

Low Cloud Point Biodiesel

Shanti Christopher Johnson

Mentors: Dr. David Hackleman

Dr. Travis Walker

School of Chemical, Biological, and Environmental Engineering

Oregon State University, 103 Gleeson Hall

Corvallis, OR 97331

BioResource Research, Bioenergy

Oregon State University, 137 Strand Agriculture Hall

Corvallis, OR 97331

David Hackleman, June 3, 2014
Department of Chemical, Biological, & Environmental Engineering

Travis Walker June 3, 2014
Department of Chemical, Biological, & Environmental Engineering

Katharine G. Field, BRR Director June 3, 2014

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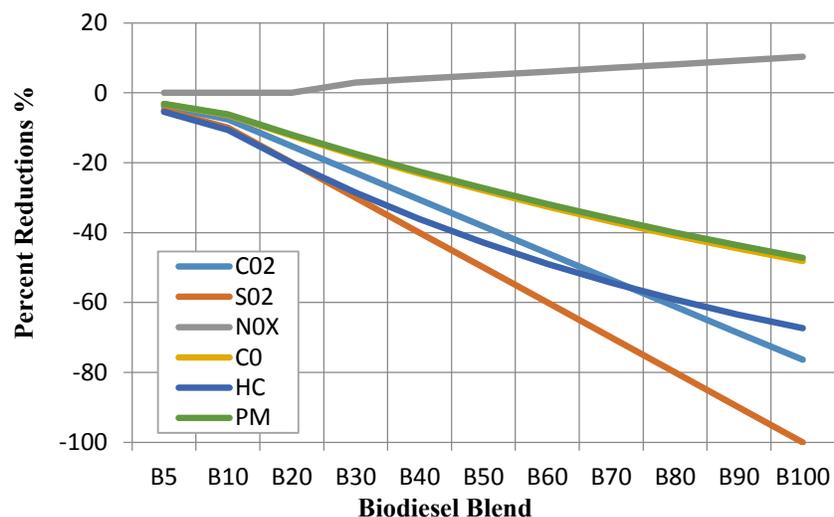
Abstract

The synergistic interplay between the removal of saturated methyl esters and the addition of deoxygenated fatty acids on depressing the cloud point temperature of biodiesel was investigated in this study. Canola biodiesel was produced in batch as a standard with a cloud point of 1.37 ± 6.3 °C. Saturated methyl esters were removed from the standard via urea fractionation resulting in a low saturate biodiesel with a cloud point of -21.06 ± 0.5 °C. Heptadecene was used as a standard for the major products produced from the deoxygenation of saturated fatty acids. Heptadecene was blended in ratios of 1 to 5 wt% in both the standard and low saturate biodiesel. The standard biodiesel blended with heptadecene did not show any statistically significant shift in the mean cloud point over the range. The low saturate biodiesel blended with heptadecene showed statistically significant deviations from the mean at 2, 4, and 5 wt%. A pseudo-eutectic system was observed between heptadecene and low saturate biodiesel with a minimum cloud point of -25.16 ± 2.5 °C at 2 wt% Heptadecene.

Introduction

Biodiesel, a drop-in fuel replacement for #2 diesel, is a blend of fatty acid esters that can be made from many different feedstocks including vegetable oil, tallow, and algal oil. One of the issues associated with biodiesel is the phase stability of the fuel during cold temperature operating conditions. The cloud point of petroleum and biodiesel is an index of the lowest temperature of utility for certain applications (ASTM). The cloud point is the temperature at which the first observable solids appear upon cooling.

A common strategy for depressing the cloud point of biodiesel is to simply blend biodiesel with petroleum diesel in volume ratios such as 50, 30, 20, and 5 % (B50, B30, B20, and B5). This is practical, and B20 is widely accepted as a suitable winter biodiesel blend (Cold Weather Guide). Unfortunately, by blending biodiesel, you are detracting from the reduced emissions B100 provides over petroleum diesel (figure 1).



A second strategy has been shown to affect the cloud point is using ethanol in the transesterification reaction as opposed to methanol (Couhtino). Making ethyl esters can decrease the biodiesel cloud point on the order of 5 °C, but the economics of using ethanol is the main deciding factor for industrial biodiesel production and the minimal cloud point reduction may not be worth the cost. Biodiesel may respond to store bought winterizing agents, but none were tested in this study of producing winter ready fuel. The two cloud point depression methods that were investigated here are urea fractionation and catalytic deoxygenation.

Figure 1. Life Cycle Emissions, Diesel Vs. Biodiesel Blends. The reduction in emissions as a function of biodiesel blend volume decreases for all emissions except NOX (Biodiesel.org). that

The cold flow properties of biodiesel are highly dependent on the fatty acid profile of the original triglyceride source. Thermodynamic models and fractionation experiments have shown that the cloud point of a biodiesel is limited by the saturated fatty acid ester content, even at low mass fractions (Figure 2). Biodiesel can be fractionated into its saturated and unsaturated components by urea fractionation. Urea has been shown to form an adduct with saturated biodiesel. Urea in the presence of an acceptable guest molecule will form hexagonal channels allowing for guest inclusion. Crystalline solids will precipitate out of a urea-methanol-biodiesel solution at room temperature, some of which are urea-saturated biodiesel adducts. A fraction that is high in unsaturated fatty acid esters will have a much lower cloud point than the fraction high in saturates.

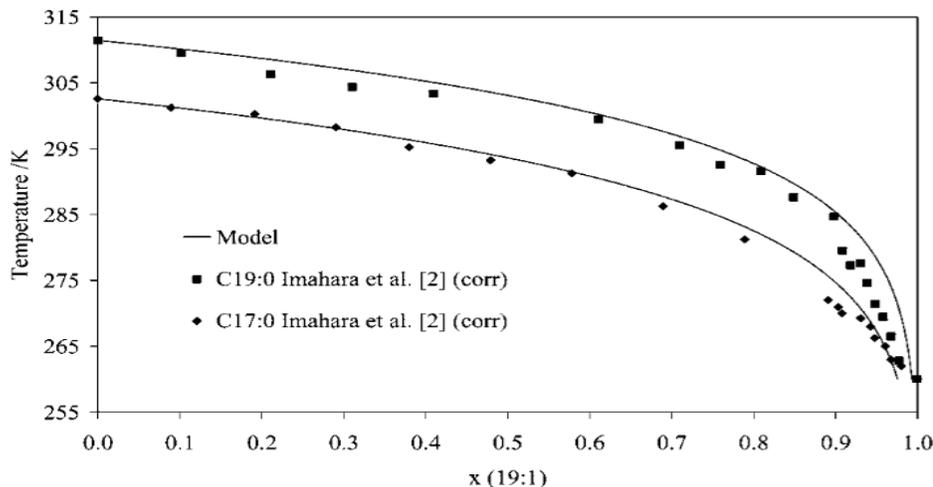


Figure 2. Experimental and predicted CPs of the methyl stearate plus methyl oleate (C19:0 plus C19:1) and methyl palmitate plus methyl oleate (C17 plus C19:1) systems. (Coutinho et al.)

Catalytic deoxygenation is under investigation by many research groups. Biodiesel and the fatty acids that make up the biodiesel may be modified under high temperature and low oxygen conditions to remove the oxygen within the carboxylic end group. Wang et al. has demonstrated a microwave-assisted process, which preferentially decarboxylates fatty acid soaps derived from biodiesel (Figure 3). Major products range from 8 to 17 n-alkenes and n-alkanes, with the major

product being heptadecene. A group from university of Oklahoma has decarboxylated methyl esters using a CSNaX catalyst at high temperature, their results indicated that major products were alkenes (Danuthia).

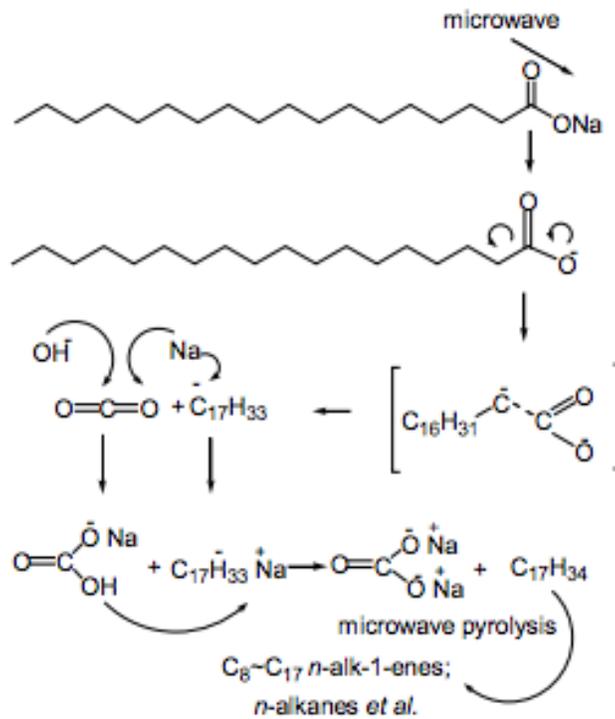


Figure 3. Reaction pathway for the decarboxylation of fatty acid soaps. A proposed pathway and methodology for saturate modification (Wang et al).

Materials and Methods

Biodiesel Production

Biodiesel was produced in 500 ml Erlenmeyer flask batches. The catalyst, 1.05 g of sodium hydroxide, was first added to the 500ml flask. Sixty ml of methanol was then added to the catalyst and the stirrer turned on without the addition of heat. Sodium hydroxide and methanol in solution is sodium methoxide. The sodium methoxide was stirred until all of the solid sodium hydroxide was dissolved, which usually required 30 minutes. Three hundred ml of canola oil was then added. Heat was set on low and the solution monitored so as not to reach 65° C, the boiling point of methanol. If the temperature gets too high, the methanol quickly evaporates, and the reaction will be incomplete. In the case of poor temperature control, excess methanol was added to ensure complete reaction. The solution of oil, sodium hydroxide, and methanol was allowed to react while being heated and mixed for one hour and thirty minutes. Once the reaction was finished, the solution would have a dark hue, indicative of free glycerin, which is darker than the produced biodiesel.

The solution was poured into a separatory flask and allowed to sit for 8 hour. The different specific gravities of the two main reaction products, glycerin and biodiesel, is the driving force that results in the solution separating out into two distinct layers. After 8 hours the glycerin was drained out of the bottom. What was left in the separatory flask is primarily biodiesel, but also contained trace amounts of glycerin, catalyst, various glycerides, and methanol. The trace contaminants could easily be removed by water washing the biodiesel.

The impure biodiesel was drained into a new 500 ml Erlenmeyer flask. A stir bar was added and the flask placed on a scientific hot plate to mix. Twenty ml of distilled water was added to the water and allowed to mix for an hour. The solution would turn a milky color indicating that there were trace contaminants in the biodiesel that were now dissolving into the water. The oil-water mixture was then placed in a new separatory flask, where it would again separate into two layers. After three days the bottom layer would be water and contaminants while the top was cleaned biodiesel. The water wash was repeated until the water cleanly and quickly separated from the oil. This usually took two cycles.

At this point the biodiesel was clean of contaminants and it was necessary to drive off any water that may still be in the biodiesel after separation. The biodiesel was poured into a new 500 ml beaker and put on the hot plate. A stir bar mixed the biodiesel while the temperature was increased to over 100° C. Reaching this temperature insured that most of the water had evaporated off. Roughly 250 ml of clean biodiesel made from canola oil esters was produced per batch.

Urea Fractionation

Laboratory grade urea (Sigma Aldrich), weighed out at 44 g, was added to a 500 ml vacuum flask. After the addition of 300 ml of methanol, the flask was mixed with a stir bar until most of the urea had dissolved. Fifty ml of the biodiesel was added. Crystals would form immediately after the biodiesel was added. The solution was continually mixed and the heat slowly increased. The temperature was stabilized at 45° C and allowed time to form a single liquid phase. After the solution was completely liquid the heat was turned off and the solution allowed to cool to room temperature while mixing.

Once the solution of methanol, biodiesel, urea crystals, and urea adduct crystals had cooled to room temperature the mixing could be stopped. The solution was allowed to sit at room temperature for at least a day. The mixture of urea crystals, biodiesel, and methanol was then filtered with a Buchner funnel and paper filter to separate the solid crystals. The liquid that was extracted would contain biodiesel that had low levels of saturated methyl esters, methanol, small urea crystals that had passed by the filter, and saturated methyl esters bound up in urea clathrate crystals. The solution was heated to drive off more of the methanol until urea started to crash out of solution. The solution was then allowed to cool while mixing and then set for a day. A solid-liquid extraction was performed on this solution. The resulting liquid phase was heated again until most of the methanol has evaporated off, leaving a two liquid phase solution of urea and biodiesel. This was allowed to cool to room temperature while being mixed, and then set for a day. The resulting crystalline matrix of urea and liquid biodiesel was finally separated using a cotton filter contained in a pipette.

The recovered biodiesel was heated to 170° C, Heating the biodiesel to 170° C would decompose most of the remaining urea. After cooling, Approximately 15 ml of biodiesel had been molecularly fractionated based on the saturation of the methyl ester species.

Heptadecene Biodiesel Blends

Standard biodiesel and low saturate biodiesel samples, in 15 ml volumes, were analyzed by the OSU Cloud Point Apparatus to baseline their cloud point temperature. Heptadecene (>90% TCI America) was added to both standard and low saturate samples in 1 weight percent (wt%) increments. Weight percent additions were measured using a scale. All Samples were analyzed by in triplicate by the Cloud Point Apparatus. Data was collected incrementally up to 5 wt% heptadecene.

Data Analysis

Urea fractionation efficacy was analyzed with a HP 5890 FID GC to qualitatively determine if the urea fractionation was successful. Biodiesel samples were made up in 5 ml vials by adding 5 drops of MSTFA, a silylation agent, and Biodiesel to react for one minute. The silylated biodiesel was then diluted with 5 ml of heptane. Integration function was not utilized for quantitative concentration data.

Cloud point temperature was determined using the OSU Cloud Point Apparatus (Figure 4). The cold box temperature was allowed to reach steady state before samples were tested. Biodiesel samples of 15 ml were tested individually and repeated in triplicates. Samples were thoroughly re-homogenized between runs to mitigate the known fractionation that occurs upon freezing. Samples were warmed in a water bath between replicates and sampling order was randomized. Run data was recorded with *Logger Pro software* and *Vernier sensor interface* (Figures 5 & 6).

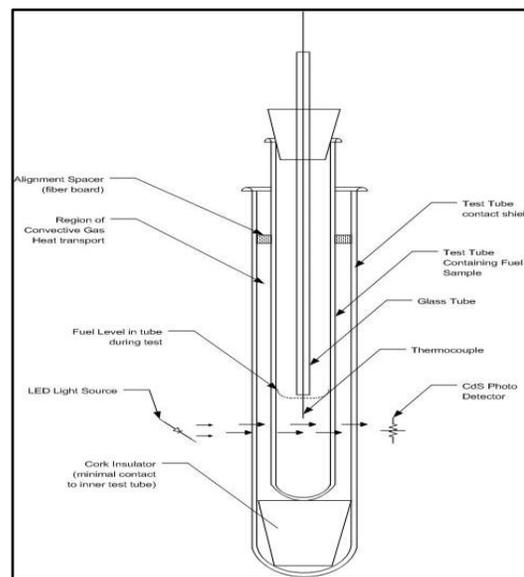


Figure 4. OSU Cloud Point Apparatus Schematic. Depiction of how a biodiesel sample's optical

property is detected in conjunction with temperature readings. The nested sample containment design ensures convective heat transfer uniformly cools the fluid. (Hackleman)

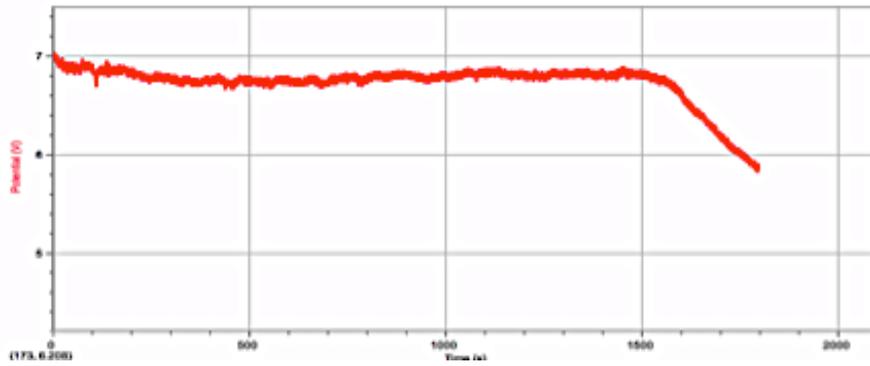


Figure 5. signal (V) over time (s) recorded in *Logger pro*

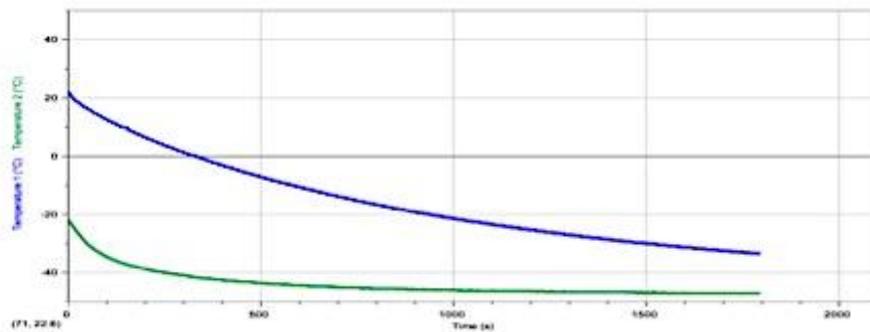


Figure 6. Temperature (°C) of the sample and the temperature (°C) of the cold box over time recorded in *Logger Pro*

Data collected in *Logger Pro* was transferred into excel so that a MATLAB algorithm could read the triplicate data arrays. The algorithm defined the cloud point temperature differently depending on the signal quality. Experience with past samples had shown that some fuels have a distinct cloud point signature defined by a local maximum in signal strength before the sample quickly clouds. The MATLAB algorithm initially searched for the local maxima indicative of the cloud point (figure 7). This method minimized the influence of time as shown in figure 8.

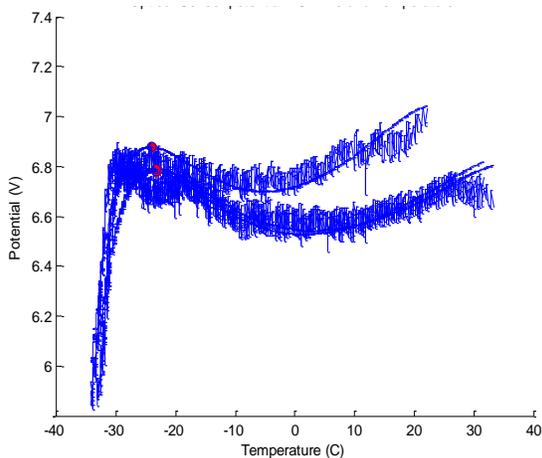


Figure 7. Signal intensity (V) vs. temperature (°C). Raw data for triplicate samples with a 3rd degree polynomial fit to each run. Local maximum method pinpoints cloud point indicated in red.

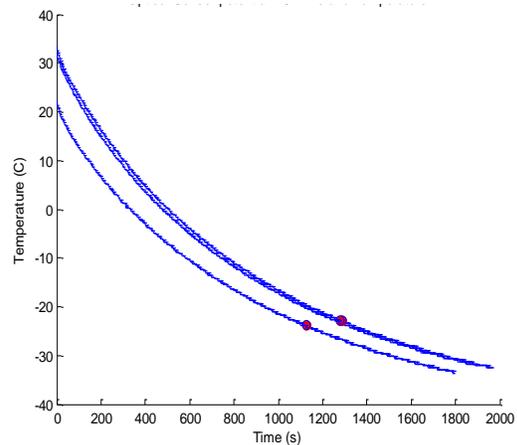


Figure 8. Temperature (°C) vs. Time (s). Triplicate runs only showing poly fit. Cloud points indicated in red appear to not be a function of time or initial temperature.

If the local maximum search cycled through the entire array, a second protocol was activated which re-analyzed the sample data using a control chart strategy. If a local maximum were not observed then it was generally true the optical signal would monotonically decrease during the clouding event. Fuels with high wax content tended to have monotonically decreasing optical signal behavior making them hard to reproducibly analyze. The control chart protocol took the first 300 points/seconds of data and found the average and range. An A_2 control limit factor of 0.308 was used because 10 point averages were compared to the lower control limit. The lower control limit was defined as the average minus the A_2 multiplied by the range. A 10 point average that fell below the lower control limit was defined as the cloud point (figure 9). Under the right circumstance the control chart method could identify cloud points with fairly low variability and with minimal influence from time (figure 10).

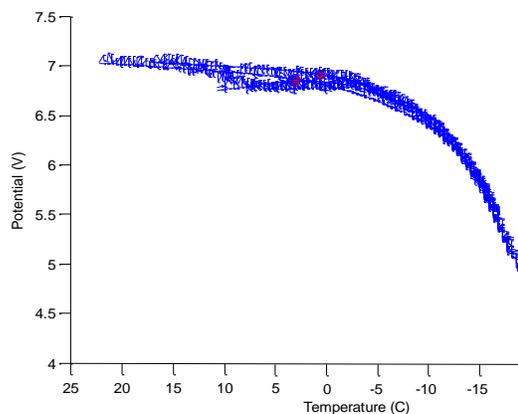


Figure 9. Signal intensity (V) vs. temperature ($^{\circ}$ C). Raw data for triplicate samples with a 3rd degree polynomial fit to each run. Control chart method pinpoints cloud point indicated in red.

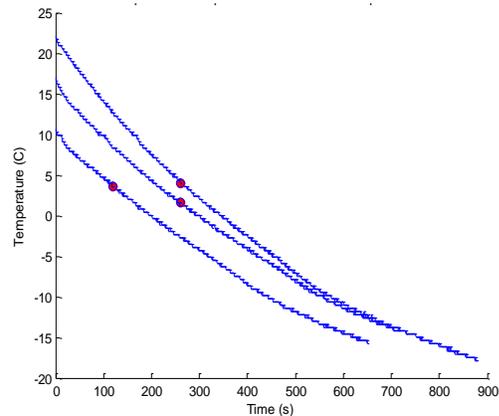


Figure 10. Temperature ($^{\circ}$ C) vs. Time (s). Triplicate runs only showing poly fit. Cloud points indicated in red appear to not be a function of time or initial temperature.

Results and Discussion

Biodiesel urea fractionation efficacy was verified using gas chromatography. Canola biodiesel has a unique signal at the methyl palmitate peak, the lowest saturated methyl ester. Removal of the methyl palmitate peak would indicate a separation of saturates from unsaturates. This studies method of urea fractionation resulted in a substantial decrease in the methyl palmitate peak (Figure 11& 12).

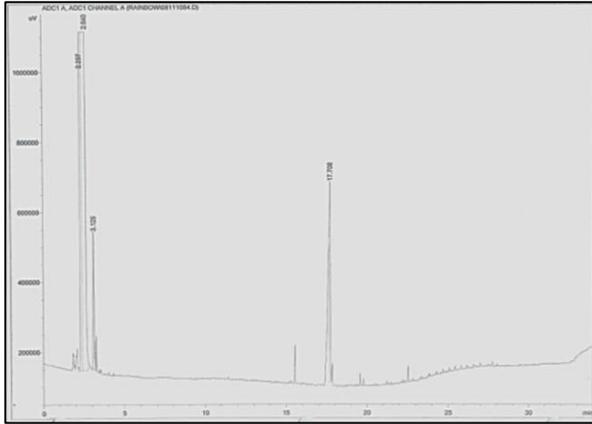


Figure 11. GC Output of Standard Canola Biodiesel. Methyl palmitate peak is distinctly present.

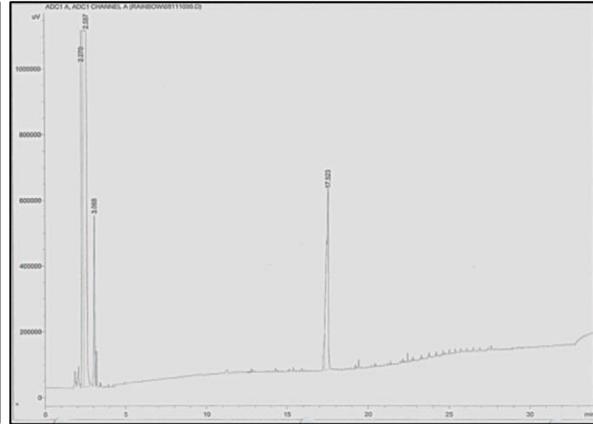


Figure 12. GC Output of Biodiesel after Urea Fractionation. Methyl palmitate peak is almost completely removed.

The standard for unmodified canola biodiesel was tested in the OSU cloud point apparatus resulting in a cloud point of 1.37 ± 6.3 °C. The low saturate biodiesel resulted in a cloud point of -21.06 ± 0.5 °C. The difference in the mean cloud point between the standard and low saturate biodiesel was 22.43 ± 4.1 °C with a P-value= 0.0001 for a null hypothesis of the means being equal. A classic solid-liquidous equilibrium model was used to compare the relative saturate concentrations (equation 1). The cloud point model assumed the chemical potential of the pure solid phase and the liquid phase are equal. Methyl palmitate thermo physical properties were used to represent the saturate fraction, $\Delta_{fus}H_i=56.85$ kJ/mol and $T_{fus}=302.59$ K. this simplified model has been shown to provide nearly identical results to a more sophisticated Uniquac method (coutinho). The cloud point model suggested the standard biodiesel contained 10 mol % saturates while the low saturate biodiesel was on the order of 1 mol % (Figure 13).

$$X_i^L = \exp \left[-\frac{\Delta_{fus}H_i}{RT} \left(1 - \frac{T}{T_{fus,i}} \right) \right]$$

Equation 1. Cloud point model assumes ideal liquid with equal chemical potential between a pure component solid phase and the liquid phase ($\mu^L=\mu^S$). Methyl palmitate thermo physical properties and fraction based on mole percent.

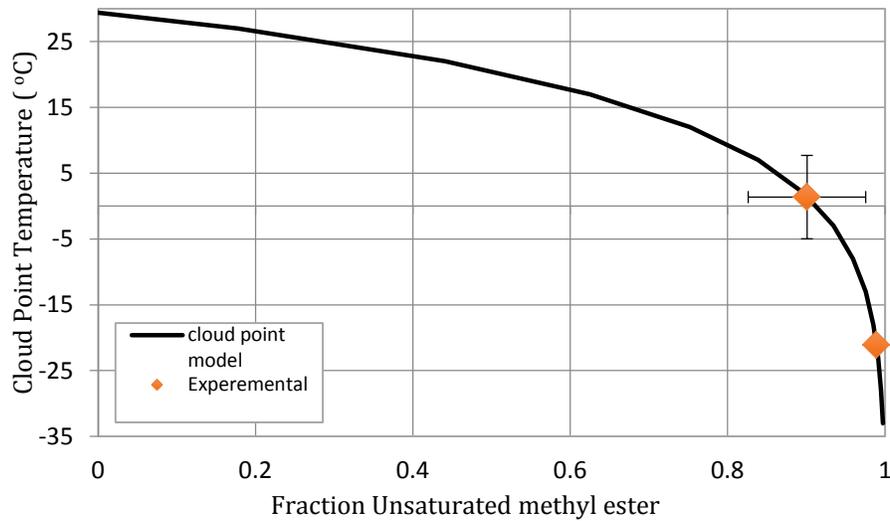


Figure 13. Cloud Point Model. The model is used to predict the mole percent of saturates for a given cloud point. The model suggests that the standard biodiesel contained roughly 10 mol% saturates while the low saturate biodiesel had roughly 1 mol% saturates

Heptadecene was used as a standard biodiesel deoxygenated biodiesel compound. Heptadecene was added to a standard canola biodiesel and a low saturate biodiesel in 1 wt% additions increments. The cloud points of the samples were measured between each addition in triplicate. Heptadecene was blended from 0 to 5 wt%. The standard biodiesel did not show a statistically significant change in the mean cloud point over the range of Heptadecene concentrations (figure 14 & 15).

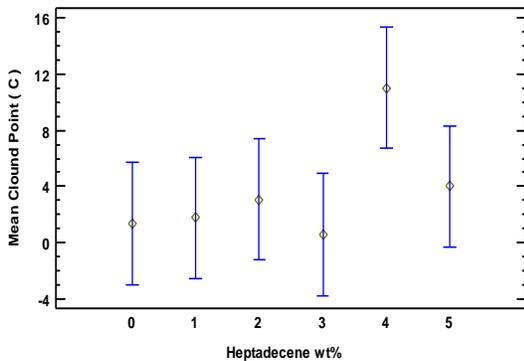


Figure 14. Comparison of the Mean Cloud Point. The mean standard biodiesel cloud point over 0 to 5 wt% heptadecene addition. 95 %Confidence intervals constructed using pooled standard error of 2.8.

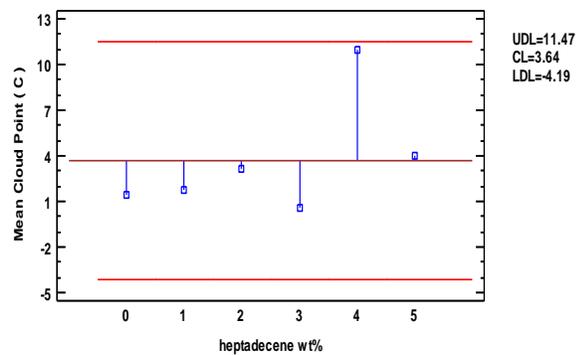


Figure 15. Upper and Lower Decision Limits. Used for determining a shift in the mean cloud point over the heptadecene addition. No sample fall outside the decision limits

Analysis of

the low saturate biodiesel revealed a statistically significant change in the mean cloud point at 2, 4, and 5 wt% heptadecene additions. Heptadecene used in these experiemnts had a measured cloud point of 14.07 +/- 11.8 °C. The trend observed over the heptadadecen addition to low saturate biodiesel could be described as a psuedo-eutectic system with minimum cloud point at 2 wt% heptadecene (Figure 16 & 17).

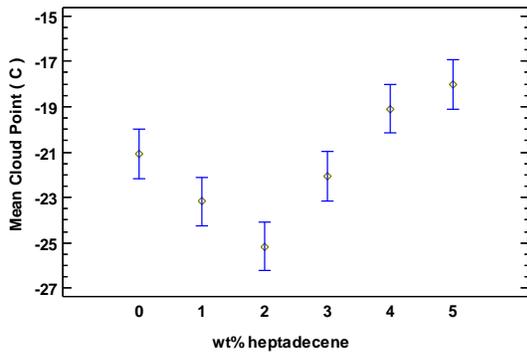


Figure 16. Comparison of the Mean Cloud Point. The mean low saturate biodiesel cloud point over 0 to 5 wt% heptadecene addition. 95 %Confidence intervals constructed using pooled standard error of 0.71. pseudo –eutectic minimum at 2 wt%.

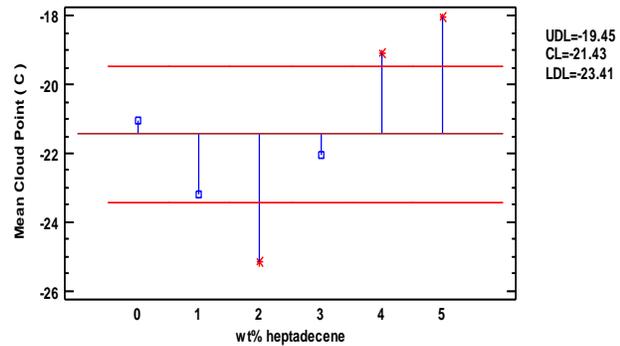


Figure 17. Upper and Lower Decision Limits. Used for determining a shift in the mean cloud point over the heptadecene addition. Samples fall outside the limits at 2, 4 ,and 5 wt%, further reinforcing the idea of a psudo eutectic system

A pseudo-eutectic system between Heptadecene and low saturate biodiesel suggests that urea fractionation in conjunction with the addition of catalytically modified saturates has a synergetic effect on cloud point depression. The low saturate biodiesel blended at 2 wt% resulted in a 26.53 +/- 4.38 °C depression in cloud point over the standard canola biodiesel. Utilizing both urea fractionation and catalytic de-oxygenation technologies could be a way of making winter 100% biodiesel. Comparing the fuels made in this experiment with two different grades of diesel and tallow biodiesel demonstrates the potential for the winter B100 proposed in this study (Figure 18).

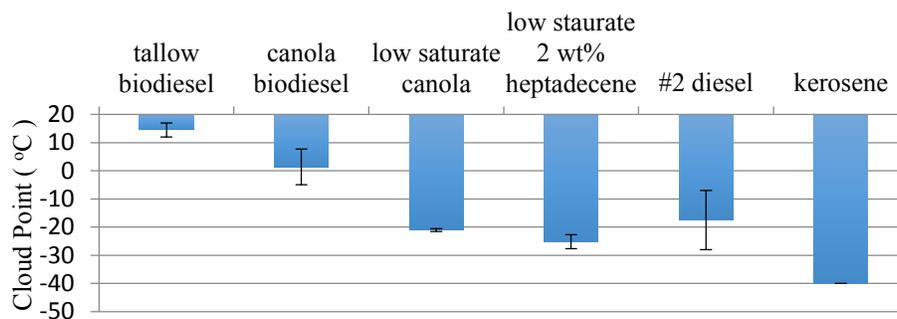


Figure 18. A comparison of tallow (cp=14.5 +/- 2.5) , canola (cp=1.37 +/- 6.32), Low saturate biodiesel (cp=-21.06 +/- .52), low saturate with 2 wt% heptadecene (cp=-25.16 +/- 2.5), #2 diesel (cp=-17.5 +/- 10.5), kerosene (cp=-40) cloud points °C

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