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ORIGINAL PAPER

Minimizing the Cost of Biodiesel Blends for Specified Cloud Points

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Abstract When used as a biodiesel fuel, isopropyl esters are expensive compared to the more common methyl esters. However, isopropyl esters have better cold flow properties than methyl esters, allowing the use of highly saturated feedstocks such as tallow or lard. It has not been determined if isopropyl esters can be part of an economical biodiesel (B100) blend for a specified cloud point, which allows for an objective material cost comparison. This work explores this question through the use of an empirical cloud point model that has been developed and validated. Constrained cost minimization was performed using the cloud point model and historical prices for alcohols and triglycerides. Case studies using 2003 and 2006 average prices are presented. The results indicate that an expensive component such as isopropyl ester can be part of an economical blend under the market conditions. For isopropyl esters to be feasible as an economical blend component, they have to be derived from a highly saturated feedstock that is less expensive than soybean oil by $0.10/lb. This price differential is most applicable to a biodiesel blend that has a cloud point between 5 and 10 °C.

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Introduction

The feedstock supply for biodiesel production can be extended through the use of highly saturated oils and fats such as palm oil, beef tallow or pork lard. While these triglyceride (TG) feedstocks are less expensive generally, the biodiesel produced from these feedstocks typically has poor cold flow behavior. For a fair cost comparison, the raw material costs for producing biodiesel should be evaluated based on equal cold flow performance. In this work, an economic analysis was performed for the blending of alkyl esters from these highly saturated feedstocks with soy methyl esters. This paper will look at minimizing the cost of a biodiesel (B100) blend subject to a target cloud point. The specific objectives are to determine the range of costs for blends that have the same cloud point. (e.g. For a blend that has a specific cloud point such as 5 °C, what is the price difference between the lowest cost blend and the most expensive blend?). The study also seeks to determine the required components for a desired cloud point that will minimize the cost of the blend and its sensitivity to the blend composition.

The fuel properties of any given biodiesel are influenced by its fatty acid composition and alkyl group [1]. Higher melting point components such as methyl stearate and methyl palmitate increase the fuel's tendency to gel at higher temperatures. On the positive side, feedstocks that contain more of these components are generally less expensive. This is demonstrated in Fig. 1 which shows the historical price trends for canola oil, soybean oil, lard, and beef tallow using data obtained from the USDA Economic Research Service [2].

It may be desirable to use isopropyl esters as a possible component for blends due to their improved cold flow properties. Haas and co-workers have calculated that soybean oil contributes about 88% of the overall production costs for producing soy methyl esters [3]. No similar work exists for the production costs of isopropyl esters, but they are likely to be more expensive because isopropanol is more expensive than methanol, and the process for producing isopropyl esters requires more energy. More alcohol and higher temperatures are used in the reaction because isopropanol is less reactive compared to methanol. For the current work, a 20:1 alcohol to oil ratio was used and boiling with reflux at around 80 °C as has previously been reported [4]. The increase in the amount of alcohol used and the higher temperature translates to higher operating costs. It needs to be determined whether isopropyl esters can play a role in minimizing the cost of the alkyl ester blend while meeting a desired cloud point.

Previously, it was shown that isopropyl esters of soybean oil have lower cloud and pour points than their methyl ester counterparts [5]. It was also shown that the difference in the crystallization onset temperature was 11 °C between the two types of esters. Isopropyl esters have also been produced from highly saturated feedstocks such as tallow [6, 7]. The exhaust emissions from isopropyl esters were not significantly different from methyl esters for both soy and yellow grease feedstocks [4]. In a B20 blend (20% biodiesel and 80% diesel fuel), the isopropyl tallowate diesel fuel blend had a cloud point of −10 °C and the methyl soyate-diesel fuel blend had a relatively close cloud point of −14 °C [7].

With this information, there appears to be no prohibition for isopropyl esters of a highly saturated feedstock to be used as part of a blend with other types of fatty acid alkyl esters.

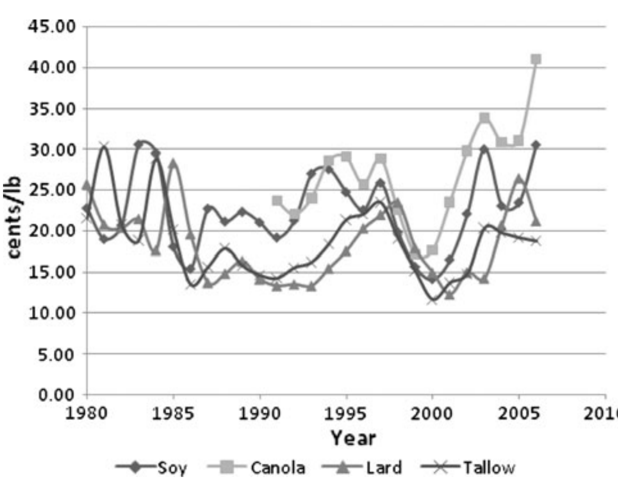

Fig. 1 Historical prices for soy, canola, lard, and tallow (USDA [13])

The key question that remains is whether it is economical from a material cost standpoint. That is, for a given cloud point, can the use of a more expensive alcohol give a less expensive fuel if it allows the use of a low cost oil or fat?

Experimental Procedures

Cloud Point Model Development

A cloud point prediction model is needed to identify the mixture components for a specified cloud point to allow for an objective cost comparison of the different blends. The cloud point (CP) test [8] (ASTM D 2500) was chosen as a measure for cold flow performance because it is a conservative estimate of impending operational problems (in the engine's fuel system) and the test is simple to perform. In addition, Dunn and Bagby [9] have shown that CP correlates well with the cold filter plugging point (CFPP) and low temperature filtration test (LTFT), which are intended to predict actual engine operating limits.

To develop the model, CP measurements were taken for biodiesel fuels produced from different alcohols and feedstocks and blends of these fuels. The cold flow tests were done manually according to the ASTM D 2500 method, with slight modifications to allow greater resolution. All of the samples were evaluated at a bath temperature of −18 °C. Type T thermocouples were used and data acquisition was performed using a Visual Basic program with a HP 3497A controller. Three independent measurements were done for each sample and the average CP was reported. In the ASTM D 2500 specification, the observer is to check for the formation of a cloud at every 1 °C interval during cooling. In this case, temperature readings and observations of crystal formation were taken at 20-s intervals to provide better than 1 °C resolution. The noted temperatures were recorded to the nearest 0.1 °C. Once a blend was prepared, it was allowed to equilibrate for at least 30 min in a separate 60-ml container before the cloud point tests were done in the standard test jars using a Neslab LT-50 low temperature bath circulator with ethanol as the cooling medium.

Two CP data sets were collected, one for model development and the other for validation. The factorial design is not a good choice for collecting data for modeling work due to the constraint that the sum of the components must equal one. Thus, a simplex-centroid design [10] was used to generate the data for modeling where the component proportions are evenly spaced. This study was limited to four parent fuels for practical purposes: tallow methyl esters (TME), tallow isopropyl esters (TPE), soy methyl esters (SME), and soy isopropyl esters (SPE). The materials and methods used to produce the esters are described later in this section.

The simplex centroid design yields 15 points and the breakdown is shown below:

- Four of the points are neat formulations of each parent fuel
- Six of the points are binary blends (0.5, 0.5)
- Four formulations for ternary blends (0.33, 0.33, 0.33)
- One quaternary blend which is central (0.25, 0.25, 0.25, 0.25).

The six binary blends represent all possible combinations from four parent fuels where the two fuels in the blend are in equal proportions. They are SPE–SME, TME–TPE, SME–TME, TPE–SPE, SPE–TME, and SPE–TME. The four formulations for ternary blends have each component being present in equal proportions. A quaternary blend was included with equal amounts of each component. The design was augmented to improve the model's predictive capabilities by adding four interior points having the composition (0.125, 0.125, 0.125, 0.625). So, the total number of points based on the design is 19. Due to material limitations, only the CP observations were replicated three times and the variability in the process of mixing was not evaluated in this study.

In addition to the 19 samples used to develop the CP model, the CPs of 68 more samples comprising pure parent fuels, binary blends, ternary blends, and quaternary blends were measured in triplicate. This expanded data set was used to validate the model derived from the data collected using the simplex centroid design.

Soy oil was purchased from a local grocery store and had the following fatty acid profile (mass%): 10.25% palmitic acid, 4.6% stearic acid, 24.5% oleic acid, 52.3% linoleic acid, and 6.3% linolenic acid. SME were prepared using a standard 6:1 methanol to oil molar ratio and 0.5% sodium methylate catalyst (based on the weight of oil). The sodium methylate catalyst (25% in methanol) was obtained from Oxychem (Dallas, TX). Isopropyl esters from this soy oil were prepared with isopropanol using a 20:1 alcohol to oil molar ratio and 3% potassium methylate (32% in methanol) catalyst (based on the weight of oil). Potassium methylate from Degussa (Parsippany, NJ) was used because it was readily available.

Tallow obtained from a commercial source containing 5.91% free fatty acids was used to make methyl and isopropyl esters. The fatty acid profile (mass%) for the tallow was as follows: 2.5% myristic acid, 24.6% palmitic acid, 21.2% stearic acid, 37.9% oleic acid, and 5.6% linoleic acid. Additional catalyst was necessary to saponify the free fatty acids and the required stoichiometric amount was added for this purpose in addition to the amount required for transesterification. A methylate catalyst was used for the reaction because the isopropylate catalysts were considered to be too expensive to be practical. It was recognized that this would result in some methyl esters being produced in addition to isopropyl esters. Sodium methylate was used as a catalyst to reduce the amount of methanol present in the reaction mixture since sodium has a lower molecular weight than potassium.

The SPE were made with potassium methylate catalyst (32% in methanol) where the methanol made up about 4% of the total alcohol weight involved in the reaction, with the rest being isopropanol. The resulting fuel consists mostly of isopropyl esters, and some methyl esters. A Gas Chromatograph–Mass Spectrometer (GC–MS) was used to estimate the amounts of isopropyl and methyl esters present and the results are presented in Table 1. Free glycerin was not detected in any of the samples. The amount of isopropyl ester content was determined through the identification of the GC peaks using a mass spectral library and the quantification of the respective areas.

This procedure to confirm the fractions of methyl and isopropyl esters in the mixture used an HP 6890 GC with an HP 5973 MS detector. The GC column was a Varian VF-5MS column (Palo Alto, CA) with the following dimensions: 30 m × 0.25 mm film thickness. A 1-ml sample was injected with a split ratio of 59.8:1 and a split flow rate of 46.5 ml/min. The carrier gas was helium at 5 psi and a flow rate of 0.8 ml/min. The temperature profile was: 50 °C for 3 min, a ramp rate of 15 °C/min to 320 °C, and then holding at 320 °C for 3 min.

Constrained Cost Minimization

The goal of the calculation was to minimize the cost of the blends subject to a cloud point constraint. There were four

Table 1 Relevant fuel properties for parent fuels

	Soy methyl esters	Soy isopropyl esters	Tallow methyl esters	Tallow isopropyl esters
Total glycerol (mass%)	0.005	0.031	0.017	<0.005
Viscosity at 40 °C (mm^2/s)	4.45	4.89	4.28	4.46
Isopropyl ester content[a] (mass%)	NA	71.7	NA	75.3

NA not applicable

[a] The isopropyl ester content was determined using GC–MS

parent fuels, and thus four variables (x_i) were used with subscripts from 1 to 4 representing TME, TPE, SME, and SPE.

The cost function is given as:

$$\text{Cost, } C = \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_4 x_4 \quad (1)$$

where x_i is the volume fraction of a single feedstock with a certain alkyl group, and α_i is the unit cost for the corresponding type of ester. On a more fundamental level, it can be argued that there are more than just four principle components since the different feedstocks are composed of different fatty acid esters. However, the individual fatty acids do not have prices affixed to them, and for simplicity, the cost is a function of the parent fuel's material cost.

The unit cost for any given alkyl ester on a \$/liter basis, α_i, is shown below in Eq. 2:

$$\alpha_i = f_1 + P'_f + P'_{\text{ROH}} \quad (2)$$

where P'_f is the TG feedstock cost for producing a liter of biodiesel and P'_{ROH} is the alcohol cost for producing a liter of biodiesel. A factor to include processing costs is given as f_1. In this work, f_1 was set to zero because only the material costs were considered. It is acknowledged that the processing cost of isopropyl esters may be higher in practice due to the higher temperatures and the greater molar excess of alcohol required for a complete reaction.

The calculation assumes quantitative yields for the transesterification reaction. Yield can have a variety of meanings. In this case, we are considering the yield to be the ratio of the weight of esters (product) to the weight of the TG feedstock (input). For example, if 100 kg of oil were used as the reactant, roughly 100 kg of methyl esters would be obtained [11]. However, 100 kg of oil would yield 110 kg of isopropyl esters. Due to the bulkier alkyl group, there is approximately a 10% gain above the initial weight of the TG feedstock. All of these factors can be adjusted to suit the requirements of the specific case being analyzed.

The objective function (i.e., the cost of the blend) has now been defined. The constraints are explained in the following section.

Material Constraint

Each component, x_i, has to be non-negative, and the sum of all the components must be equal to one.

$$x_1 + x_2 + x_3 + x_4 = 1. \quad (3)$$

The Cloud Point Constraint

This constraint is subject to the customer's requirements and the available fuels for blending. It is considered to be an input to the problem.

The problem is a *linear programming* problem and can be summarized as follows:

Minimize $C = \alpha x$

Subject to $\begin{array}{l} \mathbf{A}x = b \\ x \geq 0 \\ b \geq 0 \end{array}$ where $\mathbf{A}$ is the *coefficient matrix*,

$$A = \begin{bmatrix} 1 & 1 & 1 & 1 \\ 19.376 & 12.064 & 2.475 & -2.893 \end{bmatrix}$$

x is the *decision vector*, $x = [x_1 \quad x_2 \quad x_3 \quad x_4]^{\mathrm{T}}$, α is the *cost vector*, $\alpha = [\alpha_1 \quad \alpha_2 \quad \alpha_3 \quad \alpha_4]^{\mathrm{T}}$ and b is a column vector of the constraints (material and cloud point): $b = \begin{bmatrix} 1 \\ \text{CP} \end{bmatrix}$.

The coefficients in matrix $\mathbf{A}$ are from the material constraint and from the empirical equation as presented in Eq. 4 in the following section. Optimization through linear programming was performed using Premium Solver (Incline Village, NV), which is an add-on package for Microsoft Excel 2003 (Redmond, WA).

To evaluate the methodology for identifying conditions where isopropyl esters could be part of a least cost blend, historical data for feedstock oils and alcohols were used. Data from the years 2003 and 2006 were selected for detailed consideration because they corresponded to years where the price difference between the methanol and isopropanol were low (2003) and high (2006) while the prices for the soy oil and tallow were virtually unchanged. Thus, conclusions for these years should bracket the solutions found for other years. In modeling the 2006 cost for the blends, the prices used for the alcohol were taken from the Chemical Market Reporter [12]. The range given for anhydrous 99% isopropyl alcohol was \$0.60–0.65/lb. Methanol was priced at \$0.96 per gallon (contract price), which is \$0.146/lb. This means that IPA was about six times the price of methanol on a molar basis. The USDA ERS was used for historical triglyceride costs which were downloaded from their webpage [13]. Historical prices for the main materials used are summarized in Table 2.

Table 2 Historical prices for methanol, isopropanol, soy, and tallow

Feedstock (years)	Low price (\$/lb)	High price (\$/lb)
Methanol[a] (1999–2004)	0.04	0.14
Isopropanol[b] (1998–2003)	0.28	0.49
Soy[c] (1980–2006)	0.15	0.31
Tallow[c] (1980–2006)	0.12	0.30

[a] Chemical Market Reporter [15]

[b] Chemical Market Reporter [16]

[c] USDA [13]

Table 3 Cloud points from the simplex centroid designed study

Sample	Volume fractions				Cloud point (°C)	
	Tallow		Soy			
	Methyl esters	2-Propyl esters	Methyl esters	2-Propyl esters	Average[a]	Standard deviation
1	1.000	0.000	0.000	0.000	18.3	0.1
2	0.000	1.000	0.000	0.000	10.6	1.0
3	0.000	0.000	1.000	0.000	2.5	0.4
4	0.000	0.000	0.000	1.000	5.1	0.3
5	0.500	0.500	0.000	0.000	11.8	0.3
6	0.000	0.000	0.500	0.500	0.6	0.6
7	0.500	0.000	0.500	0.000	13.2	0.3
8	0.500	0.000	0.000	0.500	6.4	0.4
9	0.000	0.500	0.000	0.500	5.1	0.4
10	0.000	0.500	0.500	0.000	4.2	0.6
11	0.330	0.330	0.340	0.000	14.5	0.4
12	0.330	0.000	0.330	0.340	4.4	0.2
13	0.000	0.330	0.330	0.340	5.2	0.3
14	0.330	0.330	0.000	0.340	12.1	0.4
15	0.250	0.250	0.250	0.250	6.3	0.2
16	0.125	0.125	0.125	0.625	6.6	0.2
17	0.125	0.625	0.125	0.125	13.5	0.4
18	0.125	0.125	0.625	0.125	2.2	0.3
19	0.625	0.125	0.125	0.125	15.6	0.2

[a] Cloud points reported are the average of three readings

Breakeven analysis was performed to identify the conditions when isopropyl esters are part of the least cost blend for a specified cloud point. Breakeven curves were generated in relation to the price differentials between the alcohols and between the TG feedstocks. This was done by holding one price differential constant while finding the other necessary price difference required to drive the price difference between the most and least costly blends to zero. The historical prices (Table 2) were taken into consideration in the breakeven analyses for the years 2003, 2006, and 2007. The prices for methanol do not vary as much for isopropanol, and historically, tallow has been less expensive than soybean oil. So, the price differential for the alcohols was calculated by varying the price of isopropanol, and the price differential for the TG feedstocks was calculated by varying the price of tallow. The prices for methanol and soybean oil were held constant at the average value for the year.

Results and Discussion

The validated empirical cloud point model is given by the following equation

$$CP = 19.376x_1 + 12.064x_2 + 2.475x_3 - 2.893x_4 \tag{4}$$

where the values of the volume fractions x_i correspond to TME (x_1), TPE (x_2), SME (x_3), and SPE (x_4).The data used to generate the cloud point prediction model are shown in Table 3. The data demonstrate that the standard deviations for the three independent observations were all equal to or less than one degree centigrade, which is within the repeatability limits of ASTM D 2500.

The three types of blends (binary, ternary, and quaternary) have been examined for their effect on cloud point in detail in a dissertation [14]. A linear model was found to be the best predictive model when validated against the expanded study data. The empirical model given earlier in Eq. 1 was found to be the most useful because of its simplicity and the strength of the correlation was adequate ($R^2 = 0.8281$).

The cloud point prediction model was evaluated using the data from the expanded data set, which is separate from the data used to generate the model. Figure 2 shows the predicted points from Eq. 1 plotted against the observed data from the expanded data set. A 45° line has been placed in Fig. 2 to aid in evaluating the prediction capabilities of the linear model. While the prediction involves considerable scatter, it was considered acceptable for the economic analysis described here.

Higher order models fitted to the simplex-centroid data had coefficients that were not statistically significant.

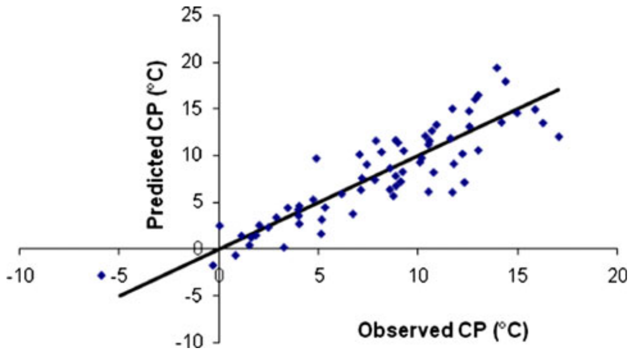

Fig. 2 Comparison of model to observed cloud points for expanded study. A 45° line is drawn through the data points

Although the R^2 value increases for a higher order model, the increase is artificial. The prediction from the higher order models had larger root-mean-square deviations from the observed cloud points from the expanded data set. The root mean square error (RMSE) for the quadratic, cubic, and quartic models were 2.63, 2.91, and 3.42 °C, respectively, while the linear model had a RMSE of 2.39 °C. The RMSE for the linear model is closer to the repeatability of the ASTM D 2500 test of ±2 °C.

While the cost of producing biodiesel is largely dependent on the lipid feedstock, the cost of isopropanol (IPA) is six times higher than methanol on a molar basis using the 2006 price data [11]. While methanol may account for about 6% of the total material (i.e., alcohol + oil) costs for methyl esters, isopropanol can amount to 35% of the total material costs if soy oil were selling at $0.25/lb, methanol at $0.14/lb and IPA at $0.65/lb. The latter two prices will be used in the rest of the discussion for the alcohol prices in 2006. Thus, the material costs for isopropyl esters are more sensitive to the price of IPA than methyl esters are to methanol.

In 2003, the average prices ($/lb) for tallow, soy, methanol, and IPA were 0.20, 0.30, 0.11, and 0.40 $/lb [13, 15, 16]. This year was chosen because the price difference between soy and tallow was about the same as in 2006, while the price difference between methanol and IPA increased from $0.29/lb in 2003 to $0.51/lb in 2006. The increase in the price difference between methanol and IPA and a similar price for the TG feedstock lends itself well to sensitivity analysis on the alcohol price.

The feedstock cost in 2003 for the four parent fuels with their corresponding alcohol and triglyceride contributions is shown in Fig. 3. In 2006, the price ($/lb) for tallow and soy oil are 0.19 and 0.31, respectively [13]. Figure 4 shows the feedstock costs for 2006 prices.

In Figs. 3 and 4, the cost of the TG feedstock for producing a gallon of biodiesel goes down when IPA is used instead of methanol. This is due to the higher yield (10%) from the reaction with IPA. However, this reduction in TG

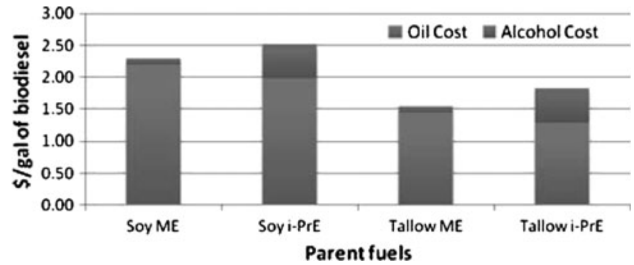

Fig. 3 Feedstock cost according to 2003 prices. In ($/lb), the prices for tallow, soy, methanol, and IPA were 0.20, 0.30, 0.11, and 0.40. *ME* methyl esters, *i-PrE* isopropyl esters

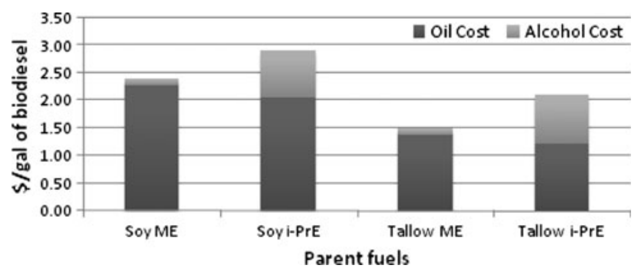

Fig. 4 Feedstock cost according to 2006 prices. Prices in $/lb for tallow, soy, methanol, and IPA were 0.19, 0.31, 0.14, and 0.65. *ME* methyl esters, *i-PrE* isopropyl esters

feedstock cost is not sufficient to compensate for the much higher price for IPA as seen in both TG feedstocks, and in the 2003 and 2006 cases. So, for the same TG feedstock, the resulting isopropyl esters are more expensive than the methyl esters. These figures also show that the isopropyl esters of tallow are less expensive than the methyl esters of soy oil. This provides the incentive for attempting to determine whether isopropyl esters can contribute to a less expensive biodiesel when the cloud point is held constant.

The increase in price of the isopropyl esters can be viewed as a premium cost to gain improved cold flow performance. This holds true for the blends in the expanded study. Blends that have high cloud points are less expensive than blends with low cloud points because they involve greater use of the less expensive tallow. Figure 5 relates the material cost of the blends from the expanded data set with their respective cloud points. If vertical lines are drawn on Fig. 5 to represent isotherms for different cloud points, there may be several blends with different material costs that have the same cloud point. This is the basic question of the current study: What is the lowest cost blend for a fixed cloud point?

Obviously, the primary value of the methodology developed here is for the marketer of biodiesel who proposes to sell biodiesel having a specified cloud point and wants to minimize production costs by blending different components. Because the model involves so many degrees of freedom, it is difficult to present results

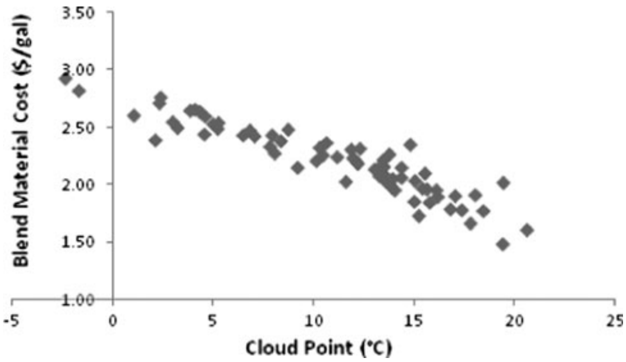

Fig. 5 Material cost for blends using 2006 prices versus cloud points

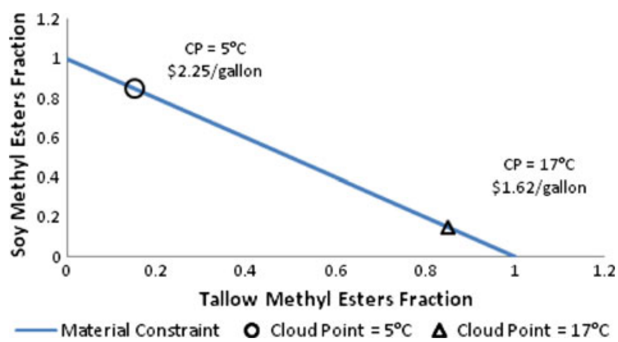

Fig. 6 Illustration for the binary blend problem

that be generalized. However, particular cases can be presented to illustrate some general observations of the solutions.

In the case of binary blends, the problem of determining the lowest cost blend is quite straightforward as illustrated in Fig. 6 for a blend of methyl esters produced from soybean oil and tallow. With binary blends, choosing a percentage for one component determines the percentage of the other component. Thus, the domain of possible blends is limited to the line shown. Along this material constraint, each point can be associated with a specific cloud point. Two points are shown for two different blends, one being 85% SME, and the other 85% TME. The predominantly tallow blend has a cost of $1.62 per gallon and a cloud point of 17 °C. The more expensive soy-dominated blend ($2.25/gallon) has a cloud point of 5 °C. Thus, the cost for a binary blend is fixed for a given cloud point, and the lowest cost can be found by comparing costs across combinations of different starting materials for a given cloud point. It is conceivable for blends to have complex composition–cloud point relationships, such as eutectics, but this behavior was never observed in this study.

For ternary blends, there may exist several blends of differing composition from the same three parent fuels that provide the same given cloud point. Consider Fig. 7 where the four faces of the tetrahedron that characterizes the possible ternary blends are shown with the contours representing different cloud point regions in 4 °C increments. If the four faces were joined at the appropriate sides, a quaternary phase diagram is generated. The contours were derived using the linear cloud point model.

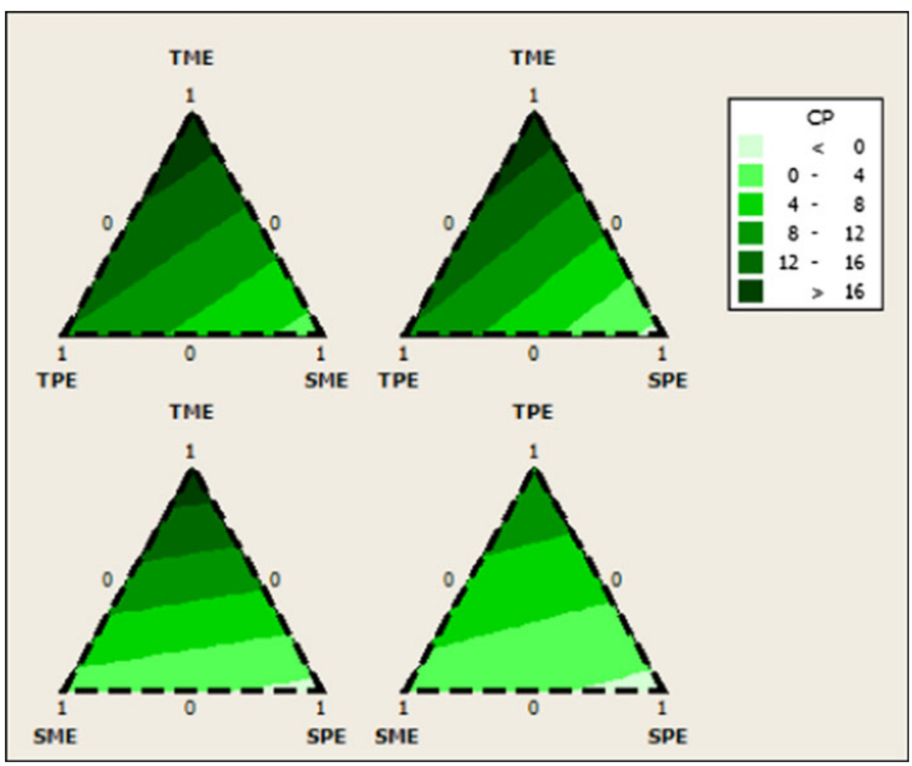

Fig. 7 Four ternary diagrams for the four parent fuels with cloud point zones. *TME* tallow methyl esters, *TPE* tallow isopropyl esters, *SME* soy methyl esters, *SPE* soy isopropyl esters

Table 4 Blend costs based on 2006

Variables	CP = 0 °C		CP = 5 °C		CP = 10 °C	
	Min	Max	Min	Max	Min	Max
TME	0.00	0.00	0.15	0.00	0.45	0.00
TPE	0.00	0.19	0.00	0.53	0.00	0.86
SME	0.54	0.00	0.85	0.00	0.55	0.00
SPE	0.46	0.81	0.00	0.47	0.00	0.14
Cost ($/gal)	2.63	2.76	2.25	2.49	1.99	2.21

Prices in $/lb for tallow, soy, methanol, and IPA were 0.19, 0.31, 0.14, and 0.65

TME tallow methyl esters, *TPE* tallow isopropyl esters, *SME* soy methyl esters, *SPE* soy isopropyl esters

Table 5 Blend costs based on 2003 prices

Variables	CP = 0 °C		CP = 5 °C		CP = 10 °C	
	Min	Max	Min	Max	Min	Max
TME	0.00	0.00	0.00	0.15	0.00	0.45
TPE	0.19	0.00	0.53	0.00	0.86	0.00
SME	0.00	0.54	0.00	0.85	0.00	0.55
SPE	0.81	0.46	0.47	0.00	0.14	0.00
Cost ($/gal)	2.39	2.40	2.15	2.18	1.92	1.95

In ($/lb), the prices for tallow, soy, methanol, and IPA were 0.20, 0.30, 0.11, and 0.40

TME tallow methyl esters, *TPE* tallow isopropyl esters, *SME* soy methyl esters, *SPE* soy isopropyl esters

In the next level up, a quaternary blend may have the same cloud point as a ternary blend or a binary blend. However, for a fixed cloud point, a quaternary blend might not be economically advantageous when compared to a ternary or binary blend.

Given that the constraints are well defined, and that the cloud point and cost models are linear, the optimal solutions to this optimization problem (i.e., the lowest cost blend or the most expensive blend) are always a point that lies on one of the edges of the tetrahedron, or a vertex, if the desired cloud point is the same as one of the parent fuels. The edges of the tetrahedron represent binary blends, and the line in Fig. 6 is one of the six edges. This simplifies the presentation of results because the lowest cost option will not involve a complex mixture. More information on linear programming and its solutions can be found elsewhere [17].

To illustrate the relationship between composition, cost, and cloud point, the material cost of blending for three different cloud points was considered for the 2006 price data set. The model developed was implemented in Microsoft Excel (Redmond, WA) for three cloud points of 0, 5, and 10 °C. The formulations that correspond to the least and most costly blends for the three cloud points in 2006 are presented in Table 4. From Table 4, optimal points (minimum or maximum cost) are always binary blends, as mentioned previously.

Since the cost of IPA is much greater than the cost of methanol, it is no surprise that the costly blends are ones that include isopropyl esters. All columns for the maximum blend cost for the three cloud point cases include SPE as part of the formulation. However, for blends that require low cloud points such as the 0 °C blend in Table 4, soy isopropyl ester is a necessary component, even in the lowest cost blend. Again, the improved cold flow performance has a price attached to it as was shown in Fig. 5. From Table 4, the price range for blends with CP = 5 °C is $2.25–$2.49 per gallon, while the price range for blends with CP = 10 °C ranges from $1.99 to $2.21 per gallon.

The minimum and maximum blend costs for the same cloud points were also calculated using 2003 material prices as an exercise in sensitivity analysis. These results are tabulated in Table 5. The feedstock and alcohol price differences from 2003 to 2006 are as follows: the price difference between tallow and soy increased from $0.10/lb to $0.12/lb, and the price difference between methanol and IPA increased from $0.29/lb to $0.51/lb. For 2003 prices, blends composed solely of isopropyl esters appear to be the lowest cost solution for the specified cloud points in all three cases (refer to Table 5). Upon closer inspection, the difference between the minimum and maximum blend cost for any of the three given cloud points appears to be small. For a 0 °C blend, the difference is only $0.01 per gallon, while the other two cases have a difference of three cents per gallon. This indicates that for the 2003 prices used here, there is little difference between using isopropyl esters or methyl esters as part of a blend to meet a specific cloud point.

Thus, for isopropyl esters to be practical for blending for the four parent fuels presented here, the price difference between soy and tallow would have to increase above $0.10/lb, where tallow is less expensive than soy oil, and the price difference between methanol and IPA will have to decrease below $0.29/lb where IPA is more costly than methanol. The threshold price difference for the alcohols is roughly three times the price difference for the TG feedstocks. This implies that the cost function for blends is more sensitive to the TG price difference than the alcohol price difference. This is not surprising considering the much larger amount of TG used in the reaction.

Figure 8 shows the breakeven curves for the three sample years of 2003, 2006, and 2007. In this case, the breakeven curves identify the price differential conditions when isopropyl esters could have been part of an economic blend that met a cloud point constraint of 5 °C.

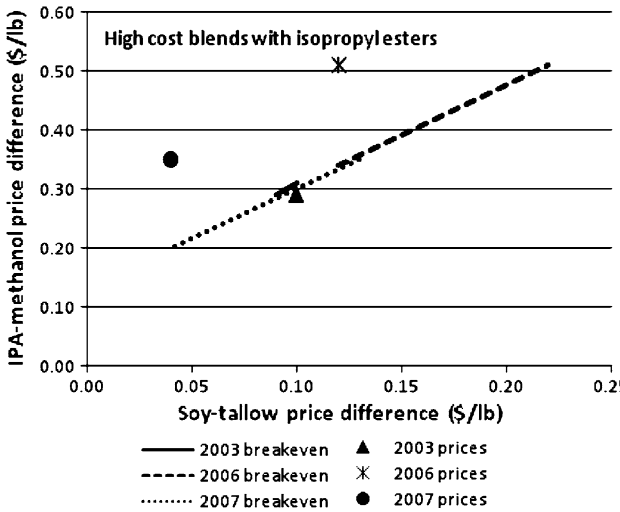

Fig. 8 Breakeven price differentials for blends with a cloud point of 5 °C. Prices of soy and methanol are fixed at their respective years

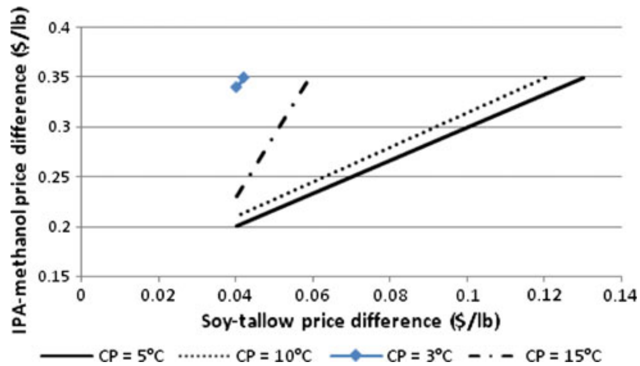

Fig. 9 Family of breakeven curves for 2007 prices. The price of soy was fixed at $0.38/lb (October 2007) and the price of methanol was fixed at $0.23/lb (2007 contract price)

The horizontal axis represents the price difference between soy and tallow, where soy is more expensive. The vertical axis represents the price difference between IPA and methanol, where IPA is more expensive. For a set of feedstock prices, the soy-tallow price difference must increase and the IPA-methanol price difference must decrease in order for SPE to be part of an economic blend. So, graphically, the lower right portion just below the breakeven lines represents the price differentials where isopropyl esters form part of the least cost blend. The breakeven curves are the diagonals of the rectangle (not shown), which encloses the feasible region for the cloud point constraint (5 °C in this case). The areas of the feasible regions vary for the different market conditions as seen by differing diagonal lengths. The actual price differentials for the three different years are also shown in Fig. 8. The markers for 2006 and 2007 are to the upper left of the breakeven curves, where it is not favorable to use isopropyl esters of tallow in blends.

Interestingly, the breakeven curves from the three different years (different market conditions) seem to form a single line. This suggests that Fig. 8 can be used as an initial estimate to determine the economic feasibility of isopropyl esters as part of a blend for a cloud point of 5 °C. A family of curves with different cloud point constraints for 2007 prices is given in Fig. 9. Observing Fig. 9, the feasible regions are largest at the midrange cloud points (5 and 10 °C) where there are more blends that can meet the cloud point constraint. Above or below this cloud point midrange, the possibilities for forming blends that can meet the cloud point constraint are limited, which in turn limits the range of blend prices.

The linear cloud point model, though simple, has been shown to be robust and can predict the cloud points for blends from any combination of the four parent fuels. Now that it has been shown that binary blends are more economical, it might be reasonable to develop a more precise cloud point model for binary blends. Due to the reduction in degrees of freedom, it is usually possible to do better predictions with higher order models. The use of higher order models, for example a quadratic one, does not invalidate the findings presented here [14]. Binary blends will still be the solution to either the most costly or least costly blend even if a higher order cloud point model is used.

The range of costs for blends that have the same cloud point depends on the cloud point constraint and the price differentials for both the TG and alcohol feedstocks. High cloud points and low cloud points have a limited number of blends due to the intrinsic cold flow properties of the parent fuels. As such, these extremes have a smaller domain of possible compositions and thus a smaller cost range. Mid-range cloud point blends have a greater price difference between the minimum and maximum cost blends because there is a greater degree of freedom to achieve the specified cloud point.

The minimum and maximum cost blend for the specific cloud point of 5 °C was considered for the 2003 and 2006 price data sets. In 2003, the difference between the minimum and maximum cost blends were $0.25 per gallon, while in 2005, the difference was only $0.03 per gallon. Thus, market conditions determine the range of costs for a given cloud point.

While isopropanol can account for about a third of the material costs for producing isopropyl esters, the use of isopropyl esters in a blend for a specified cloud point diminishes the severity of the high isopropanol costs. As a rule of thumb, for mid-cloud point ranges (5–10 °C), if the highly saturated feedstock is $0.10/lb less than the soybean oil price, isopropyl esters from highly saturated feedstocks may be part of the least cost blend.

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