechanism for the branching of unsaturated fatty acids, forms a carbocation ring structure at the double bond, followed by the carbocation ring breaking and reforming the double bond and a methyl or ethyl side chain [8, 9, 24]. This process of double bond reforming changes the configuration of the

Table 4 GC/MS analyzed isomerization products of esterified oleic acid

Run #	Temperature (°C)	Pressure (MPa)	Water (wt%)	Conversion ^a (%)	Area (wt%) ^b								Cloud point (°C)	
					3	2.1	2.2	2.3	2.4	5	6	4		
C1	23	0	0	0	0	0	0	0	0	0	0	0	0	−15.6
C2	250	1.5	0	3	0	0	0	0	0	0	0	2	0	−15.7
1	200	0.1	0	31	22	2	1	2	1	0	2	0	−15.1	
2	225	0.1	2	42	19	5	4	3	2	0	3	0	−13.4	
3	250	0.1	1	63	24	8	3	3	2	1	3	1	−8.5	
4	275	0.1	0	57	34	7	4	3	2	0	2	1	−6.7	
5	300	0.1	2	69	42	9	5	3	2	0	3	2	−1.3	
6	200	1.5	1	42	28	5	1	1	0	1	2	0	−8.1	
7	225	1.5	0	50	29	5	3	2	1	3	4	0	−8.3	
8	250	1.5	2	67	22	10	5	2	3	3	3	2	−0.1	
9	275	1.5	2	75	25	15	6	5	3	3	4	2	2.9	
10	300	1.5	0	80	50	8	5	4	3	0	4	2	0.3	
11	200	3.0	2	42	27	3	1	1	1	1	3	0	−7.4	
12	225	3.0	1	63	25	9	4	2	2	1	3	1	−4.9	
13	250	3.0	0	65	41	8	6	3	1	3	2	1	−6.2	
14	275	3.0	1	70	21	10	6	3	3	2	2	2	−0.7	
15	300	3.0	1	71	10	16	8	6	5	2	2	2	0.7	

3 Methyl Isooctadecenoates, 2.1 *trans* methyl 9-octadecenoate, 2.2 *trans*-methyl 11-octadecenoate, 2.3 *trans*-methyl 8-octadecenoate, 2.4 *trans*-methyl 6-octadecenoate, 5 stearolactone, 6 Shorter chain methyl esters (cracked products), 4 methyl hydroxyoctadecenoate, C1 control #1 no reaction pure product, C2 control #2 exposed to median reaction conditions for 5 h with no catalyst

^a Conversion is defined as $(100 - \text{unreacted methyl oleate}) \times 100\%$

^b GC separated area curves using dodecane as internal standard

Table 5 Response optimization of reaction conditions based on cloud point (°C) and branch chain conversion (wt%)

#	Factors optimized	Optimal reaction conditions			Response (predicted)	Response (experimental)	Difference ^a (%)
		Temperature (°C)	Pressure (MPa)	co-catalyst (wt%)			
1	CP (MO)	200	0.1	2	−17.5	−15.8	9.7
2	CP (OA)	200	0.1	0	−15.2	−15.5	−2.0
3	BC (MO)	200	3	0	39	36	7.6
4	BC (OA)	300	1.5	0	53	50	5.7
5	CP (MO) & BC (MO)	200	3	0	−16.7	−15.4	7.8
					39	35	10.3
6	CP (OA) & BC (OA)	200	0.1	0	−15.2	−15.5	−2.0
					36	40	−11.1
7	CP (MO), CP (OA), BC (MO) & BC (OA)	200	1.25	0	−15.2	−14.9	2.0
					−11.6	−12.2	−5.2
					25	31	−24.0
					32%	40%	−25.0

CP cloud point, BC branch chain product, MO methyl oleate starting material, OA oleic acid starting material esterified post reaction

^a % difference of predicted versus experimental results

double bond from the *cis* configuration to the *trans* configuration. This is due to the fact that it is thermodynamically more stable to reform as a *trans* bond [25, 26]. The

experimental results show that there is *trans* isomers formed without concomitant branching. Therefore, when the double bond is reformed it may or may not reform with

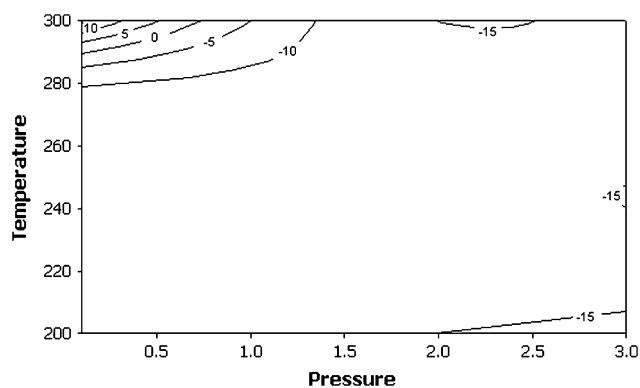


Fig. 4 Contour plot of two-way interaction of temperature (°C) and pressure (MPa) on cloud point (°C) for isomerization reactions carried out on methyl oleate

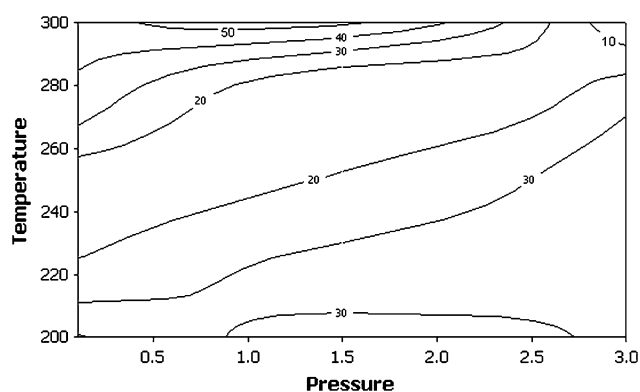


Fig. 5 Contour plot of two-way interaction of temperature (°C) and pressure (MPa) on branch chain conversion (wt%) using oleic acid as a starting material

a branch chain, depending on the reaction conditions. A *trans* bond ester without a methyl side chain is a negative by-product because of its high melting point and can be attributed to the rise in cloud point of the experimental results. Therefore, future efforts will focus on finding optimal conditions for increasing the branched isomers while reducing the unbranched *trans* isomer by-products.

Conclusion

Branch chain isomerization was achieved for all reaction conditions using a beta zeolite catalyst. Both oleic acid and methyl oleate were isomerized with oleic acid showing higher conversion values. The optimal conditions for skeletal isomerization are oleic acid run at 300 °C and 1.5 MPa. However, when the cloud point of the ester is taken, the optimal results are methyl oleate run at 200 °C and 3 MPa. The optimal cloud point and branch chain conversion based on experimental results were −15.2 °C (methyl oleate at 200 °C and 3 MPa) and 50% (oleic acid

at 300 °C and 1.5 MPa). This contrast between optimal branching and optimal cloud point is due to the fact that increasing the temperature had the negative effect of increasing the cloud point of the samples. The rise in cloud point was due to the undesired side reaction of *trans* isomerization, which straightens the hydrocarbon chain thereby increasing the cloud point. Although GC/MS analysis detected small concentrations of hydroxyl side chains and cracked products, they did not possess the high melting point of the *trans* bond methyl esters or large enough concentrations to significantly affect the cloud point. Though there is a potential benefit to creating a branch chain isomer, efforts are needed to reduce the amount of unbranched *trans* isomer production. The ideal goals of this study were to branch the FA and FAME as well as lower the cloud point. Although the first objective was accomplished, the cloud point of the FAME was not improved. However, this study provided an insight as to why creating a branch chain can negatively affect the cold flow properties of the methyl oleate.

Acknowledgments The authors wish to acknowledge the financial contribution of the Natural Sciences and Engineering Research Council of Canada.

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