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# Improving the Cold Flow Properties of Biodiesel by Fractionation

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## 1. Introduction

Biodiesel is generally defined as the mono-alkyl esters of fatty acids derived from transesterification of agricultural lipids with a short-chain alcohol. Biodiesel must conform to fuel property specifications such as those outlined in the American Society of Testing and Materials (ASTM) standard D 6751 or the European Committee for Standardization EN 14214 (ASTM, 2008b; CEN, 2003). Although the most common form of biodiesel in the U. S. is made from soybean oil, many other types of lipid feedstocks have been developed. Biodiesel is compatible with compression-ignition (diesel) engines. It may be utilized in neat (100%) form or in blends with conventional diesel fuel (petrodiesel). Biodiesel has been applied as an alternative fuel in transportation trucks, farm and other off-road vehicles, automobiles, locomotives, aircraft, power generators, boilers and heaters.

The advantages and disadvantages of biodiesel as an alternative diesel fuel have been efficiently documented (Erhan et al., 2008; Graboski & McCormick, 1998; Knothe & Dunn, 2001, 2005). One major disadvantage is the performance of biodiesel in cold weather which may compromise its year-round commercial viability in moderate temperature climates. Although field studies on cold weather performance are scarce, there is evidence that soybean oil fatty acid methyl esters (SME) develop operability issues as ambient temperatures approach 0-2°C. In contrast, petrodiesel develops similar problems at a significantly lower temperature range, typically between -16 and -20°C.

This chapter examines fractionation as an effective process step that may be applied to improve the properties and performance of biodiesel and its blends in petrodiesel during cold weather. This technology is based on separating biodiesel into low- and high-melting point fractions. Unless otherwise noted, the term *alkyl esters* refers to fatty acid alkyl esters which may specifically include fatty acid methyl esters (FAME), ethyl esters, propyl esters, etc. Similarly, the term *petrodiesel* refers to petroleum middle distillate fuel, either grade No. 1 or No. 2, as defined in ASTM fuel standard D 975 (ASTM, 2008a).

## 2. Cold flow properties

Regardless of origin, all diesel fuels are susceptible to start-up and operability problems when vehicles and fuel systems are exposed to cold temperatures. As ambient temperatures cool toward their crystallization temperature, high-molecular weight paraffins (C<sub>18</sub>-C<sub>30</sub> *n*-alkanes) in petrodiesel nucleate and form wax crystals suspended in a liquid phase

composed of shorter-chain *n*-alkanes and aromatics (Botros, 1997; Brown et al., 1989; Chandler et al., 1992; Lewtas et al., 1991; Owen & Coley, 1990). Left unattended overnight, solid wax crystals may plug or restrict flow through filters causing start-up and operability problems the next morning.

### 2.1 Properties of diesel fuels

At low temperatures, higher-melting point (MP) components in the fuel nucleate and grow to form solid crystals. The cloud point (CP) of the fuel is defined as the temperature where crystals become visible (diameter exceeds 0.5  $\mu\text{m}$ ) forming a hazy or cloudy suspension (Chandler et al., 1992; Westbrook, 2003). Prolonged exposure of the fuel to temperatures at or below CP causes crystals to grow and cling together forming agglomerates that restrict flow. Pour point (PP) is defined as the lowest temperature where the fuel flows or can be pumped (Westbrook, 2003; Westbrook & LeCren, 2003).

Both CP and PP are easily measured in the laboratory. However, neither parameter efficiently predicts how diesel fuels will perform in tanks and fuel systems during cold weather (Owen & Coley 1990; Westbrook, 2003; Westbrook & LeCren, 2003). Consequently, data from field trials were correlated to develop bench-scale tests that more effectively predict temperature limits where start-up or operability problems may be expected to occur in the fuel after prolonged exposure. The first such test, cold filter plugging point (CFPP), is accepted nearly world-wide and listed among the limiting fuel parameters in the aforementioned European biodiesel fuel standard EN 14214. CFPP is defined as the lowest temperature where 20 mL of fuel passes safely through a 45  $\mu\text{m}$  wire mesh filter under 200 mm H<sub>2</sub>O (0.019 atm) vacuum within 60 s (Westbrook, 2003).

Despite the wide acceptance of CFPP for testing cold weather performance of diesel fuels, this test does not correlate well with field test data in North America (Brown et al., 1988; Owen & Coley, 1990). Therefore, the less user-friendly low-temperature flow test (LTFT) was developed as a standard test for predicting operability of diesel fuels and fuel systems prevalent in North America (Chandler et al., 1992; McMillan & Barry, 1983). Analogous to CFPP, LTFT is defined as the lowest temperature where 180 mL of fuel passes through a 17  $\mu\text{m}$  wire mesh filter under 0.2 atm vacuum within 60 s (Westbrook, 2003). The LTFT test method also requires a slower cooling rate (1°C/hr) than CFPP limiting its practicality as a bench-scale test.

### 2.2 Cold flow properties of biodiesel

Data in Table 1 demonstrate that CP, PP, CFPP and LTFT of biodiesel (FAME) from many lipid feedstocks are generally higher than corresponding data for petrodiesel. Cold flow properties of biodiesel generally depend on fatty acid composition. Straightforward transesterification to biodiesel does not greatly alter the fatty acid composition based in the parent feedstock. Fatty acid compositions occurring in several biodiesel feedstocks are summarized in Table 2. Shown in the bottom row of this table are MP data of the corresponding pure FAME compound.

Soybean oil-FAME (SME) generally consists of a mixture of high-melting ( $C_{16}$  and  $C_{18}$ ) and low-melting ( $C_{18:1}$ ,  $C_{18:2}$  and  $C_{18:3}$ ) components. A recent study (Dunn, 2010) on eight different SME products showed that for total saturated fatty acid ester concentration ( $\Sigma\text{Sats}$ ) = 14.8-19.2 mass%, CP was in the range -2.0 to 1.2°C. In contrast, tallow-FAME (TME) had  $\Sigma\text{Sats}$  = 49.8% and CP = 14.3°C.

Fuel	CP (°C)	PP (°C)	CFPP (°C)	LTFT (°C)	Reference
Canola	0	-9	-7		Moser, 2008
Coconut	5	-3			Chiou et al., 2008 Serdari et al., 2000
Corn	-3	-4	-7		Peterson et al., 2000
Jatropha	4	3	2		Sarin et al., 2007
Olive	-2	-3	-6		Kalligeros et al., 2003
Palm	16	15	12		Sarin et al., 2007
Rapeseed, < 5% erucic	-3	-9	-9		Rashid & Anwar, 2008
Soybean	0	-2	-2	0	Dunn & Bagby, 1995
Tallow	17	15	9	20	Foglia et al., 1997
No. 1 petrodiesel	-31	-46	-42	-27	Dunn & Bagby, 1995
No. 2 LSD	-16	-27	-18	-14	Dunn & Bagby, 1995
No. 2 ULSD	-11	-20	-16		Unpublished data

Table 1. Cold flow properties of fatty acid methyl esters (FAME) and petrodiesel fuels (defined according to ASTM standard D 975). CP = cloud point; PP = pour point; CFPP = cold flow plugging point; LTFT = low-temperature flow test; LSD = low-sulfur diesel ( $\leq 500$  ppm); ULSD = ultra-low sulfur diesel ( $\leq 15$  ppm).

The cold flow properties of biodiesel may be estimated based on  $\Sigma$ Sats portion of the alkyl ester mixture. The following correlation for CP was reported (Dunn et al., 1997):

$$CP = 1.44(\Sigma\text{Sats}) - 24.8 \quad (1)$$

where CP is in °C and  $\Sigma$ Sats is in mass%. Equation 1 is based on data correlated for  $\Sigma$ Sats = 6-20 mass% in SME. Although significant scatter was evident as indicated by an adjusted correlation coefficient ( $R^2$ ) = 0.79, standard error of the y-estimate ( $\sigma_y$ ) was only 2.4°C.

A more complex correlation of CP based on concentrations of the five main FAME found in SME was also reported (Davis et al., 2007). The empirical equation consisted of 21 terms with permutations of singular, squared and two-product mass fractions of each FAME. It was shown to calculate CP within  $\pm 2^\circ\text{C}$  of measured values for 29 of 39 total samples.

Extrapolating Eqn. 1 to  $\Sigma$ Sats = 0 mass% suggests a finite minimum CP =  $-24.8^\circ\text{C}$  ( $\pm 2.4^\circ\text{C}$ ) for the remaining components in SME. Another recent study (Bist et al., 2009) reported a nearly linear correlation between CP and  $\Sigma$ Sats for FAME mixtures with  $\Sigma$ Sats = 2.3-15

Oil or Fat	Fatty Acid (mass%)								
	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18</sub>	C <sub>18:1</sub>	C <sub>18:2</sub>	C <sub>18:3</sub>	C <sub>20:1</sub>	C <sub>22:1</sub>
Canola			3.6	1.5	61.6	21.7	9.6	1.4	0.2
Coconut <sup>a</sup>	45-53	17-21	7-10	2-4	5-10	1-3	≤ 0.2	≤ 9.2	
Corn		≤ 0.3	12-14	1-3	22-32	52-62	≤ 0.9		
Jatropha <sup>b</sup>		0.1	14-15	7	34-45	31-43	0.2		
Olive			10.5	2.6	76.9	7.5			
Palm <sup>c</sup>	0.2	1.1	44.1	4.4	39.0	10.6	0.3		
Rapeseed			4	1	14.8	14.2	9.1	10	45.1
Soybean			2-13	2-6	18-31	49-57	2-11		≤ 0.3
Tallow		3.4	29.5	26	34.9	1.5			
FAME MP (°C)	4.3	18.1	28.5	37.7	-20.2	-43.1	-55.5	-7.8	-3.0

<sup>a</sup>Coconut oil also contains 4-9% C<sub>8</sub> (octanoic acid), 5-8% C<sub>10</sub> (decanoic acid), and ≤ 0.2% C<sub>20</sub> (arachidic acid).

<sup>b</sup>Jatropha oil also contains 0.1% C<sub>10</sub>, 0.2-0.3% C<sub>20</sub> and ≤ 0.2% C<sub>22</sub> (behenic acid).

<sup>c</sup>Palm oil also contains 0.2% C<sub>20</sub>.

Table 2. Fatty acid composition of biodiesel feedstock lipids and melting points (MP) of corresponding FAME. Sources: Fatty acid profile data from Knothe et al., 2010 & references therein; MP data from Knothe & Dunn, 2009 except for C<sub>18:3</sub> (unpublished data). C<sub>12</sub> = Dodecanoic acid; C<sub>14</sub> = myristic acid; C<sub>16</sub> = palmitic acid; C<sub>18</sub> = stearic acid; C<sub>18:1</sub> = oleic acid; C<sub>18:2</sub> = linoleic acid; C<sub>18:3</sub> = linolenic acid; C<sub>20:1</sub> = eicosenoic acid; C<sub>22:1</sub> = erucic acid.

mass%. However, this study showed that decreasing  $\Sigma$ Sats below 2.3 mass% resulted in sharp non-linear decreases in CP. This suggested that accurate calculation of CP depended on factors other than  $\Sigma$ Sats in a FAME mixture.

The following correlation was reported for calculating CFPP as a function of  $\Sigma$ Sats based on studies conducted on used cooking oil-FAME (UCOME):

$$\text{CFPP} = 0.99(\Sigma\text{Sats}) - 19.0 \quad (2)$$

for  $\Sigma$ Sats = 14-26 mass% (González Gómez et al., 2002). This equation was nearly linear with respect to  $R^2 = 0.95$ . The following correlation based on cold flow properties of admixtures of SME and FAME from palm, canola and high-oleic sunflowerseed oils was similarly reported:

$$\text{CFPP} = 0.438(\Sigma\text{Sats}) - 8.93 \quad (3)$$

for  $\Sigma$ Sats up to 48.2 mass% (Moser, 2008). This equation had  $R^2 = 0.86$  and relatively high degrees of scatter were observed at lower concentrations. For  $\Sigma$ Sats exceeding 12 mass%,  $R^2$  increased to 0.98.

In contrast, a curvilinear relationship was reported for CFPP increasing from -12 to +12°C as  $\Sigma$ Sats in biodiesel increased from 5 to 45 mass% (Hilber et al., 2006). This study also noted that CFPP of biodiesel derived from animal fats generally exceeds 0°C. Similar results were obtained by correlating CFPP with respect to  $\Sigma$ Sats for blends of SME and FAME derived from rapeseed and palm oils (Park et al., 2008). Results indicated a higher degree of scatter and a sharp negative slope as unsaturated FAME content exceeded 85%.

### 2.3 Cold flow property correlations

A recent survey (Dunn & Moser, 2010) was conducted on cold flow properties of neat (100%) biodiesel derived from a variety of vegetable and plant oil, animal fat, used cooking oil, waste grease and other lipid feedstocks. Least-squares linear regression analysis were applied to PP, CFPP and LTFT versus CP of the corresponding biodiesel fuel. The following three correlations were reported:

$$PP = 0.98(CP) - 5.1 \quad (4)$$

$$CFPP = 1.0(CP) - 4.5 \quad (5)$$

$$LTFT = 1.0(CP) + 5 \quad (6)$$

where CP, PP, CFPP and LTFT are in °C. These equations had  $R^2 = 0.73, 0.78$  and  $0.54$  indicating significant scatter in the data and  $\sigma_y$  were between 3.4 and 4.4. Slopes were close to unity suggesting PP, CFPP and LTFT may be estimated by only measuring CP of the fuel.

### 2.4 Biodiesel/Petrodiesel blends

A detailed discussion on the cold flow properties of biodiesel/petrodiesel blends is presented elsewhere (Dunn & Moser, 2010). Summarizing, CP and PP curves generally show an increase with respect to increasing blend ratio (defined as vol% biodiesel in the blend). This was true for blends in No. 2 low-sulfur petrodiesel ( $S \leq 500$  ppm) and ultra-low sulfur petrodiesel (ULSD;  $S \leq 15$  ppm) as well as blends in jet fuel and No. 1 petrodiesel (kerosine). Cold flow properties of several biodiesel/petrodiesel blends are summarized in Table 3.

For blends shown in Table 3, ratios are defined as the vol% biodiesel in the blend and denoted as 'Bx' where x refers to the vol% biodiesel. Compared with corresponding data in Table 1, biodiesel/petrodiesel blends tend to yield cold flow properties that are close to volumetric average values based on blend ratio. At blend ratios as low as B20-B30, much of the influence of biodiesel on cold flow properties is minimized by dilution with petrodiesel. Consequently, blending biodiesel with petrodiesel may be advantageous for mitigating the poor cold flow properties of biodiesel from many lipid feedstocks. On the other hand, blending at higher ratios may compromise cold flow properties.

The aforementioned survey on cold flow properties of biodiesel derived from a variety of lipid feedstocks was also extended to compare properties of biodiesel/petrodiesel blends (Dunn & Moser, 2010). Similar to equations discussed earlier for neat (unblended) biodiesel, PP, CFPP and LTFT were found to correlate with CP as shown in the following equations:

$$PP = 1.10(CP) - 5.5 \quad (7)$$

$$CFPP = 0.95(CP) - 4.3 \quad (8)$$



Oil or Fat (FAME)	Petrodiesel	CP (°C)	PP (°C)	CFPP (°C)	LTFT (°C)	Reference
Soybean oil	No. 1	-17	-30	-27	-19	Dunn & Bagby, 1995
Chicken fat	No. 2 LSD	-10	-14			Wyatt et al., 2005
Chicken fat	No. 2 ULSD	-9	-10	-14		Unpublished data
Palm oil	Winter ULSD	-2	-16	-6		Tang et al., 2008
Soybean oil	No. 2 LSD	-14	-21	-14	-12	Dunn & Bagby, 1995
Soybean oil	No. 2 ULSD	-11	-17	-14		Unpublished data
Tallow	No. 2 LSD	-5	-9	-8		Foglia et al., 1997
Used Cooking Oil	No. 2 ULSD	-10	-13	-15		Unpublished data
Waste Grease	Winter ULSD	-17	-24	-24		Tang et al., 2008

Table 3. Cold flow properties of biodiesel/petrodiesel blends. Blend ratio = B20 (20 vol% biodiesel in blend). FAME = fatty acid methyl esters; LSD = low-sulfur petrodiesel ( $S \leq 500$  ppm); ULSD = No. 2 ultra-low sulfur petrodiesel ( $S \leq 15$  ppm); Winter ULSD = blend of No. 1 and No. 2 grade ULSD.

$$LTFT = 1.10(CP) + 3.3 \quad (9)$$

where CP, PP, CFPP and LTFT are in °C. These equations were nearly linear with respect to  $R^2 = 0.90, 0.92$  and  $0.94$ , respectively, and  $\sigma_y$  were between 3.3 and 4.0. Comparing with corresponding Eqns. 4-6, intercepts deviated by less than 2.0 and slopes by less than 0.12, suggesting the Eqns. 7-9 may be applied to blends with very low biodiesel blend ratios. Slopes for Eqns. 7-9 were also close to unity suggesting PP, CFPP and LTFT may be estimated by only directly measuring only CP. Overall, results from the survey showed that biodiesel has a predominant role in determining the cold flow properties and performance in blends with petrodiesel.

### 3. Thermodynamics of crystallization

Biodiesel is essentially a mixture of fatty acid alkyl ester components. For example, as shown in Table 2, SME is a mixture of methyl esters of  $C_{16}$ ,  $C_{18}$ ,  $C_{18:1}$ ,  $C_{18:2}$  and  $C_{18:3}$  fatty acids. Thermodynamic contributions related to alkyl ester composition may be accounted for by applying freezing point depression theory.

Crystallization phase behavior in model lipid mixtures was studied by application of the Hildebrand equation to results from isothermal and non-isothermal DSC analyses (Toro-Vazquez et al., 2000; Zhou & Hartel, 2006). Both studies employed the form of the equation for ideal mixtures, shown as follows:

$$\ln(x) = -\frac{\Delta H_{\text{fus}}}{R_g} \left[ \frac{1}{T_f} - \frac{1}{\text{MP}} \right] \quad (10)$$

where the mole fraction of crystallized fat ( $x$ ) is a function of its enthalpy of fusion or melting ( $\Delta H_{\text{fus}}$ ), the gas constant ( $R_g$ ), its crystallization onset temperature ( $T_f$ ) in a mixture and its MP in pure form.

Phase behavior resembling freezing point depression was observed in dewaxed gas oil spiked with pairs of long-chain ( $C_{20}$ - $C_{28}$ )  $n$ -alkanes (Holder & Winkler, 1965). Freezing point depression theory accurately predicted the cold flow behavior of mixtures by following crystallization behavior of a binary system in a solvent that did not freeze at the temperatures studied. The theory also explained how small mass fractions of heavy wax can disproportionately influence cold flow properties of mixtures.

Another study (Suppes et al., 2000) examined several theoretical and empirical models for mixtures composed of  $n$ -alkanes, olefins and other hydrocarbons and determined that freezing point depression was the only fundamentally correct theory for describing crystallization processes in organic liquid mixtures. One equation derived for mixtures where independent crystallization of solute species is prevalent was as follows:

$$\ln(\gamma_i x_i) = -\frac{\Delta H_{\text{fus}}}{R_g} \left[ \frac{1}{T_f} - \frac{1}{\text{MP}} \right] - \frac{\Delta C_p}{R_g} \left[ 1 - \frac{\text{MP}}{T_f} + \ln \left( \frac{\text{MP}}{T_f} \right) \right] \quad (11)$$

where  $\gamma_i$  and  $x_i$  are activity coefficient and mole fraction of component 'i' in the liquid phase,  $\Delta H_{\text{fus}}$ , MP and  $T_f$  are parameters for component 'i' as defined in Eqn. 10 and  $\Delta C_p$  is the differential heat capacity of species 'i' between liquid and solid phases ( $C_p^L - C_p^S$ ). The activity coefficient accounts for non-ideal behavior in the liquid phase, while the second term on the right-hand-side corrects for variation in  $\Delta H_{\text{fus}}$  with respect to temperature. Another form of Eqn. 11 was derived for mixtures where a solid solution forms upon crystallization. This equation replaces the left-hand side with the term  $\ln([\gamma_i x_i]/[\gamma_i^S x_i^S])$ , where  $\gamma_i^S$  and  $x_i^S$  are activity coefficient and mole fraction of species 'i' in the solid phase.

Equation 10 was applied to determine CP of biodiesel based on studies with mixtures of long-chain ( $C_{16}$ - $C_{18}$ ) FAME (Imahara et al., 2006). This model was derived by setting  $\gamma_i = 1$  due low ambient pressure and assuming  $\Delta C_p$  as shown in Eqn. 11 was negligible. FAME mixtures showed good agreement between corresponding  $T_f$  and CP data. Eutectic points were predicted for mixtures with methyl palmitate ( $C_{16}$ )/stearate ( $C_{18}$ ) mole ratios of 2.3:1. Similar observations were noted for mixtures of methyl palmitate with dodecanoate ( $C_{12}$ ) and myristate ( $C_{14}$ ). Deviations between  $T_f$  and measured CP data were less than 5°C for mixtures with up to five FAME. Results also demonstrated that  $T_f$  was independent of the species of unsaturated FAME in the solvent phase.

A recent study (Dunn, 2008) compared results from application of Eqns. 10 and 11 to model crystallization of methyl palmitate and stearate in solutions with methyl oleate ( $C_{18:1}$ ). MP and  $\Delta H_{\text{fus}}$  values for pure FAME components were measured by DSC. Results for binary



mixtures indicated non-ideal behavior with respect to high-MP solutes, in contrast to results reported by Imahara et al. (2006). Osmotic coefficient data indicated that the methyl oleate behaved independently of the type of solute in the liquid phase (Dunn, 2008). The  $\Delta C_p$  term in the right-hand side of Eqn. 11 was not significant in calculation of  $T_f$  values. Results for ternary mixtures indicated a eutectic point at  $C_{16}/C_{18}$  mole ratio of 3.1:1. Although deviations between calculated and measured  $T_f$  values averaged less than 2.3°C, larger deviations occurred at  $C_{16}/C_{18}$  mole ratios close to the eutectic point, suggesting that methyl palmitate and stearate did not undergo independent crystallization under these conditions. Calculated results were generally more accurate when accounting for non-ideal behavior in the liquid phase. Adding *n*-propyl, isopropyl or *n*-butyl stearate also disrupted independent crystallization of solute species in ternary mixtures with methyl stearate and oleate (Dunn, 2009).

#### 4. Improving the cold flow properties of biodiesel

Results from the aforementioned cold flow property survey (Dunn & Moser, 2010) generally agreed with conclusions reported in earlier research studies (Dunn & Bagby, 1995, 1996; Dunn et al., 1996) on developing approaches to reduce CP, PP, CFPP and LTFT of biodiesel. The main conclusion based on correlations shown in Eqns. 8 and 9 was that approaches that emphasize reducing the CP of biodiesel will have the greatest potential for improving CFPP and LTFT. In addition, improving the properties of biodiesel will have the added benefit of improving the properties of its blends with petrodiesel.

As discussed earlier, blending with petrodiesel at relatively low blend ratio mitigates most performance-related issues with cold flow properties of neat biodiesel depending on its original feedstock. Splash blending biodiesel and petrodiesel may also present problems during cold weather. A recent report (Cold Flow Blending Consortium, 2005) recommended that biodiesel be stored at temperatures no lower than 6°C above its CP before splash blending with petrodiesel. Increased reliance on palm oil, tallow and other feedstocks with relatively high  $\Sigma$ Sats (see Table 2) continues to drive research efforts to improve cold flow properties. Another driver may be applications where higher blend ratios are necessary to improve exhaust emissions from combustion of fuels formulated with biodiesel.

A comprehensive discussion on experimental approaches evaluated for improving the performance of biodiesel and its blends is presented elsewhere (Dunn & Moser, 2010). Summarizing, these approaches include:

1. Treating with commercial petrodiesel cold flow improver additives
2. Developing new additives for biodiesel
3. Mixing FAME with alkyl esters made from transesterification with medium- and branched-chain alcohols
4. Decreasing crystallization temperature ( $T_f$ ) by reducing total saturated FAME concentration.

The remainder of this chapter is an in depth examination of fractionation technologies that have or may be explored to address the fourth outlined approach.

#### 5. Fractionation

The objective of fractionation is to modify the fatty acid alkyl ester composition of biodiesel such that the concentration of high-MP components decreases. *Crystallization fractionation* takes advantage of the aspect that saturated alkyl esters have a significantly higher MP than

unsaturated alkyl esters with the same chain length. For example, MP data in Table 2 show values of 37.7°C for methyl stearate (C<sub>18</sub>) and -20.2°C for methyl oleate (C<sub>18:1</sub>). With few exceptions biodiesel from most lipid feedstocks is composed of saturated and unsaturated long-chain (C<sub>14</sub>-C<sub>18</sub>) fatty acid alkyl esters where higher-melting components have MP at least 38°C higher than lower-melting components. This large differential means a mixture would typically experience nucleation and crystal growth kinetics similar to precipitation of solutes (MP > 18.1°C) from a solvent mixture (MP < -20°C). Applying this paradigm to multi-component alkyl ester mixtures suggests that an effective approach for improving cold flow properties is to separate and remove the high-MP components from the mixture.

Commercial fractionation processes for application to edible oils and fats have been extensively reviewed (Anderson, 1996; Bailey, 1950; Illingworth, 2002; Kellens & Hendrix, 2000; Kellens et al., 2007; Krishnamurthy & Kellens, 1996; O'Brien, 1998; Rajah, 1996). One popular process is crystallization fractionation which separates lipid components based on differences in crystallizing temperatures (MP). Crystallization fractionation has been successfully applied to vegetable oils, hydrogenated vegetable oils, animal fats, fish oils, fatty acids, fatty acid esters, monoacylglycerols, diacylglycerols and other fatty derivatives (Brown & Kolb, 1955; Illingworth, 2002; Kellens & Hendrix, 2000; O'Brien, 1998).

The traditional process is performed in two steps, crystallization followed by separation into liquid and solid fractions. Product yield is defined by separation of high- and low-melting fractions and depends on maintaining strict control during both steps of the process. In the first step, the oil is cooled at a controlled rate with gentle agitation in a chiller (or crystallizer) to promote selective nucleation and crystal growth. Cooling rate in the chiller must be constantly monitored because it determines the rate of nucleation and number, size distribution and shape of the crystals. Crystallization modifiers may be added to promote nucleation, modify crystal growth rate and habit or reduce entrainment of liquid within solid crystal agglomerates (Illingworth, 2002; Krishnamurthy & Kellens, 1996). Agitation regulates crystalline growth by reducing buildup of heat transfer-reducing crystals on walls of the chiller and agglomeration of small crystals which causes entrainment of liquid phase. Agitation also reduces the effects of increasing viscosity that occur during the cooling cycle. Increasing viscosity decreases mass transfer rate to the crystal surface and reduces heat transfer away from the crystals (Krishnamurthy & Kellens, 1996). It must be tightly controlled to prevent detrimental effects of high shear rates, which can fragment or destroy crystals, and limit addition of mechanical work to the system (Anderson, 1996; Krishnamurthy & Kellens, 1996). Other process variables include composition of source oil or fat, final crystallization temperature and total time in the chiller. The latter two variables will also significantly affect crystalline growth rates (Illingworth, 2002; Kellens & Hendrix, 2000).

Once well-defined crystals with narrow size distribution and specified shape are formed, the resulting slurry is transferred to the second step for separation. Separation of solid and liquid phases is usually performed by filtration, centrifugation or decantation. Most commercial filtration equipment employs plate and frame, flat-bed vacuum band, rotary drum vacuum, membrane (polypropylene or synthetic rubber), hydraulic press or pressure leaf type filters. Conditions are also tightly controlled and generally determine optimal crystal sizes that should be generated in the crystallization stage (Illingworth, 2002; Krishnamurthy & Kellens, 1996).

### 5.1 Dry fractionation

Dry (melt) fractionation, defined as crystallization from a melt without dilution in solvent, is the simplest, least expensive and most common process for separating high- and low-

melting fatty derivatives (Anderson, 1996; O'Brien, 1998). Dewaxing and winterization are limited forms of dry fractionation often associated with oil refining because the total wax content removed is relatively small (< 2 mass%) and physical properties other than appearance are not affected. Winterization is typically associated with crystallization during long-term storage in cold temperatures. Dry fractionation generally refers to a modification process where substantial changes in composition are accompanied by significantly modified CP, MP, cold stability test, dropping point and iodine value. Crystallization and separation stages are technologically sophisticated and require a higher degree of control to separate fatty derivatives with higher selectivity than dewaxing or winterization (Kellens & Hendrix, 2000; Krishnamurthy & Kellens, 1996). Cold flow properties of liquid fractions obtained from dry fractionation of SME and UCOME are summarized in Table 4. Earlier studies (Dunn et al., 1996, 1997) showed that dry fractionation of SME decreased CP to -20°C and LTFT to -16°C, values that compared well to the properties of low sulfur No. 2 petrodiesel. PP and CFPP were also significantly reduced. Although  $\Sigma$ Sats decreased to as low as 5.6 mass%, liquid fraction yields were only 25-33 mass% relative to the starting material. Step-wise crystallization in 2-3°C-increments was necessary to maintain control over crystallization. Residence time in the cooling bath for each step was 16 h (overnight).

FAME	Modifier	Steps	T <sub>B</sub> (°C)	Yield (g/g)	$\Sigma$ Sats (mass%)	CP (°C)	PP (°C)	CFPP (°C)
SME	None	6	-10	0.334	6.3	-20	-21	-19
SME	None	11	-10.0	0.255	5.5	-7.1 <sup>a</sup>		
LP-SME	None	7	-13.2	0.857	3.8	-11.2 <sup>a</sup>		
UCOME	None	1	0	0.30	13.0			-5
UCOME	None	1	-6	NR	9.6			-9
SME	<i>DFI-200<sup>b</sup></i>	6	-10	0.801	9.8	-11		-12
SME	<i>Winterflow<sup>b</sup></i>	6	-10	0.870	9.3	-11		-11

<sup>a</sup>Crystallization onset temperature from differential scanning calorimetry analysis.

<sup>b</sup>Petrodiesel pour point depressants, 2000 ppm. Vendors: Du Pont (*DFI-200*) and Octel-Starreon (*Winterflow*).

Table 4. Cold flow properties of dry fractionated biodiesel. Sources: Dunn, 1998; Dunn et al., 1997; González Gómez et al., 2002; Kerschbaum et al., 2008; Lee et al., 1996. T<sub>B</sub> = Coolant bath temperature (final step); Yield = mass ratio liquid fraction/starting material;  $\Sigma$ Sats = total saturated alkyl concentration; SME = soybean oil-FAME; LP-SME = low-palmitic (4.0 mass%) SME.

The effects of dry fraction on cold flow properties of "normal" and low-palmitic (4.0 mass%) SME were investigated (Lee et al., 1996). Dry fractionation of normal SME was conducted by step-wise crystallization with incremental residence times varying with respect to time required for significant crystal formation to occur. Typical liquid fraction yields for each

step were 84-90 mass%. After 11 steps and a total residence time of 84 h, the final liquid fraction had  $\Sigma\text{Sats} = 5.5$  mass% and crystallization onset temperature =  $-7.1^\circ\text{C}$  (measured by differential scanning calorimetry), compared to values of 15.6 mass% and  $+3.7^\circ\text{C}$  for non-fractionated SME. However, final liquid yield was only 25.5%. Fractionation of low-palmitic SME under similar conditions required seven steps and increased liquid yield to 85.7%. The liquid fraction had  $\Sigma\text{Sats} = 3.8$  mass% and onset temperature =  $-11.2^\circ\text{C}$  compared to values of 6.8 mass% and  $-3.7^\circ\text{C}$  for the non-fractionated low-palmitic SME.

Comparing results from these two studies, the former employed a constant crystallization time (16 h) for each fractionation step (Dunn et al., 1996, 1997) while the latter increased control of nucleation and crystal growth by keeping the crystallized mass constant for each step (Lee et al., 1996). Both schemes collected liquid fractions with significantly improved cold flow properties at the expense of poor liquid fraction yields for normal SME. Trapping of liquid within solid crystals during growth and agglomeration phases led to substantial losses of liquid after filtration. Contrasting the control schemes also suggests the rate of crystalline growth and agglomeration was rapid causing substantial entrainment of liquid phase during early stages of crystallization.

Results from two studies applying dry fractionation to decrease CFPP of UCOME are also shown in Table 4. One study (González Gómez et al., 2002) cooled the liquid UCOME to  $0^\circ\text{C}$  at a slow cooling rate ( $0.1^\circ\text{C}/\text{min}$ ) for 15-24 h. After filtration,  $\Sigma\text{Sats}$  decreased to 13.0 mass% and CFPP to  $-5^\circ\text{C}$ , compared to values of 19.2 mass% and  $-1^\circ\text{C}$  for non-fractionated UCOME. Liquid fraction yields were poor at 30%. The second study (Kerschbaum et al., 2008) circulated UCOME through a cross-flow micro heat exchanger (channel diameter =  $200\ \mu\text{m}$ ) while slowly decreasing the temperature of water-ethylene glycol coolant flowing through other channel. Employing a very slow cooling curve over a period of 8 days reduced  $\Sigma\text{Sat}$  by 11.4 mass% and CFPP by  $11^\circ\text{C}$ , compared to non-fractionated UCOME. Animal fat-FAME and UCOME were dry fractionated with separation mainly occurring between saturated and unsaturated FAME (Falk & Meyer-Pittroff, 2004). Oils were first cooled in a flask until large crystal structures formed and the solid phase removed by filtration through a  $300\ \mu\text{m}$  pore-size filter and centrifugation at  $1200 \times g$ . Dry fractionation of TME under controlled conditions resulted in 60-65% yields of liquid fraction characterized by an increase in iodine value from 41 to 60 and a decrease in CP from 11 to  $-1^\circ\text{C}$  (Krishnamurthy & Kellens, 1996).

A pilot-scale process study (Delafontaine et al., 2005) demonstrated that SME could be fractionated in a scraped-surface heat exchanger operating in continuous mode. The heat exchanger operated with efficient heat transfer and during trials retention times were less than 60 min. The biodiesel was pre-chilled to  $10^\circ\text{C}$  before being pumped into the heat exchanger and steady state crystallization occurred at  $-3^\circ\text{C}$  within the exchanger. A light-scattering probe in the collection vessel confirmed the slurry consisted of near-Gaussian distribution about a median crystal size of  $15\ \mu\text{m}$ . Filtrate temperatures were as low as  $-4.6^\circ\text{C}$  before the product began to gel. Pumping the slurry through a membrane press filter at a rate of 4 L/min, CP of the filtrate was only  $1.2^\circ\text{C}$ , suggesting this step may be insufficient to maintain good separation between fractions.

## 5.2 Wax crystallization modifiers

Crystallization modifiers may be applied to promote nucleation or adsorb onto crystal surfaces (co-crystallization) to disrupt otherwise orderly patterns and limit growth and agglomeration. Modifiers can improve separation efficiency and reduce entrainment by



slowing the rate of agglomeration. Examples of modifiers for fatty derivatives include commercial lecithins, monoacylglycerols, diacylglycerols, citric acid esters of monoacylglycerols and diacylglycerols, free fatty acids and fatty acid esters of sorbitol and polyglycerol (Illingworth, 2002; Krishnamurthy & Kellens, 1996).

An earlier study (Dunn et al., 1996) reported that a number of commercial petrodiesel cold flow improver additives also significantly reduced PP and CFPP of neat SME. It was concluded that these additives decreased the rates of crystalline growth and agglomeration at temperatures below the CP of SME. Two of the most effective additives, *DFI-200* and *Winterflow*, were subsequently evaluated as crystallization modifiers for dry fractionation of SME in another study (Dunn et al., 1997). Some results from the second study are summarized in Table 4.

Results from the step-wise fractionation of SME treated with 2000 ppm *DFI-200* and *Winterflow* additives are shown in Table 4. Six incremental crystallization-filtration cycles were conducted on succeeding liquid fractions as coolant temperature for each step decreased by 2-3°C. The additives significantly increased final liquid fraction yields to 80-87 mass%. Both trials resulted in decreasing CP to -11°C, a value close to the final cooling bath temperature (-10°C). These results demonstrated that treating biodiesel with crystallization modifiers hindered growth and agglomeration of crystals which subsequently reduced entrainment of liquid within the solid crystal phase. These conditions improved separation efficiencies leading to significant increases in liquid fraction yield (Dunn et al., 1997).

### 5.3 Solvent fractionation

Crystallization fractionation from dilute solution in organic solvent offers many advantages over dry fractionation. Solvent fractionation reduces viscosity and entrainment of liquid within and between solid crystals. The process is characterized by short crystallization time and ease of filterability leading to high separation efficiency and improved yield. It is the most efficient fractionation process, though it may raise concerns associated with safety, handling and recovery of solvent. Decontaminating fractions from trace concentrations of residual solvent may also prove difficult and problematic. It is more expensive than dry fractionation and generally employed in production of high quality oils or fats or products with unique properties (Illingworth, 2002; Krishnamurthy & Kellens, 1996; O'Brien, 1998).

Factors affecting solvent selection include polarity, relative solubility of components to be fractionated and the presence of unsaturated fatty acids. Solvent polarity affects crystal morphology which influences growth rate and habit (Gunstone, 1967; Larsson & Quinn, 1994). Alkyl esters have higher solubility in a given organic solvent than corresponding free fatty acids and will require much lower crystallization temperatures. Acetone, methanol, Skellysolve B and ether have been employed as solvents for fractionation of alkyl esters from cottonseed and soybean oils and other long-chain (C<sub>18</sub>) fatty acids (Brown & Kolb, 1955). Other solvents employed in fractionation of lipids include, chloroform, ethanol (95%), ethyl acetate, hexane, isopropanol, methanol and 2-nitropropane (Brown & Kolb, 1955; Krishnamurthy & Kellens, 1996; O'Brien, 1998).

Cold flow properties of liquid fractions obtained from solvent fractionation of SME in hexane and isopropanol are summarized in Table 5. An earlier study (Dunn et al., 1997) investigated effects of hexane and isopropanol on crystallization fractionation of SME. Fractionation was achieved in one step with crystallization times of 3.5-5 h. As shown in

Table 5, fractionation from hexane at  $-25^{\circ}\text{C}$  resulted in a liquid fraction with  $\text{CP} = -10^{\circ}\text{C}$ . Although yield improved to 78.4 mass% with respect to dry fractionation (see Table 4),  $\Sigma\text{Sats}$  in the liquid fraction decreased by only 3.5 mass% compared to non-fractionated SME. This suggested its CP may have been influenced by residual hexane left behind after evaporation of the solvent. Decreasing crystallization temperature to  $-30^{\circ}\text{C}$  reduced  $\Sigma\text{Sats}$  in the liquid fraction to 11.3 mass% allowing reduction in CP to  $-10^{\circ}\text{C}$  and PP to  $-11^{\circ}\text{C}$ . However, liquid product yield decreased to 59.6%. Fractionation of SME from isopropanol at  $-15^{\circ}\text{C}$  resulted in comparable results after only one step. Product yield was 86.0% and  $\Sigma\text{Sats}$  was 10.8 mass%, resulting in significant decreases in CP, PP and CFPP as shown in Table 5.

Solvent	SME/Solvent (g/g)	Steps	$T_B$ ( $^{\circ}\text{C}$ )	Yield (g/g)	$\Sigma\text{Sats}$ (mass%)	CP ( $^{\circ}\text{C}$ )	PP ( $^{\circ}\text{C}$ )	CFPP ( $^{\circ}\text{C}$ )
Hexane	0.284	1	-25	0.784	16.2	-10	-11	-10
Hexane	0.217 <sup>a</sup>	3	-28.4	0.77	6.0	-5.8 <sup>b</sup>		
Isopropanol	0.228	1	-15	0.860	10.8	-9	-9	-9

<sup>a</sup>In g/mL.

<sup>b</sup>Crystallization onset temperature from differential scanning calorimetry analysis.

Table 5. Cold flow properties of solvent fractionated soybean oil-FAME (SME). Sources: Dunn, 1998; Dunn et al., 1997; Lee et al., 1996.

Similarly, fractionation of SME from hexane solvent in three steps was evaluated (Lee et al., 1996). Crystallization times were 16, 16 and 5 h, respectively, and the final cooling temperature was  $-28.4^{\circ}\text{C}$ . The final liquid fraction yield increased significantly to 77 mass% compared to dry fractionation of SME (see Table 4). The liquid fraction had  $\Sigma\text{Sats} = 6.0$  mass% and an crystallization onset temperature =  $-5.8^{\circ}\text{C}$  (measured by differential scanning calorimetry). Results also showed the importance of the nature of the solvent. Dilution in methanol resulted in separation into two liquid layers as coolant temperature approached  $-1.6^{\circ}\text{C}$ . Acetone mixtures resulted in no significant reduction in onset temperature and crystals failed to form in mixtures with chloroform at cooling temperatures below  $-25^{\circ}\text{C}$ .

Crystallization of TME in blends with ethanol, No. 2 petrodiesel and ethanol/No. 2 petrodiesel solvents was investigated (Hanna et al., 1996). Experimental procedures closely resembled traditional winterization where samples were stored for three weeks in walk-in freezers for a series of incremental crystallization/filtration steps performed at 10, 0,  $-5$ ,  $-10$  and  $-16^{\circ}\text{C}$ . Ethanol decreased formation of crystals in TME and TME/No. 2 petrodiesel mixtures. Winterization of 1:9 (vol) TME/No. 2 petrodiesel and 16.5:13.5:70 (vol) TME/ethanol/No. 2 petrodiesel mixtures reduced CP below  $-5^{\circ}\text{C}$ .

Effects of adding wax crystallization modifiers on fractionation of SME diluted in hexane and isopropanol were investigated (Dunn et al., 1997). *DFI-200* and *Winterflow* at 2000 ppm concentration (in SME) were added to 0.20 g/g SME/solvent mixtures and processed in one step. Compared to mixtures without modifiers, lower cooling bath temperatures were necessary to promote shorter crystallization times. Liquid fractions were collected in very high yield (95-103 mass%), indicating that residual solvent was likely retained following



evaporation. Results from these trials were compared to those for solvent fractionation of SME with no modifiers present (see Table 5). For mixtures with modifiers, liquid fractions from SME/isopropanol had slightly higher  $\Sigma$ Sats (12.8-13.3 mass%) than those for mixtures without modifiers. Liquid fractions from mixtures with modifiers had higher CP (-6 to -5°C) while PP was in the same range (-12 to -9°C) as those from mixtures without modifiers present. It was concluded that adding crystallization modifiers offered no significant advantages in performing solvent fractionation on SME.

#### 5.4 Urea fractionation

Clathrates are well-defined addition compounds formed by inclusion of *guest* molecules within cavities formed by crystal lattices or present between large molecules. Urea inclusion compounds (UIC) were discovered by accident in 1940. While studying the effects of urea on pasteurized milk, it was shown that urea formed solid crystals when mixed with *n*-octanol (Hayes, 2002). This work reported that *n*-alkanes, *n*-alcohols, fatty acids, fatty acid esters, aldehydes and ketones demonstrated formation of UIC. It was subsequently shown that UIC readily form with straight-chain guest molecules having six or more carbon atoms in length with stability of the clathrates increasing with increasing chain-length. In contrast, molecules with less than six carbon atoms or with branched or cyclic moieties in their structure formed less stable clathrates when mixed with urea (Bengen & Schlenk, 1949; Hayes, 2002; Schlenk, 1954). Furthermore, increasing the degree of unsaturation, particularly with respect to *cis*-type double bonds, in fatty acids and esters also decreases the tendency to form stable UIC (Abu-Nasr et al. 1954; Domart et al., 1955; Newey et al. 1950; Schlenk & Holman, 1950; Swern & Parker, 1952a, 1952b, 1953). These early findings suggested that processes for separating mixtures of organic compounds with high degrees of selectivity could be based on their tendencies to form clathrates when mixed with urea.

##### 5.4.1 Theory and methodology

The theory of UIC-based fractionation summarized herein is explained more thoroughly in other reviews (Hayes, 2002; Schlenk, 1954; Swern, 1955). Urea clathrates do not form unless guest molecules are present. Clathrates consist of a series of parallel channels approximately 55-58 nm in average inside diameter. Urea molecules ( $\text{H}_2\text{N}-[\text{CO}]-\text{NH}_2$ ) are aligned along the channel walls and held in place by hydrogen bonding. Clathrates form needle-like hexagonal crystals with channels aligned side-by-side in contrast to the tetragonal crystalline structures formed from pure urea. These channel walls are considered smooth such that guest molecules with sufficiently small cross-sectional diameter will randomly pack inside them.

In practice, UIC are prepared by dissolving urea and guest compounds into solution typically at elevated temperature and in presence of a polar solvent that does not form clathrates (for example, methanol or ethanol) then cooling the resulting heterogeneous solution until solid crystals appear. Operational conditions depend on solubility of compounds being studied and desired yield and fractionation efficiency of the intended products. Presence of UIC in solid phases may be confirmed analytically by X-ray diffraction, differential scanning calorimetry or infrared spectroscopy.

Solid (UIC) and liquid phases are typically separated by vacuum filtration. If fractionated molecules within the UIC are to be recovered, adding slightly acidic (pH = 3-4) warm water dissolves urea leaving a separate solid precipitate or liquid layer that can subsequently be vacuum-distilled to remove traces of organic solvent. Alternatively, guest molecules may be

extracted with a solvent such as benzene, isooctane or carbon tetrachloride. Similar process steps are applied when fraction(s) of interest remain in the filtrate (liquid phase) after separation. Urea and organic solvents employed in the fractionation steps may be recovered and recycled within the process.

#### 5.4.2 Applications

Urea clathrates were initially applied in fractionation of petroleum based on MP of *n*-alkanes present in the oil. However, availability of inexpensive petroleum allowed less complex distillation refining, hindering progress in the development of UIC methodologies. Nevertheless, at least one recent study (Zabarnick et al., 2002) demonstrated that urea fractionation significantly reduces CP, PP and freezing point of Jet-A aviation fuel. The best results were obtained by forming a slurry where Jet-A fuel is mixed with 25 mass% urea and 1 mass% methanol at 23°C for 3 h. Results indicated substantial decreases in concentration of *n*-tetradecane (C<sub>14</sub>) and higher *n*-alkanes in the filtrate after passing the slurry through a chromatographic syringe.

Urea clathrates were also demonstrated to form for several common saturated fatty acids as well as alkyl esters of myristic, palmitic and stearic acids. Microscopic examination shows that UIC formed with saturated fatty acids and esters appear as thin or coarse needles. In contrast, unsaturated fatty acids and esters formed flat hexagonal leaflets. Formation of UIC is an exothermic process where guest molecules that more readily form clathrates have higher molar heats of formation. Increasing chain length or decreasing the degree of unsaturation generally increases molar heat of formation. Mostly owing to hydrogen bonding, fatty acids have higher molar heats of formation than fatty esters (Schlenk, 1954).

Urea binds with fatty acids or esters at a mass ratio of 3:1, though it is often necessary to add excess urea to obtain good yields. For example, 1 g fatty derivative dissolved in a hot mixture of 30 mL methanol plus 5 g urea (solubility limit at room temperature) forms precipitates when cooled to room temperature. Temperatures and concentrations may be varied for guest molecules with lower tendencies to form clathrates such as unsaturated fatty esters. Fatty acid or alkyl ester mixtures may be fractionated into saturated and unsaturated components after one urea precipitation step. However, for mixtures of palmitic, stearic, oleic, linoleic and linolenic acids or esters, separation is generally most efficient between saturated/monounsaturated and polyunsaturated components. Also, increasing urea concentration generally increases the concentration of oleic acid or ester contained within the clathrates (Schlenk, 1954).

Initially, applications that were explored for UIC processing in the field of fats and oils chemistry were removal of free fatty acids from plant oils and fats and fractionation of fatty acids, esters, alcohols and other derivatives. Taking advantage of UIC not oxidizing when exposed to air, storage of polyunsaturated fatty materials as UIC solids was explored. Finally, isolation of fatty peroxides and determining the configuration of diastereoisomers (for example, 9,10-dihydroxystearic acid) by formation of clathrates were also studied (Swern, 1955).

More recently, urea fractionation was applied in laboratory- and industrial-scale reduction of saturated fatty acid content of low-erucic acid rapeseed oil (Hayes et al., 1998). UIC were employed in fractionation of fatty acid mixtures of marine, borage, canola, linseed, lesquerella, rapeseed and meadowfoam oils (Hayes et al., 2000; Hayes, 2006). This technique was applied in isolation and purification of linoleic acid from sunflowerseed oil (Wu et al., 2008) and oleic and linoleic acids from various vegetable oils (Lee, 2003). Urea fractionation

was utilized in selective enrichment of conjugated linoleic acid isomers ( $C_{18:2-9c,11t}$  and  $C_{18:2-10t,12c}$ ) in fatty acids obtained from safflower oil (Ma et al., 1999). UIC were employed in the purification of gamma-linolenic acid ( $C_{18:3-6c,9c,12c}$ ) from borage oil fatty acids (Shimada et al., 1998) and blackcurrant seed oil fatty acids (Traitler et al., 1988). Urea fractionation was applied in the enrichment of eicosapentaenoic acid ( $C_{20:5-5c,8c,11c,14c,17c}$ ) and docosahexaenoic acid ( $C_{22:6-4c,7c,10c,13c,16c,19c}$ ) obtained from marine oils (Lee, 2003; Bretton, 2003). Finally, UIC were utilized in isolation and purification of stearidonic acid ( $C_{18:4-d6,9,12,15}$ ) from fatty acids derived from blackcurrant and marine oils (Lagarde et al., 1992). Many of the experimental techniques outlined in these studies employed methanol or ethanol, anhydrous or with the presence of 5-10 vol% water, as solvents because they could be easily removed by evaporation. Some processes coupled urea fractionation with other steps such as vacuum distillation, solvent fractionation and preparative high performance liquid chromatography to isolate and purify the compounds of interest.

#### 5.4.3 Fatty acid alkyl esters (biodiesel)

Processing of fatty derivatives is frequently made easier by first converting fatty acids into their corresponding esters. Consequently, urea fractionation was applied to alkyl ester mixtures employing methanol or ethanol, anhydrous or aqueous (5-15 vol%), as polar solvents. UIC were employed to isolate and purify malvalic (*cis*-9,10-methyleneheptadec-8-enoic) and sterculic (*cis*-9,10-methyleneoctadec-9-enoic) acid methyl esters from crude FAME mixtures derived from *Bombax munguba* and *Sterculia foetida* seed oils (Fehling et al., 1998). A continuous UIC-based process was developed to isolate gamma-linoleic acid esters from linseed and marine oil fatty acid ethyl esters (Traitler & Wille, 1992). For that process, solid crystals were precipitated by cooling heterogeneous solutions to below room temperature in a series of scraped-surface heat exchangers. Another process coupled urea fractionation with vacuum distillation to isolate eicosapentaenoic acid ethyl esters from marine oil (Fujita & Makuta, 1983). A process integrating transesterification and urea fractionation step was also patented (Bertioli et al, 1997). After separation of the glycerol layer, product alkyl esters were mixed with urea and ethanol to perform the fractionation step. This process was designed for industrial-scale production of highly pure gamma-linoleic, eicosapentaenoic and docosahexaenoic acid esters.

There is a paucity of scientific studies directly applying urea fractionation to improve the cold flow properties of biodiesel. Nevertheless, the following general procedure was derived from studies on fatty acid mixtures (Bist & Tao, 2005; Bist et al., 2007, 2009):

1. Mix urea with FAME and methanol or ethanol
2. Heat mixture to form a heterogeneous solution
3. Cool the mixture to between 15-30°C
4. Separate solids crystals from liquid by vacuum filtration, centrifugation or decantation.

The filtrate is processed to remove alcohol by evaporation and trace urea concentrations by extraction with organic solvent and slightly acidic (pH = 3-4) water. The final product biodiesel is enriched in unsaturated FAME content and has a significantly reduced CP. Product yields are adjusted by varying urea concentration, solvent volume and cooling temperature.

Experimental conditions and results from several UIC trials on fractionation of SME are summarized in Table 6. These data show that increasing urea/SME mass ratio at constant alcohol volume decreases  $\Sigma$ Sats and CP of the final liquid product. These improvements come at the expense of reduced yield and monounsaturated FAME (methyl oleate)

concentration in the product. Losses caused by increasing urea/SME mass ratio may be partially recouped by crystallization of UIC at a higher cooling temperature.

A pilot-scale process directly integrating urea fractionation and transesterification for conversion of lipid feedstock into biodiesel with enhanced cold flow properties was developed (Bist et al, 2007, 2009). The urea fractionation step was designed to accept crude products from the transesterification step where biodiesel is mixed with glycerol co-product. Fractionation was demonstrated with methanol and ethanol solvents. For fractionation of SME, a 44.6 mass% yield of liquid product with  $\Sigma\text{Sats} = 1.7$  mass% and CP =  $-34^\circ\text{C}$  was recovered. Decreases in CP were non-linear with respect to increasing urea/SME mass ratio especially for ratios exceeding 0.5:1. Concentrations of all unsaturated FAME components were enriched in liquid products from fractionation with urea/SME mass ratios less than 0.5:1. In contrast, higher mass ratios decreased methyl oleate ( $\text{C}_{18:1}$ ) concentrations in liquid products.

Urea/SME/Alcohol (g/g/mL)	Alcohol	$T_{\text{Soln}}$ ( $^\circ\text{C}$ )	$T_{\text{B}}$ ( $^\circ\text{C}$ )	Yield (g/g)	$\Sigma\text{Sats}$ (mass%)	$\text{C}_{18:1}$ (mass%)	CP ( $^\circ\text{C}$ )
Non-fractionated SME	None				12.9	23.5	0
24.1/10.1/160	Ethanol	67	20	0.783	7.7	24.6	-10
24.1/16.0/160	Ethanol	72	30	0.759	2.3	22.5	-16
Non-fractionated SME	None				15.0	25.9	3
24.0/16.8/120	Methanol	55	25	0.517	2.3	24.4	-23
24.0/24.0/120	Methanol	55	20-25	0.429	0.0	19.2	-57

Table 6. Urea fractionation of soybean oil-FAME (SME). Sources: Bist & Tao, 2005; Bist et al., 2009.  $T_{\text{Soln}}$  = temperature where heterogeneous solution formed;  $\text{C}_{18:1}$  = methyl oleate; NA = not applicable.

Another study (Davis et al., 2007) more broadly investigated the effects of increasing urea/SME mass ratio on yield,  $\Sigma\text{Sats}$  and CP of recovered liquid fractions. Results confirmed that increasing urea/SME mass ratio from 0:1 to 1:1 decreased  $\Sigma\text{Sats}$  and CP at the expense of reduced final product yield. Furthermore, increasing urea concentration increased the mass of methyl oleate bound to the clathrates during cooling which led to lower concentrations in the liquid filtrate. It was demonstrated that 80 mass% yield of fractionated SME with CP of  $-9^\circ\text{C}$  could be produced by applying a urea/SME mass ratio of 0.3:1. Increasing the mass ratio to 0.5:1 reduced methyl stearate ( $\text{C}_{18}$ ) content in the filtrate to 0.0 mass%. Product from the liquid phase was recovered with 67 mass% yield and had CP below  $-15^\circ\text{C}$ . Further increasing mass ratio to 1:1 produced a 44 mass% yield of fractionated SME with essentially  $\Sigma\text{Sats} = 0.0$  mass% and CP below  $-55^\circ\text{C}$ .

### 5.5 Other fractionation processes

Many other fractionation processes have been applied in fractionation of fatty acid alkyl esters and other fatty derivatives for a variety of purposes. Processes that may show



potential to directly improve the cold flow properties of biodiesel include vacuum distillation, adsorption, membrane separations and supercritical fluid extraction. Each of these techniques are discussed below.

### 5.5.1 Vacuum distillation

This technique is frequently applied in refining of fatty derivatives. Distilled fractions are collected based on differences in volatility (boiling point) of components and fractions may be isolated according to relative chain length. Application under reduced pressure and with packed-columns operating at low temperatures are generally required to maintain thermal stability of fatty acids and esters. Due to energy requirements and cost, this technique is mainly employed in production of high quality products with low impurity levels (Krishnamurthy & Kellens, 1996). Distillation may also be coupled with other fractionation steps in refining of fatty derivatives.

One recent study (Falk & Meyer-Pittroff, 2004) applied vacuum distillation in fractionation of UCOME and animal fat-FAME. Distillation was conducted at 0.05 Pa absolute pressure and temperature did not exceed 180°C. Distillate fractions had elevated concentrations of  $\Sigma$ Sats while unsaturated FAME concentrations were enriched in the residuum (undistilled) fraction. For UCOME and animal fat-FAME,  $\Sigma$ Sats decreased from 31 to 15 mass% and from 43.5 to 30 mass%, respectively.

A process was developed for fractionation of palm kernel oil-FAME to produce technical grade methyl oleate (Heck et al., 2006). The process was performed under an absolute pressure of 25 mbar (2.5 Pa) with a reflux ratio of 2:1. The input stream consisted of mainly pre-distilled  $C_{16}$ - $C_{18}$  FAME. These FAME were then distilled at 180°C to separate  $C_{16}$  (distillate) and  $C_{18}$  (residuum) fractions. The residuum was subsequently distilled at 219.2°C to obtain a mixture of predominantly unsaturated  $C_{18}$  plus some  $C_{16}$  in the distillate. The distillate from the second step was again distilled at 219.7°C to enrich the methyl oleate ( $C_{18:1}$ ) product. Final yield was 52.1 mass% liquid FAME composed of 80.1 mass% methyl oleate and  $\Sigma$ Sats = 1.58 mass%. Increasing the reflux ratio to 2.5:1 significantly increased yield to 95.8% and decreased  $\Sigma$ Sats to 1.48 mass%, though methyl oleate content also decreased to 64.4 mass%.

An earlier review (Dunn & Moser, 2010) examined the effects of trace concentrations of saturated monoacylglycerols and free (non-acylated) steryl glucosides on cold weather storage stability of biodiesel. High-vacuum distillation has been applied by fuel producers to remove these and other minor constituents from biodiesel during production and processing. However, other lower cost processes involving cooling and filtering the biodiesel as it leaves the production facility are also being developed.

### 5.5.2 Adsorption

Adsorption was applied in fractionation of triacylglycerols and other mixtures of fatty materials into high-purity components. Separation is based on specific components adsorbing either on solids suspended in solution or on the surface of a stationary phase. Recovery of adsorbed components is made by isolating the solid phase and extracting (desorbing) them with liquid solvent. This technology is known to reduce saturates in triacylglycerols (Krishnamurthy & Kellens, 1996).

Saturated fatty acids were removed from a fatty acid mixture by passing a 10 vol% solution in acetone solvent through a solid bed molecular sieve composed of amorphous crystalline

silica (Cleary et al., 1985). The sieves were packed in a separation column and flooded with acetone at 120°C with sufficient pressure applied to maintain the liquid phase. The feed mixture was injected in pulses into the column and separated fractions were collected as withdrawn at the bottom of the column. Processes for separating polyunsaturated fatty acids based on preparative high performance liquid chromatography columns packed with Ag-silica or Ag-alumina stationary phases were also developed. These processes were coupled with urea fractionation to purify eicosapentaenoic (C<sub>20:5</sub>) and stearidonic (C<sub>18:4</sub>) acids from marine or blackcurrant oils (Lagarde et al., 1992; Lee, 2003).

Applications for biodiesel were developed to reduce concentrations of monoacylglycerols, steryl glucosides and other minor constituents and for cleaning trace contaminants from transesterification product streams. Selective adsorption was applied in fractionation of a mixture of saturated and unsaturated FAME employing X- and Y-type zeolites embedded with sodium and potassium exchange cations (Neuzil & Derosset, 1977). Selectivity for adsorption increased with increasing degree of unsaturation allowing separation of methyl oleate and linoleate from a feed mixture that also contained methyl palmitate and stearate in a 25 vol% blend with *n*-heptane. Separation was carried out at 125°C and under 50 psig (345 kPa) pressure and bound unsaturated FAME were recovered by desorption with *p*-diethylbenzene. The best results were observed for columns packed with 20-24 U.S. mesh particle size X-type zeolites embedded with potassium cations.

More recently, SME was fractionated to enrich polyunsaturated FAME concentration by passing a mixture diluted in hexane solvent at room temperature through a gravity filtered column packed with silver nitrate (AgNO<sub>3</sub>)-impregnated silica (SiO<sub>2</sub>) gel (Ghebreyessus et al., 2006). Separations were performed at room temperature and a very high 100:1 (vol) dilution ratio in hexane. The SME/hexane mixture was gravity filtered down the vertical column packed with adsorbent. Selectivity increased with increasing degree of unsaturation and polyunsaturated components were desorbed with diethyl ether. From the perspective of isolating FAME enriched in unsaturated components, a column packed with 1:9 g/g AgNO<sub>3</sub>/SiO<sub>2</sub> adsorbent yielded 45 vol% liquid with  $\Sigma$ Sats = 2.1 mass%. Although increasing AgNO<sub>3</sub>/SiO<sub>2</sub> mass ratio increased the yield and decreased  $\Sigma$ Sats, this improvement was accompanied by a disproportionate decrease in monounsaturated FAME (C<sub>18:1</sub>) content.

### 5.5.3 Membrane separations

This technology was also developed for extraction and separation of components from fatty derivatives. Flat porous nitrocellulose membranes may selectively transfer long chain free fatty acids from mixtures with triacylglycerols into an aqueous phase (Kocherginsky & Grishchenko, 2000). Oil phases with higher viscosities demonstrated slower transfer (diffusion) rates. Non-porous cellulose acetate membranes were studied in fractionation of free fatty acids and monoacylglycerols, diacylglycerols and triacylglycerols formed by hydrolysis of high-oleic sunflowerseed oil (Koike et al., 2002). Stirred cells were operated at 40°C and 6 MPa pressure and the hydrolysate mixture was diluted in ethanol. Results showed the rates of retention in descending order were triacylglycerol > diacylglycerol > monoacylglycerol > fatty acids suggesting this technique may be useful in cleaning transesterification product streams or reducing effects of monoacylglycerol on cold weather storage stability of biodiesel.

Low-pressure dialysis was applied in the partial separation of UCOME into saturated and unsaturated FAME-rich fractions (Wichmann et al., 2008). The experimental apparatus consisted of a pocket shaped from the dialysis membrane holding within it the UCOME and



surrounded on the outside by *n*-hexane. Permeation of unsaturated FAME components was hindered due to the bend in the tailgroup about the double bond(s) in contrast to the straight-chained tailgroup of saturated FAME. Although a polyisoprene-based rubber membrane (MWCO < 3200 daltons) had a larger permeation rate, a polyethylene membrane (MWCO < 530 daltons) was more chemically resistant. Both membranes performed well with respect to diffusion of saturated FAME into the dialysate (permeate).

#### 5.5.4 Supercritical fluid extraction

This process is more expensive than other fractionation techniques and considered to be a scientific curiosity. Its practical use is generally limited to extraction of high-value components such as eicosapentaenoic and docosahexaenoic acids from marine and other oils (Illingworth, 2002). Fractionation is based on solubility (that is, density) of components in the supercritical fluid. Applications have been developed to fractionate milk fat into short-, medium- and long-chain triacylglycerols, remove cholesterol from animal fats, prepare cold spreadable butters, separation of monoacylglycerols and diacylglycerols from triacylglycerols and fractionation of fatty acids and esters derived from vegetable oils and fats. The process generally requires high pressure and a high degree of technical complexity which hinder its application on a large-scale (Krishnamurthy & Kellens, 1996).

Supercritical fluid extraction is frequently applied to fractionate fatty acid alkyl esters of vegetable and marine oils to enrich polyunsaturated fatty acid components. Carbon dioxide (CO<sub>2</sub>) has a relatively mild critical temperature (31.1°C) making it an attractive choice for processing of fatty derivatives (Nilsson et al., 1988). Partition coefficients of alkyl esters between CO<sub>2</sub> and liquid phase decrease with increasing chain length due to an increase in density. Partition coefficients may be increased by decreasing temperature or increasing pressure. Separation based on degree of unsaturation is less selective than variation in chain length (Nilsson, 1996).

This technique was demonstrated to isolate and purify ethyl esters of eicosapentaenoic and docosahexaenoic acid derived from menhaden oil after preparative concentration by urea fractionation (Nilsson et al., 1988, 1989). Another study (Perretti et al., 2007) reported a reduction in  $\Sigma$ Sats (C<sub>16</sub>-C<sub>20</sub>) in marine oil ethyl esters from 10.1 to 1.8 mass% after extraction by supercritical CO<sub>2</sub> in a column packed with stainless steel rings and operated at 40°C and 150 bar (15 MPa). Increasing pressure or CO<sub>2</sub> flowrate increased partition coefficient for extracted saturated ethyl esters.

Based on a review of available scientific literature, very little activity has been devoted to the direct application of supercritical fluid extraction to improve the cold flow properties of biodiesel. However, it may be inferred from studies with fatty acid ethyl esters that this technique will be useful in reducing the content of smaller chain length saturated FAME. Thus, supercritical CO<sub>2</sub> extraction may be productively applied to biodiesel since many feedstocks for biodiesel typically have saturated fatty acid components that are predominantly palmitic as opposed to stearic and larger acids.

## 6. Effects of fraction on other fuel properties

Many fuel properties are directly related to the fatty acid composition of biodiesel. Reducing  $\Sigma$ Sats through fractionation may affect properties besides cold flow properties. An earlier study (Dunn, 1998) examined the effects of dry and solvent fractionation on the fuel properties of SME. With respect to kinematic viscosity at 40°C and acid value,

fractionated SME remained within specifications outlined in ASTM standard D 6751 for biodiesel. Although specific gravity increased slightly after dry fractionation, it was not affected by solvent fractionation. Peroxide value increased slightly after dry and solvent fractionation. As expected, enriching the total concentration of unsaturated FAME in SME increased the iodine value. Liquid fractions exhibiting larger reductions in CP and other cold flow properties demonstrated larger increases in iodine value, though iodine values remained within range of values for non-fractionated SME.

Dry and solvent fractionation of SME significantly decreased oxidative stability as determined by the oil stability index (OSI) measured isothermally at 50°C (Dunn, 1998). In this case, reduction in  $\Sigma$ Sats caused concentrations of unsaturated and polyunsaturated FAME to increase in the final liquid fraction making it more susceptible to oxidation from contact with air. Another study (Sahlabji et al., 2007) showed that dry fractionation of animal fat-FAME led to increased concentrations of oxidation inhibitors (antioxidants)  $\alpha$ -tocopherol and butylated hydroxytoluene (BHT). It was suggested that these antioxidants were sterically hindered from aligning along the surface of solid crystal nuclei as they form causing them to remain in the bulk liquid phase during cooling. Similar results have been reported for enriched  $\beta$ -carotene concentrations in unsaturated fractions collected from palm olein (Illingworth, 2002).

Regardless of the enriching effects of fractionation on antioxidant concentrations in low-melting products, it is likely that the increase in total unsaturated, especially polyunsaturated alkyl ester content, causes a net reduction in oxidative stability with respect to non-fractionated esters. For example, distillate fractions from vacuum distillation of animal fat-FAME generally had higher OSI (at 110°C) than the undistilled FAME because these fractions had higher  $\Sigma$ Sats (Falk & Meyer-Pittroff, 2004). Despite an increase in total antioxidant concentration, the non-distilled (residuum) fraction had OSI < 1 h compared to a value of 1.3 h for the undistilled FAME. This result suggested that enriching the unsaturated and polyunsaturated FAME contents in the residuum fraction had a stronger influence on oxidative stability than enrichment of antioxidant concentration. Similar results were observed for residuum fractions obtained from vacuum distillation of UCOME. Ignition quality of diesel fuels is related to ignition delay time, which is correlated to the cetane number of the fuel. Cetane number may be adversely affected by fractionation of biodiesel. Increasing the degree of unsaturation in a hydrocarbon structure decreases cetane number with respect to constant chain length (Harrington, 1986; Knothe et al., 1996, 1997). Decreasing cetane number generally increases ignition delay time, an effect that may worsen engine performance and emissions.

Technologies such as solvent, UIC, adsorption and membrane fractionation may employ organic solvents and other reagents that have special requirements for safe storage and handling. After fractionation is complete the solvents and reagents need to be separated and removed to collect the desired liquid products. Some organic solvents may need to be recycled to reduce costs. Distillation and supercritical fluid extraction processes will require special equipment for handling fluids at very low or very high pressures.

Fractionation itself may impact biodiesel production economics. Separating and removing high-MP components increases cost per unit mass. Secondary effects may be assumed if special conditions and equipment are required to maintain fuel quality of fractionated biodiesel during storage and handling. Another consideration is the disposition of byproduct fractions with enriched  $\Sigma$ Sats. Derivatives from these byproducts might be utilized in formulation of lubricants, surfactants, detergents, plasticizers, pharmaceuticals,

water-proofing agents and cosmetics as well as fuel additives for heavy-grade petrodiesel or residual fuels.

## 7. Conclusions

Cold flow properties and performance continue to influence the development of biodiesel as an alternative diesel fuel or extender. On-road transportation, power generation, heaters and boilers, locomotives, farm vehicles and aviation applications may provide incentives for development of commercial-scale processes to improve cold flow properties of biodiesel.

The fatty acid composition of biodiesel is the main factor in determining their CP, PP, CFPP and LTFT. Development of feedstocks with inherently higher  $\Sigma$ Sats, such as animal fats or used cooking oils, will direct research efforts in development of processing technologies to improve their cold flow properties. In some cases, the influences of  $\Sigma$ Sats composition may be linearly correlated to CP or CFPP. However, the cold flow properties of biodiesel from various feedstocks can be calculated from thermodynamic models based on freezing point theory provided the crystallization properties of each individual component in an alkyl ester mixture are known.

Previous research demonstrated that the most promising approaches for improving the cold flow properties of biodiesel are those that reduce CP. This conclusion was subsequently extended to biodiesel/petrodiesel blends with at least 10 vol% biodiesel (blend ratio = B10). Several studies have examined a number of process technologies for improving the cold flow properties of biodiesel. Among these, fractionation demonstrated great potential for effectively reducing CP of biodiesel.

Fractionation improves cold flow properties of biodiesel by modifying its fatty acid profile to remove high-melting components resulting in reduced crystallization onset temperatures. For biodiesel such as SME or TME, this generally means separating and removing saturated FAME which are mainly methyl palmitate (MP = 28.5°C) and stearate (MP = 37.7°C) enriching the concentration of methyl oleate, linoleate and linolenate (MP < -20.2°C). Dry fractionation, with and without crystallization modifiers, solvent fractionation and urea fractionation may significantly reduce CP. In some cases, yields exceeded 80-90 mass% liquid fractions based on the starting material. Other fractionation technologies evaluated were vacuum distillation, adsorption, membrane separations and supercritical fluid extraction. Urea clathrates, vacuum distillation and adsorption were also applied in the removal of trace concentrations of saturated monoacylglycerols and steryl glucosides, minor constituents that may be problematic to the cold weather storage stability of biodiesel and biodiesel/petrodiesel blends.

Other adaptations to the fractionation technology may be explored in future studies for application to biodiesel. An example is surfactant fractionation. Applied mostly to fats and vegetable oils, this process is similar to dry fractionation where after the crystallization the separation of solid crystals is assisted by adding a cool aqueous solution of surfactant (sodium dodecyl sulfate) containing an electrolyte (magnesium or aluminum sulfate). The combination of surfactant wetting agent and electrolyte allows solid crystals to be suspended in the aqueous phase. After separation of oil and aqueous phases by centrifugation, fractions are heated, washed and dried to remove additives. Surfactant fractionation is more efficient than dry fractionation with respect to separation efficiency and yield of liquid fractions. Its main disadvantages are high operating costs and decontamination of end products (Illingworth, 2002; Kellens & Hendrix, 2000; Krishnamurthy & Kellens, 1996; O'Brien, 1998).

Another example may be to inject a low-boiling point coolant such as ammonia, CO<sub>2</sub> or halogenated hydrocarbon into the alkyl ester mixture. It was shown that applying this approach to fatty acid mixtures with or without solvent improved separation efficiency of solid and liquid phases (Zondek, 1978). The injection of rapidly evaporating coolant promoted formation of a slurry with crystals sufficiently large to facilitate separation by filtration.

Most studies on supercritical fluid extraction of unsaturated fatty acids and esters have been performed with supercritical CO<sub>2</sub>. However, attention might be put into supercritical ethylene or propane as biodiesel and other derivatives demonstrate much higher solubilities in these solvents (Illingworth, 2002). Liquid-based extraction may also be explored for application to biodiesel. For example, dodecanoic and myristic acid were separated by crystallizing the mixture in aqueous ethanol and collecting solid crystals on a Nylon monofilament filter (Maeda et al., 1999).

## 8. Abbreviations

CFPP	Cold filter plugging point
CP	Cloud point
FAME	Fatty acid methyl esters
LTFT	Low-temperature flow test
MP	Melting point
PP	Pour point
ΣSats	Total concentration of saturated fatty acid alkyl esters
SME	Soybean oil-FAME; methyl soyate
TME	Tallow-FAME; methyl tallowate
UCOME	Used cooking oil-FAME
UIC	Urea inclusion compounds
ULSD	Ultra-low sulfur petrodiesel fuel

## Symbols

$C_{M[N]}$	Chain length of fatty acid group (R-COO); M = number of carbon atoms, N = total number of double bonds
$C_p$	Heat capacity
$\Delta H_{fus}$	Enthalpy of fusion (or melting)
$R^2$	Adjusted correlation coefficient
$R_g$	Gas constant
$T_f$	Crystallization onset temperature of a component in a mixture
$x_i$	Mole fraction of component 'i'
$\gamma_i$	Activity coefficient of component 'i'
$\sigma_y$	Standard error of the y-estimate

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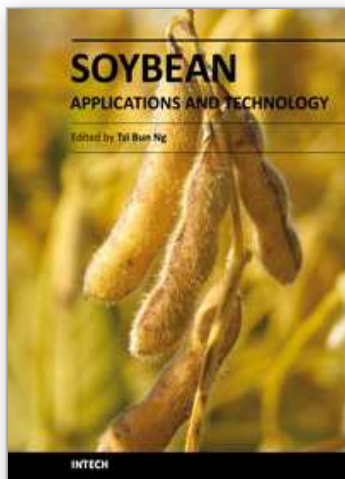
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