

Article

Use of Isomerization and Hydroisomerization Reactions to Improve the Cold Flow Properties of Vegetable Oil Based Biodiesel

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Abstract: Biodiesel is a promising alternative to petroleum diesel with the potential to reduce overall net CO₂ emissions. However, the high cloud point of biodiesel must be reduced when used in cold climates. We report on the use of isomerization and hydroisomerization reactions to reduce the cloud point of eight different fats and oils. Isomerization was carried out at 260 °C and 1.5 MPa H₂ pressure utilizing beta zeolite catalyst, while hydroisomerization was carried out at 300 °C and 4.0 MPa H₂ pressure utilizing 0.5 wt % Pt-doped beta zeolite catalyst. Reaction products were tested for cloud point and flow properties, in addition to catalyst reusability and energy requirements. Results showed that high unsaturated fatty acid biodiesels increased in cloud point, due to the hydrogenation side reaction. In contrast, low unsaturated fatty acid biodiesels yielded cloud point reductions and overall improvement in the flow properties. A maximum cloud point reduction of 12.9 °C was observed with coconut oil as the starting material. Results of the study have shown that branching can reduce the cloud point of low unsaturated fatty acid content biodiesel.

Keywords: cloud point; fatty acids; hydrolysis; methyl branching; zeolites

1. Introduction

Increases in the use of fossil fuels are leading to a noticeable effect on the Earth's climate and ecosystems. In 2009 alone, some 84,000 MT of carbon in the form of CO₂ was released from fossil fuel burning and related uses [1]. Up until now, the World's oceans have absorbed most of the CO₂, allowing for a slight rise in atmospheric CO₂ to 385 ppm, up from 300 ppm in the year 1900 [2]. Fossil fuels are finite resources; society's dependence upon them could lead to catastrophic results once the fuel has disappeared. There is not one solution to replacing fossil fuels, however, there are various alternatives, including biodiesel. As studies have shown, use of biodiesel indicates a clear life cycle reduction in CO₂ emissions (57%–66%) when taking into account all fossil fuel usage in crop cultivation, harvesting and biodiesel production [3,4].

Biodiesel consists of the esters of fatty acids that are contained in vegetable oils and fats. While biodiesel has many benefits, a negative aspect towards its use is most notably the use of edible food oil for fuel, which includes appropriating farm land for energy crops. This problem can be alleviated by the use of waste oils, animal fats, and non-edible oils such as *Jatropha*. Another way to alleviate the problem is to use high yield vegetable oils for biodiesel production. If palm, coconut and, to a smaller extent, rapeseed oils are used, better use of the land is achieved. Furthermore, if a proper balance between fuel, food and feed is achieved, an increase in food production can be accomplished [5]. There is currently a need for high volumes of biodiesel due to legislation in many countries that mandate a minimum percentage to be used in transportation fuels [5]. Biodiesel does have issues before it can be used as a transportation fuel, including cost, cloud point and stability. Biodiesel contains two main classes of fatty acids: saturated fatty acids (SFA); and unsaturated fatty acids (UFA). SFA methyl esters have excellent fuel stabilities [oxidative stability index (OSI) > 40 h] and high melting points. UFA methyl esters have poor fuel stability (OSI 1.5–3 h) with low melting points (<−19 °C). Branched chain fatty acids (BCFA), which are not found in vegetable oils but can be created through catalytic reactions, yield methyl esters with superior fuel stability (OSI > 40 h) and low melting points (< 20 °C) [6]. Two methods used to branch a fatty acid are isomerization and hydroisomerization. These methods lower the melting point of the ester by adding a methyl branch on the hydrocarbon chain of the molecule, ultimately lowering the cloud point of the mixture [7].

Isomerization (I) uses solid acid catalysts to create a carbocation within the hydrocarbon chain at a double bond site. That carbocation then rearranges forming a methyl or ethyl branch, followed by the cation being de-protonated leaving a branched hydrocarbon [8]. Hydroisomerization (HI) is similar in that the only difference is an extra hydrogenation/dehydrogenation step is required. This is due to the fact that the starting material does not have a carbon-carbon double bond [8]. The two different reactions are needed because there are two different types of fatty acid methyl esters that make up biodiesel. The catalysts required are solid acid catalysts (H⁺ donors) for the I reactions. For the HI reactions, a solid acid catalyst with a hydrogenation/dehydrogenation metal is required. The metal used most frequently for this is platinum. These reactions have to be run in an I then HI combination in order to minimize some of the side reactions that can take place. The side reactions are *cis/trans* isomerization and hydrogenation. *Cis/trans* isomerization changes the biodiesel molecule to a straight configuration negatively affecting the cloud point. For example, the melting point of *cis* methyl oleate is −20 °C and that of the *trans* methyl elaidate is 10 °C [7]. Hydrogenation changes the unsaturated

molecule into a saturated molecule, again negatively affecting the cloud point. This is exemplified in the melting point of the unsaturated methyl oleate being $-20\text{ }^{\circ}\text{C}$, and that of the saturated methyl stearate being $37\text{ }^{\circ}\text{C}$ [7]. The reaction order of I, followed by HI, allows the unsaturated molecule to form a branch before being hydrogenated in the HI reaction, which negates some of the effects of the side reactions.

The design of the experiments has been developed from previous work on I/HI of fatty acids [9]. The vegetable oils in their original state are too large for the I/HI reactions, so they have to undergo hydrolysis to release the fatty acids. The fatty acids are then subjected to the I reaction, followed by the HI reaction. This process was found to be the optimal process for cloud point reduction of a SFA/UFA mixture [9]. In this study, fatty acids from a variety of vegetable oils and fats are reacted under isomerization and hydroisomerization conditions. The products undergo esterification to test for various fuel qualities and composition. The objective of this study is to find an optimal vegetable oil with reference to cloud point improvement based on the I and HI reactions.

2. Methods

2.1. Catalyst Preparation

Two different zeolite catalysts were prepared for this study: with and without platinum. The beta zeolite used for both reactions (isomerization and hydroisomerization) was CP814E (Zeolyst International, Conshohocken, PA, USA) with the specifications of Si/Al molar ratio of 25, and surface area of $680\text{ m}^2/\text{g}$. The catalyst used for the isomerization reaction was calcined at $500\text{ }^{\circ}\text{C}$ for 3 h, while that for the hydroisomerization reactions was impregnated with platinum. The compound used for impregnation was tetraammonium platinum (II) chloride $[(\text{NH}_3)_4\text{PtCl}_2]$. A solution of 0.0205 M $(\text{NH}_3)_4\text{PtCl}_2$ (10 mL) was added to beta zeolite (8 g) by incipient wetness to give a platinum loading of 0.5 wt %. The sample was then dried in an oven at $110\text{ }^{\circ}\text{C}$ for 24 h. In order to achieve platinum in the ground state it was reduced in a tube furnace at $350\text{ }^{\circ}\text{C}$ in a H_2 environment for 3 h.

2.2. Hydrolysis

Fatty acids contained in the oils must be hydrolyzed prior to undergoing isomerization and hydroisomerization, due to the large size of the triglyceride molecules. An Autoclave Engineers mini reactor was charged with water (20 g) and a select amount of vegetable oil to give a water to oil molar ratio of 20:1. The reactor was heated to $230\text{ }^{\circ}\text{C}$, pressurized to 4.0 MPa with N_2 gas and stirred at 500 rpm. The reaction was allowed to proceed for 2 h after which time the mixture was cooled to $80\text{ }^{\circ}\text{C}$, depressurized and moved to a separatory funnel. The mixture separates into two phases: the water and glycerol heavy phase; and the fatty acid light phase. The fatty acids are removed and stored in a cool dry place to await isomerization/hydroisomerization.

2.3. Isomerization

The beta zeolite catalyst without Pt was used for isomerization. A Parr 4848 autoclave was charged with fatty acid (30 g) and catalyst (1.2 g) to give a 4 wt % catalyst. The reactor was purged with H_2 gas for 5 min and heated up to $260\text{ }^{\circ}\text{C}$ while pressurized with H_2 to 1.5 MPa and stirred at a rate of

600 rpm. The reaction was allowed to proceed for 6 h. When the reaction was complete the reactants were cooled to 80 °C. The reactor was then depressurized and contents removed. The products were centrifuged to remove all traces of catalyst from the reacted fatty acid. Lastly, the reaction product was stored in a cool, dry, dark place to await analysis.

2.4. Hydroisomerization

The beta zeolite containing 0.5% Pt by weight was used for the hydroisomerization reaction. A Parr 4848 autoclave was charged with fatty acid (30 g) and catalyst (1.2 g) to give a 4 wt % catalyst. The reactor was then purged with H₂ gas for 5 min, heated up to 300 °C while pressurized to 4.0 MPa, and stirred at 600 rpm. After 16 h, the reactor was cooled to 80 °C, and depressurized. The reaction products were removed from the vessel and centrifuged at 12,000 rpm for 5 min. The supernatant was cooled and stored for further analysis.

2.5. Esterification

Fatty acids were esterified with methanol to create a fatty acid methyl ester (FAME) prior to testing for cloud point and composition. This was due to the high cloud point of saturated fatty acids, which is above the limit of the cloud point analyzer (50 °C). Additionally, fatty acids have much higher melting points leading to very high residence times in the gas chromatography (GC) column. Esterification was carried out in an Omni Reacto Station (Thermo Scientific, Ottawa, ON, Canada) using sulphuric acid as a catalyst. Approximately 20 g of reacted fatty acids were charged into the reactor with methanol (25 g) and sulphuric acid (0.4 g). This gave a methanol to fatty acid molar ratio of 10:1 and a 2 wt % catalyst. The sulphuric acid and methanol were added and allowed to mix thoroughly at 350 rpm; next, the fatty acid was added to the mixture and the temperature was set to 65 °C. The reaction was allowed to proceed for 2 h under reflux conditions. Once the reaction was complete the ester was cooled and water washed three times to remove all traces of methanol, acid and other impurities. The washed ester was then dried using anhydrous CaCl₂ and an acid number was taken to ensure >99% conversion.

2.6. Gas Chromatograph/Mass Spectrometer (GC/MS)

Analysis of the reaction products was carried out with the use of a Varian CP 3800 GC and Varian 4000-8 mass spectrometer. The column used was a 60 m × 0.25 mm inner diameter (i.d.) CP 50 wax column. The injector temperature was set at 230 °C. The column oven temperature started at 100 °C and was held for 0.5 min; increased to 150 °C at 10 °C/min and held for 5 min; then increased to 220 °C at 5 °C/min and held for 5.5 min. The carrier gas (He) began at a flow rate of 0.5 mL/min for 15 min; then increased to 2.0 mL/min at 0.3 mL/min/min and held for 10 min for a total run time of 30 min. A 10 mg sample was measured out and dissolved into enough heptane to give a total mass of 10 g. The solution was then mixed at 3000 rpm for 30 s. A sample of the solution (1 g) was then dissolved in heptane (9 g) and mixed at 3000 rpm for 30 s, to yield 100 mg/kg concentration of original sample. This process was repeated for all samples.

2.7 Cloud and Pour Point

The cloud and pour point analysis was carried out on the Cloud, Pour and Freeze Point Analyzer, Model PSA-70X (Phase Technologies, Richmond, BC, Canada) with an accuracy of ± 1 °C. In order to ensure proper accuracy of the instrument, a sample of known cloud point was tested to be within ± 1 °C of its cloud point. The sample cup was then cleaned with heptane and flushed twice with sample (150 μ L). The cloud point was tested by placing sample (150 μ L) inside the analyzer and lowering the temperature at a rate of 1.5 °C/min until crystals first appeared. The cloud point tests were performed in triplicate samples to ensure the reproducibility of the results. The cloud point analyzer meets and complies with ASTM D5773 method for testing of cloud point.

2.8. Carbon Deposition, CO Adsorption and Viscosity

The amount of carbon deposited on the catalyst was determined through the use of thermal gravimetric analysis (TGA). A SDT 600 (TA Instruments, Mississauga, ON, Canada) was used as the TGA unit. Catalyst samples were degassed overnight at 120 °C in a N₂ flow of 10 mL/min prior to loading into an alumina sample cup and into the TGA furnace. The gas was set to air and a flow rate of 100 mL/min was started. The furnace was set to isothermal for 5 min at 30 °C and then ramped up to 600 °C at 20 °C/min for a total time of 33.5 min. Weight loss of the material was taken as carbonaceous material that burned off in the O₂ rich environment.

CO adsorption was taken with the use of the TA Instruments SDT 600 TGA unit. Catalyst samples were degassed overnight at 120 °C in a N₂ flow of 10 mL/min loaded into an alumina sample cup and placed into the TGA furnace. The furnace was set to 30 °C and held for 10 min at a N₂ flowrate of 25 mL/min. Next the gas was switched to 50 mL/min CO/CO₂/N₂ mix and held for 15 min. The gas was then switched back to N₂ at 25 mL/min and held for 5 min. Finally, the temperature was ramped up to 500 °C at 20 °C/min for a total time of 53.5 min.

Viscosity measurements were taken using a Brookfield DV-E viscometer (Middleboro, MA, USA) at 40 °C. The rotor was set at 30 rpm giving shear rates of 36.7/s. Sample measurements were allowed to stabilize for 15 min and a viscosity reading was taken.

2.9. Acid Number

For the acid number test, sample (1 g) was added to propanol (10 mL) with 3 drops (0.15 mL) of phenylthaline and stirred at 180 rpm. A 0.1 M solution of KOH was added to the mixture drop by drop until the end point was detected. The volume of KOH was recorded and used to calculate the acid number. The hydrolyzed sample was split into two: one for original sample; and the second to undergo the isomerization/hydroisomerization reactions. The samples were then esterified and two different acid numbers generated for the original and reacted samples (Table 1). The acid number measurement ensures that the esterification reaction conversions are high enough such that only minute amounts of fatty acids are present in the final sample, thus not affecting the cloud point analysis.

Table 1. Acid number results for hydrolysis and esterification reactions.

Sample		Hydrolysis		Esterification	
		Acid number (mg KOH/g oil)	Conversion (%)	Acid Number (mg KOH/g fatty acid)	Conversion (%)
Palm oil	Original	197.3	95.2	3.71	98.21
	Reacted			2.98	98.56
Coconut oil	Original	249.6	96.9	4.02	98.64
	Reacted			2.94	98.84
Rapeseed oil	Original	189.3	94.7	1.72	99.14
	Reacted			3.26	98.37
Corn oil	Original	192.3	96.2	2.42	98.47
	Reacted			3.01	98.50
Soybean oil	Original	190.4	95.25	1.98	98.75
	Reacted			2.85	98.96
Animal fat	Original	187.9	94.9	2.22	98.69
	Reacted			2.04	98.84
Lard	Original	185.2	92.4	3.51	98.25
	Reacted			3.01	98.50
Olive oil	Original	189.6	94.9	1.79	99.08
	Reacted			3.02	98.47

2.10. Surface Area

Surface area analysis of the catalyst was conducted with the use of single point Brunauer, Emmett, and Teller (BET) analyzer. Catalyst samples were degassed overnight at 120 °C in a N₂ flow of 10 mL/min. A selected amount of catalyst was loaded into the glass sample tube and set into the unit. The sample tube was then immersed in liquid N₂ and an adsorption reading was taken. The liquid N₂ was then removed and a subsequent desorption value was taken. The two values were compared to assess accuracy of the results and the surface area was calculated.

2.11. Oligomer Determination

Oligomers (dimers) were analyzed using a TA instruments SDT Q600 Thermogravimetric Analyzer (TGA). Esterified product (30 mg) was added to an alumina sample cup and inserted into the TGA furnace. The furnace was then flushed with N₂ at 50 mL/min for 15 min at 30 °C. Next the flowrate was set to 25 mL/min N₂ and heated to 250 °C at 20 °C/min and held for 5 min. Then the furnace was heated to 360 °C at 20 °C/min and held for 5 min, for a total time of 41.5 min. The maximum temperature was chosen to be above the boiling points of fatty acids (approximately 360 °C) and below the boiling point of oleic acid dimers (approximately 660 °C), in addition to be lower than the temperature required for significant cracking to take place. The leftover residue from 5 runs (required five repeats due to small amount of residue leftover) was mixed and analyzed by Varian 3100 Excalibur (Agilent Technologies, Mississauga, ON, Canada) Fourier Transform Infrared Spectroscopy (FTIR). A scan range was set at 4500–600 cm⁻¹ with 128 scans co-added together. The wavelengths of note were the 1711 cm⁻¹ (C=O group of dimer acids) [10] and the 1742 cm⁻¹ (C=O group of FAMES) [11].

3. Results

3.1. Cloud Point Analysis

The results of the GC/MS compositional analysis (Table 2) show a substantial reduction in the unsaturated fatty acid (UFA) portion after the I/HI reactions. This was because the HI reaction hydrogenates the carbon-carbon double bond creating saturated fatty acid (SFA) compounds. This has the negative effect of raising the cloud point of the high UFA-containing vegetable oil biodiesels. However, the low UFA oil (palm and coconut) esters showed significant improvements in cloud point, as indicated in Figure 1. Coconut oil biodiesel had a greater cloud point improvement than palm oil biodiesel. This was due to coconut oil having a higher percentage of medium chain fatty acids (MCFA), which are fatty acids with C_{10} – C_{14} chain lengths. Results in Table 2 show that MCFAs yield greater conversions to the branch chain species over the long chain fatty acids (LCFA), which are composed of $>C_{14}$ length fatty acids. Smaller chain hydrocarbons are shown to have higher initial reaction rates over long chain hydrocarbons. This is consistent with the study by Claude and Martens [12], where the initial reaction rate decreases with carbon number increase from C_{10} to C_{18} alkanes. Similar interpretation may be applied to fatty acids, as it is the hydrocarbon chain that undergoes the hydroisomerization reaction.

The change in cloud point of the samples is in direct correlation with UFA content and the production of branched chain fatty acids (BCFA). The largest increase in cloud point was shown for the high UFA oil biodiesels, rapeseed and olive oil, because of high UFA to SFA hydrogenation, in addition to a low BCFA yield. The oils with low initial UFA content such as coconut and palm oils benefit from the reactions, yielding biodiesel cloud point reductions of -16.5 and -4.7 °C, respectively. This is attributed to the high BCFA production with modest UFA to SFA hydrogenation. High UFA content oils can benefit from branching as well. Corn oil, for example, had a BCFA yield of 40%, the largest of the high UFA oils, and had only a 4.4 °C increase in cloud point, despite losing 95% of its UFA content. This is compared to the 10.9 – 19.5 °C increase of other high UFA content oils (e.g., soybean and olive oils). However, high UFA samples do not follow any specific trend with respect to cloud point changes. In other words, cloud point changes cannot be predicted solely from the initial fatty acid profiles. For example, corn and soybean oils (having similar initial fatty acid profiles as shown in Table 2) show different cloud point changes of $+4.4$ and $+10.9$ °C, respectively (Figure 1).

As explained by Knothe [13], fatty acid profile of vegetable oils strongly affects many properties of the fuel, including cloud point, viscosity, and oxidative stability. Based on Moser [14], low UFA biodiesel results in high OSI. With improved coconut oil biodiesel showing low UFAs, it is inferred that a biodiesel with high OSI and the low cloud point of -2.3 °C is achieved. Table 3 shows the effect of the reactions on the flow properties. Note that as the cloud point decreases due to the I/HI reactions, the flow properties (pour point, viscosity and density) improve as well. Conversely, as the cloud point increases due to the I/HI reactions, the flow properties become increasingly inferior.

Table 2. GC/MS compositional analysis of reactant and product stream.

Sample		Unsaturated FAME (wt %)		Saturated Long Chain FAME (>C ₁₆ chain length) (wt %)		Saturated Medium Chain FAME (C ₁₀ –C ₁₄ chain length) (wt %)	
		Poly	Mono	SC	BC	SC	BC
Palm oil	Original	10	40	49	0	1	0
	Reacted	0	18	33	36	2	2
Coconut oil	Original	2	6	12	0	71	0
	Reacted	0	0	13	9	34	39
Rapeseed oil	Original	32	62	6	0	0	0
	Reacted	2	4	57	26	3	0
Corn oil	Original	59	28	13	0	0	0
	Reacted	0	4	48	40	0	2
Soybean oil	Original	61	24	15	0	0	0
	Reacted	2	3	43	21	5	14
Beef fat	Original	4	43	43	0	3	0
	Reacted	0	12	62	17	0	0
Lard	Original	10	44	40	0	2	0
	Reacted	0	3	59	25	2	2
Olive oil	Original	11	71	16	0	0	0
	Reacted	0	0	74	21	0	0

Original: Neat fat or oil sample; Reacted: Reacted under Isomerization/Hydroisomerization conditions; FAME: Fatty acid methyl ester; Poly: Poly-unsaturated fatty acid methyl esters; Mono: Mono-unsaturated fatty acids; SC: Straight chain fatty acid methyl esters; BC: Branch chain fatty acid methyl esters.

Figure 1. Cloud point changes of the various vegetable oil biodiesels before and after the isomerization and hydroisomerization reactions.

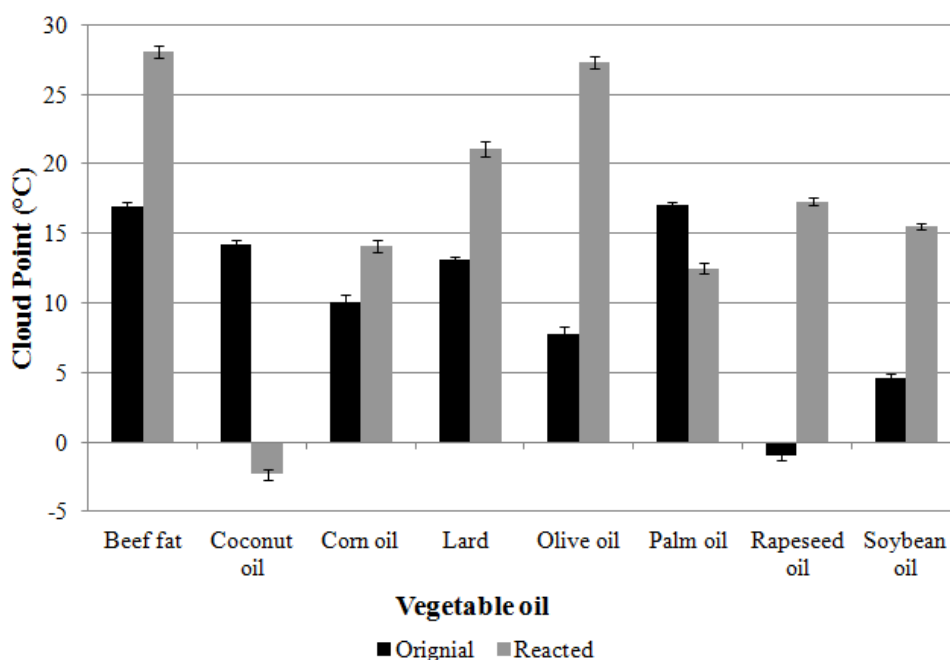


Table 3. Effect of isomerization/hydroisomerization reactions on fuel quality.

Sample		Cloud Point (°C)	Pour Point (°C)	Viscosity (mm ² /s) (@40 °C)	Density (kg/m ³) (@15 °C)
Palm oil	Original	17.5	15	4.42	882
	Reacted	12.8	9	4.08	864
Coconut oil	Original	14.2	9	4.58	850
	Reacted	−2.3	−3	3.57	824
Rapeseed oil	Original	−1.0	−15	4.53	874
	Reacted	17.3	18	6.95	902
Corn oil	Original	11.5	9	5.01	880
	Reacted	15.9	12	6.52	894
Soybean oil	Original	4.6	0	4.62	882
	Reacted	15.5	9	6.68	886
Animal fat	Original	16.9	15	5.84	892
	Reacted	28.1	24	6.99	905
Lard	Original	13.1	0	5.02	873
	Reacted	21.1	18	6.04	865
Olive oil	Original	7.8	−3	4.21	875
	Reacted	27.3	27	7.03	903

Branched chain esters have been shown to have lower melting points than their straight chain counterparts. Several studies [15] show melting point reductions using branched alcohols opposed to methyl alcohol. Additionally, studies by Yori *et al.* [16,17] were able to achieve cloud point and melting point reductions using isomerization reactions on biodiesel and oleic acid methyl ester, respectively. This study further cements the idea that branching biodiesel is a sound method of cloud point reduction. The two classes of fatty acids that cause low cloud points are UFA and BCFA methyl esters; however, these fatty acids lower the cloud point of biodiesel in different ways. As shown by Reaume and Ellis [9], the addition of BCFA methyl esters lower the cloud point in a linear fashion; whereas, the addition of UFA methyl esters only lowers the cloud point significantly at concentrations greater than 60%. Therefore, unless the oil contains a significant amount of UFAs, the cloud point will remain high, yielding greater importance to increasing BCFA content for biodiesel cloud point reduction.

3.2. Catalyst Recycle

The catalysts used for the I/HI reactions were studied for their reusability using as model compounds UFA oleic acid for isomerization and SFA palmitic acid for hydroisomerization. Note that vegetable oils were not used for the catalyst reusability study in order to avoid errors and inconsistencies in the fatty acid content of vegetable oils. Both the beta zeolite and Pt doped zeolite were washed with acetone after the reaction and tested for surface area, carbon deposition, and CO adsorption. Results in Table 4 show a correlation between carbon deposition and surface area. Calcination was used to remove the deposits and study the catalyst post reaction with no coke deposits. After calcination in air, the used catalysts surface area increased substantially. This indicates that the carbon deposits are blocking pore spaces leading to surface area decrease. Adsorption of CO shows that the carbon deposits also block the Pt on the catalyst surface. The carbonaceous material that

covers the catalyst was predominantly soluble in fatty acids. The uncalcined catalyst was immersed in a fatty acid solution and heated to 150 °C for 15 min. The catalyst was then cooled and washed with acetone and analyzed for surface area, carbon deposition and CO adsorption. The ester washed catalyst performs much better than the acetone-only washed catalyst, shown in Table 4. All three tests show an improvement in surface area and CO adsorption, though, not as well as calcination. The fatty acid wash was performed to investigate whether the coke deposited on the catalyst dissolves off in the first 15 min of the reaction. As confirmed by the increased surface area and CO adsorption, a certain amount of coke was removed, contributing to the catalytic activity of the used, uncalcined catalyst. The catalyst deposits can be categorized into soluble and insoluble residues. The ratio of soluble to insoluble coke (*i.e.*, the ratio of coke content from the reacted catalyst to coke content of the fatty acid washed catalyst) was 17:3 by weight, as shown in Table 4. This result is in agreement with a study by Villegas *et al.* [18], which shows an insoluble coke content on a hydroisomerization Pt zeolite catalyst of 13%–20%. The reduction in product yield for the recycled catalyst was 44% to 27%, giving a 40% reduction. This is consistent with a study by Lee *et al.* [15], which found a 47% reduction using a recycled hydroisomerization Pt zeolite catalyst.

In the isomerization results (Table 4) the cloud point of the isomerized product increases with BCFA yield. This is caused by the negative *cis/trans* isomerization side reaction, which turns the *cis* oleic acid to *trans* elaidic acid [19]. The melting points for the oleic acid ester is −20 °C, and for the elaidic acid ester is 10 °C [7]. In addition the *cis/trans* isomerization reaction rate is higher than the reaction rate for branching [19]; therefore, with increased catalyst activity, more elaidic acid is produced raising the cloud point of the product mixture. In contrast, the hydroisomerization reaction has no major side reactions, leading to cloud point decreasing with increasing BCFA yield.

Table 4. Physical properties of isomerization and hydroisomerization catalysts before and after the reactions.

Catalyst Sample	Yield of BCFA (%)	Cloud point of reacted ester (°C)	Surface area (m ² /g)	Carbon deposition (% w/w)	CO adsorption (% w/w)
Isomerization (original)	22	2.3	556	0	N/A
R1	14	−3.8	65	8	N/A
R2	11	−7.2	49	9	N/A
R1 ^c	17	0.8	297	0	N/A
R1 ^h	12	−4.1	125	3	N/A
Hydroisomerization (original)	44	20.1	374	0	1.1
R1 ^c	44	20.4	294	0	1
R1	27	23.8	50	17	≅0
R1 ^h	40	21.2	143	3	0.25
R2 ^c	41	21.9	219	0	0.95
R2	32	24.0	42	10	≅0

BCFA: Branched chain fatty acids; R1: catalyst used once before current reaction; R2: catalyst used twice before current reaction; ^c calcined in air at 500 °C for 2 h; ^h heated in a fatty acid bath.

3.3. Reaction By-Products

The two main reasons for the large cloud point increases are the *cis/trans* isomerization and hydrogenation side reactions [9,19]. These two reactions raise the melting point of a UFA methyl ester. For example, *cis* methyl oleate has a melting point of $-20\text{ }^{\circ}\text{C}$; while, the *trans* methyl elaidate has a melting point of $10\text{ }^{\circ}\text{C}$. The saturated methyl stearate has a melting point of $37\text{ }^{\circ}\text{C}$, and lastly the branched methyl isostearate has a melting point of $26\text{ }^{\circ}\text{C}$. The increases in melting point from the side reactions cannot be made up solely by the decrease caused by branching. Therefore, branching must be maximized while minimizing the side reactions.

The I/HI reaction creates other by-products aside from the fatty acids. These are cracking products (smaller chain fatty acids, alkanes and olefinic hydrocarbons), hydroxyls, dimers and coke material left on the catalyst. Dimers are formed from the oligomerization of two UFA compounds, creating a double fatty acid molecule attached at the carbon carbon double bond site [16]. These compounds cannot be classified using our GC/MS, due to their high boiling points; therefore, an isolation of dimers was conducted using a TGA unit under N_2 atmosphere. During heating of the samples the FAMES, cracking products, hydroxyls and any unesterified fatty acids evaporate off (due to their boiling points of $< 360\text{ }^{\circ}\text{C}$) leaving a small amount of residue. This residue (boiling point $> 360\text{ }^{\circ}\text{C}$) is analyzed with FTIR for dimer C=O bonds. The residue was less than 2% of the overall material and FTIR analysis showed it was $>95\%$ dimer fatty acids. The cracking products and hydroxyls were analyzed by the GC/MS analysis. The total weight of the reaction by-products was less than 7 wt %, with small chain fatty acids accounting for the bulk of the material.

3.4. Energy Use

The I/HI process uses more energy than the standard production process. However, due to the coconut oil yielding the highest BCFA yield and greatest cloud point reduction, there is no need for the isomerization process. This is because the isomerization process is for UFA compounds, of which coconut oil has very low amounts; hence, hydroisomerization alone is sufficient. The extra energy was calculated to examine whether there is still a net energy gain from producing improved biodiesel. Energy use for the hydroisomerization improvement process was calculated against the standard biodiesel production process. Energy calculations were based on the energy it takes to raise the temperature of the reactants to reaction temperatures. This was accomplished using specific heats of the reactants, in addition to calculating the heat losses through insulated reaction vessel walls and pressurization of gases. Heat capacities were calculated using differential scanning calorimetry (DSC) using a saffire standard and the following equation:

$$\frac{C_p}{C_p'} = \frac{m y}{m' y'} \quad (1)$$

where C_p = heat capacity of sample ($\text{J/g}^{\circ}\text{C}$); C_p' = heat capacity of saffire standard ($\text{J/g}^{\circ}\text{C}$); m = mass of sample (g); m' = mass of saffire (g); y = distance to baseline of sample (mm); y' = distance to baseline of saffire (mm).

The energy required to heat the materials present was calculated using Equation (2):

$$Q = mC_p\Delta T \quad (2)$$

where Q = Energy (J); ΔT = difference in temperature between reaction temperature and initial temperature ($^{\circ}\text{C}$); m = mass of sample (g); C_p = heat capacity of sample (J/g $^{\circ}\text{C}$).

The heat loss through the reaction vessel walls was calculated using Equation (3):

$$Q = \frac{\Delta T}{RA_s} \quad (3)$$

where Q = Energy (J); ΔT = difference in temperature between reaction temperature and initial temperature ($^{\circ}\text{C}$); R = insulation thermal resistance (m²K/Wm); A_s = surface area of vessel (m).

The R value was assumed for a high temperature insulation material which had a value of 145.7 m²K/Wm. Lastly, the energy required to compress the hydrogen to 4.0 MPa was calculated using the formula [20]. The compression was assumed to be adiabatic (isentropic) with three stages of compression:

$$\text{HP} = \left\{ \left[\frac{144NP_fVk}{33000(k-1)} \right] \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{Nk}} - 1 \right] \right\} \quad (4)$$

where HP = horsepower (W); P_f = Pressure drop (kPa); V = volume (m³); k = ratio of specific heats; P_2 = pressure required (kPa); P_1 = initial pressure (kPa); N = number of compression stages.

The two processes are defined as:

(1) Hydroisomerization improvement:



(2) Standard process:



The process comparison based on energy usage is shown in Table 5. Calculations gave total energy usages of 83.19 kJ and 4.04 kJ based on a 25 g sample of vegetable oil for the hydroisomerization and standard process, respectively. The extra 79.15 kJ of energy for the improvement process is substantial compared to the low energy use of the standard process; however, the energy content of biodiesel and glycerol by-product is 1030 kJ and 58 kJ, respectively. This gives the total energy for the additional process at <10% of the energy yielded from the biodiesel for the scale we have examined. Furthermore, some other side benefits to the process are: not using the transesterification reactions using KOH, thus avoiding emulsification problems [21]; and the hydrolysis method producing cleaner glycerol product which can be sold as pure glycerol as opposed to crude glycerol [22].

Similar processes are used to upgrade petroleum based fuels. Catalytic cracking and octane upgrading utilize similar solid acid catalysts and H₂ gas at high pressures and temperatures >500 $^{\circ}\text{C}$ [7]. The major difference in the petroleum industry is the lower cost of crude feedstock and much larger volumes available to process, *versus* the higher cost and lower volume vegetable oils. If a combined biofuel/petroleum process can be integrated into existing petroleum processing facilities, costs of upgrading biofuels can be significantly reduced or absorbed by the higher profit petroleum products.

Table 5. Energy use comparison for the hydroisomerization improvement biodiesel production process *versus* the standard biodiesel production.

Production Stage	Improvement (kJ/25 g oil)	Standard (kJ/25 g oil)
Hydrolysis		
Heating	14.08	N/A
Loss	4.60	N/A
Gas compression	0.01	N/A
Mixing	0.11	N/A
Hydroisomerization		
Heating	14.30	N/A
Loss	42.05	N/A
Gas compression	0.01	N/A
Mixing	0.88	N/A
Esterification/Transesterification		
Heating	6.24	3.04
Loss	0.79	0.89
Gas compression	0	0
Mixing	0.11	0.11
Total Energy Use	83.19	4.04

4. Conclusions

A reduction in cloud point of vegetable oil biodiesels has been shown through the use of isomerization/hydroisomerization. Improvements were successful on low UFA-containing vegetable oils, yielding reductions of 4.7 and 16.5 °C for palm and coconut oils, respectively. The reactions were unsuccessful at reducing the cloud points of the high UFA vegetable oils. Of the biodiesels that were improved, other fuel qualities were improved along with the cloud point, including viscosity and pour point. With the implementation of I/Hi reactions, there was a sizable energy increase (<10% of the energy contained in biodiesel is needed for the improvement process), due to the high reaction temperatures and additional hydrolysis step. However, cloud point reduction along with reduced biodiesel washing and cleaning help to offset the negatives associated with the energy increase.

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References

1. Friedlingstein, P.; Houghton, R.; Marland, G.; Hackler, J.; Boden, T.A.; Conway, T.; Canadell, J.; Raupach, M.; Ciais, P.; Le Quéré, C. Update on CO₂ emissions. *Nat. Geosci.* **2010**, *3*, 811–812.
2. Lammertsma, E.I.; de Boer, H.J.; Dekker, S.C.; Dilcher, D.L.; Lotter, A.F.; Wagner-Cremer, F. Global CO₂ rise leads to reduced maximum stomatal conductance in Florida vegetation. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 4035–4040.

3. Kaltschmitt, M.; Reinhardt, G.; Stelzer, T. Life cycle analysis of biofuels under different environmental aspects. *Biomass Bioenergy* **1997**, *12*, 121–134.
4. Beer, T.; Grant, T.; Williams, D.; Watson, H. Fuel-cycle greenhouse gas emissions from alternative fuels in Australian heavy vehicles. *Atmos. Environ.* **2002**, *36*, 753–763.
5. Amonette, J.E.; Woolf, D.; Street-Perrott, F.A.; Lehmann, J.; Joseph, S. Mitigation of climate change with biomass: Technical potentials and factors affecting implementation. In *Proceedings of 17th International Palm Oil Conference and Exopalma*, Cartagena, Colombia, 27 September 2012.
6. Karmakar, A.; Karmakar, S.; Mukherjee, S. Properties of various plants and animals feedstocks for biodiesel production. *Bioresour. Technol.* **2010**, *101*, 7201–7210.
7. Knothe, G.; Dunn, R.O. A comprehensive evaluation of the melting points of fatty acids and esters determined by differential scanning calorimetry. *J. Am. Oil Chem. Soc.* **2009**, *86*, 843–856.
8. Ono, Y. A survey of the mechanism in catalytic isomerization of alkanes. *Catal. Today* **2003**, *81*, 3–16.
9. Reaume, S.J.; Ellis, N. Synergistic effects of skeletal isomerization on oleic and palmitic acid mixtures for the reduction in cloud point of their methyl esters. *Energy Fuels* **2012**, *26*, 4514–4520.
10. Ismail, A.; van de Voort, F.; Emo, G.; Sedman, J. Rapid quantitative determination of free fatty acids in fats and oils by Fourier transform infrared spectroscopy. *J. Am. Oil Chem. Soc.* **1993**, *70*, 335–341.
11. Doumenq, P.; Guiliano, M.; Bertrand, J.; Mille, G. GC/FT-IR analysis of fatty acid methyl esters. *Appl. Spectrosc.* **1990**, *44*, 1355–1359.
12. Claude, M.C.; Martens, J.A. Monomethyl-branching of long *n*-alkanes in the range from decane to tetracosane on Pt/H-ZSM-22 bifunctional catalyst. *J. Catal.* **2000**, *190*, 39–48.
13. Knothe, G. “Designer” biodiesel: Optimizing fatty ester composition to improve fuel properties. *Energy Fuels* **2008**, *22*, 1358–1364.
14. Moser, B.R. Comparative oxidative stability of fatty acid alkyl esters by accelerated methods. *J. Am. Oil Chem. Soc.* **2009**, *86*, 699–706.
15. Lee, I.; Johnson, L.A.; Hammond, E.G. Use of branched-chain esters to reduce the crystallization temperature of biodiesel. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1155–1160.
16. Yori, J.C.; D’Amato, M.A.; Grau, J.M.; Pieck, C.L.; Vera, C.R. Depression of the cloud point of biodiesel by reaction over solid acids. *Energy Fuels* **2006**, *20*, 2721–2726.
17. Ngo, H.L.; Nuñez, A.; Lin, W.; Foglia, T.A. Zeolite-catalyzed isomerization of oleic acid to branched-chain isomers. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 214–224.
18. Villegas, J.; Kumar, N.; Heikkilä, T.; Lehto, V.P.; Salmi, T.; Murzin, D.Y. Isomerization of *n*-butane to isobutane over Pt-modified Beta and ZSM-5 zeolite catalysts: Catalyst deactivation and regeneration. *Chem. Eng. J.* **2006**, *120*, 83–89.
19. Reaume, S.J.; Ellis, N. Optimizing reaction conditions for the isomerization of fatty acids and fatty acid methyl esters to their branch chain products. *J. Am. Oil Chem. Soc.* **2011**, *1*, 1–11.
20. Horsepower required to compress air. The Engineering Toolbox Website. Available online: http://www.engineeringtoolbox.com/horsepower-compressed-air-d_1363.html (accessed on 13 November 2012).
21. Souza, M.S.; Aguiéiras, E.C.G.; da Silva, M.A.P.; Langone, M.A.P. Biodiesel synthesis via esterification of feedstock with high content of free fatty acids. *Appl. Biochem. Biotechnol.* **2009**, *154*, 74–88.

22. Thompson, J.; He, B. Characterization of crude glycerol from biodiesel production from multiple feedstocks. *Appl. Eng. Agric.* **2006**, *22*, 261–265.

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