PART I

BIODIESEL

CHAPTER 1

Fuel Properties and Performance of Biodiesel

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Table of Contents

1.1. INTRODUCTION

When being used as “alternative” diesel fuel, the mono-alkyl esters of vegetable oils or animal fats are referred to as biodiesel. Biodiesel is playing an

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increasingly important role in the fuel landscape, with production and use growing exponentially and standards being established around the world. It is produced by transesterifying the oil or fat in the presence of a catalyst with an alcohol—usually methanol—to the corresponding mono-alkyl esters. The reduced viscosity of the mono-alkyl esters in comparison to the parent oil or fat is critical for the production of biodiesel.

Biodiesel is technically competitive with petroleum-derived diesel fuel (petrodiesel). Correspondingly, research on biodiesel has continued to expand. Advantages of biodiesel include biodegradability, safer handling (as documented by a higher flash point), inherent lubricity, reduction of most regulated exhaust emissions, renewability, domestic origin, and compatibility with the existing fuel distribution infrastructure. Technical problems with biodiesel include oxidative stability, low-temperature properties, and an increase in NOx exhaust emissions. Accordingly, this chapter reviews some recent research results related to cetane numbers and exhaust emissions, cold flow, oxidative stability, and the viscosity and lubricity of biodiesel, besides providing a brief historical introduction.

1.2. HISTORY

At the Paris World Exposition in 1900, one of five diesel engines exhibited ran on peanut oil (Knothe, 2005), which is the first known use of a vegetable oil as a diesel fuel. The French government at that time was interested in a local energy source for its African colonies, as Rudolf Diesel (1858–1913), the inventor of the engine that bears his name, states in some of his writings (Diesel, 1912a, 1912b). The common statement that Diesel invented "his" engine to specifically use vegetable oils as fuel is therefore incorrect. Diesel's primary objective was to develop a more efficient engine, as he states in the first chapter of his *Die Entstehung des Dieselmotors (The Development [or Creation or Rise or Coming] of the Diesel Engine)* (Diesel, 1913). However, Diesel conducted later experiments with vegetable oils as fuels.

Considerable interest existed in some European countries from the 1920s through the 1940s in the use vegetable oils as diesel fuel, especially in countries with African colonies (Knothe, 2001, 2005). The objective was similar to the original demonstration in 1900 and to current background, namely to provide these colonies a local and renewable source of energy. There also was interest in countries such as Brazil, China and India. Especially in China, pyrolyzed vegetable oils were studied as fuel.

This early work documented results that are still valid today. For example, the high viscosity of vegetable oils was identified as a major problem causing engine deposits, and the fact that exhaust emissions of diesel engines are "cleaner" when running on vegetable oils than with petroleum-based diesel fuel was observed visually, although no quantitative exhaust emissions studies were performed (Knothe, 2001, 2005).

Walton (1938) also recognized that the glycerol moiety has no fuel value and suggested splitting it off and running the engine on the residual acids. However, the first documentation of esterified vegetable oil, biodiesel, as a fuel is the Belgian patent 422877 issued August 31, 1937, to Chavanne (Chavanne, 1937). Several other publications discuss the use of these esters as fuel (Chavanne, 1943; van den Abeele, 1942). The fuel was ethyl esters of palm oil. A commercial passenger bus apparently used this fuel on the Brussels-Louvain route (Leuven). In this work, the first cetane number testing of biodiesel, again in the form of ethyl esters of palm oil, was carried out (van den Abeele, 1942). The biodiesel fuel possessed a higher cetane number than the petroleum-based reference fuels.

The energy crises of the 1970s and early 1980s sparked interest in renewable and domestic sources of energy around the world. In this context, vegetable oils were remembered as potential feedstocks for alternative diesel fuels. In 1980, Bruwer *et al.* (1980) reported that diesel engines running on sunflower oil methyl esters were less prone to the build-up of engine deposits. Together with work in other countries, this research eventually led to the now-existing interest in biodiesel. Later developments included the development of standards and legislation and regulations in many countries around the world promoting the use of biodiesel.

1.3. COMBUSTION: CETANE NUMBERS AND EXHAUST EMISSIONS

1.3.1. Cetane Numbers

The cetane number (CN) is an indicator of the ignition quality of a diesel fuel. It is conceptually similar to the octane number (ON) used for gasoline. Generally, a compound that has a high ON tends to have a low CN and vice versa. The CN of a diesel fuel is related to the ignition delay (ID) time, *i.e.*, the time that passes between injection of the fuel into the cylinder and onset of ignition. A shorter ID corresponds to a higher CN and vice versa.

American Society for Testing and Materials (ASTM) method D 613 and International Organization for Standardization (ISO) method 5165 exist for determining the CN. Hexadecane ($C_{16}H_{34}$; trivial name cetane, giving the cetane scale its name) is the high quality standard on the cetane scale with an assigned CN of 100. A highly branched compound, 2,2,4,4,6,8,8,-heptamethylnonane (HMN, also $C_{16}H_{34}$), a compound with poor ignition quality, is the low-quality standard and has an assigned CN of 15. The two reference compounds on the cetane scale show that the CN decreases with decreasing chain length and increasing branching. Aromatic compounds, which occur in significant amounts in petrodiesel, have low CNs, but their CNs increase with the increasing size of *n*-alkyl side chains (Clothier *et al.*, 1993; Puckett and Caudle, 1948). The cetane scale is arbitrary and compounds with CN > 100 or CN < 15 have been identified. The standard specification for petrodiesel, ASTM D

975 (Anon., 2003a), requires CN ≥ 40, while those for biodiesel prescribe minimums of 47 for ASTM standard D 6751 (Anon., 2007a) and 51 for European Committee for Standardization (CEN) standard EN 14214 (Anon., 2003b). Due to the high CNs of many fatty compounds, which can exceed the cetane scale, the term "lipid combustion quality number" for these compounds was suggested (Freedman *et al.*, 1990).

Higher CN have been correlated with reduced nitrogen oxides (NOx) exhaust emissions (Ladommatos *et al.*, 1996), which has led to efforts to improve the CN number of biodiesel fuels by means of cetane-improving additives (Knothe *et al.*, 1997). Despite the inherently relatively high CNs of fatty compounds, NOx exhaust emissions usually increase slightly when operating a diesel engine on biodiesel. The connection between structure of fatty esters and exhaust emissions was investigated (McCormick *et al.*, 2001) by studying the exhaust emissions caused by enriched fatty acid alkyl esters used as fuel. NOx exhaust emissions increase with increasing unsaturation and decreasing chain length, which can also lead to a connection with the CNs of these compounds. Particulate emissions, on the other hand, were hardly influenced by the aforementioned structural factors. The relationship between the CN and emissions is complicated by many factors including the technological sophistication of the engine.

The influence of compound structure on CNs of fatty compounds was discussed (Harrington, 1986) and hypotheses confirmed by practical cetane tests (Freedman *et al.*, 1990; Ladommatos *et al.*, 1996; Klopfenstein, 1985; Knothe *et al.*, 2003). CNs of neat fatty compounds are given in Table 1.1. In summary, CNs decrease with increasing unsaturation and increase with increasing chain length, *i.e.*, uninterrupted CH_2 moieties. However, branched esters derived

TABLE 1.1. Cetane number (CN) of biodiesel and selected fatty acid alkyl esters.

Material	CN
Rapeseed (canola) oil methyl esters	47.9–56
Methyl soyate	48.7–55.9
Sunflower oil methyl ester	54–58
Methyl laurate	61.4; 60.8
Methyl myristate	66.2; 73.5
Methyl palmitate	74.5; 74.3; 85.9
Methyl stearate	86.9; 75.6; 101
Methyl oleate ($C_{18:1}$; Δ9 *cis*)	55; 59.3
Methyl linoleate ($C_{18:2}$; Δ9,Δ12-all *cis*)	42.2; 38.2
Methyl linolenate ($C_{18:3}$; Δ9,Δ12,Δ15-all *cis*)	22.7
Triolein	45
Ethyl oleate	53.9; 67.8
Propyl oleate	55.7; 58.8
Butyl oleate	59.8; 61.6

Source: Knothe *et al.*, 2005.

from alcohols such as *iso*-propanol have CNs competitive with methyl or other straight-chain alkyl esters (Knothe *et al.*, 2003; Zhang and Van Gerpen, 1996). Thus, one long, straight chain suffices to impart a high CN even if the other moiety is branched. Branched esters are of interest because they exhibit improved low-temperature properties. The CNs of most biodiesel fuels are in the range of about 48–60, as can be seen in Table 1.1 (Knothe *et al.*, 2005).

The CNs of fatty compounds have been investigated with an instrument termed the Ignition Quality Tester™ (IQT™) (Knothe *et al.*, 2003), which is a further, automated development of a constant volume combustion apparatus (CVCA) (Aradi and Ryan, 1995; Ryan and Stapper, 1987). The CVCA was originally developed for determining CNs more rapidly, with greater experimental ease, better reproducibility, and reduced use of fuel and therefore less cost than ASTM method D 613 utilizing a cetane engine. The IQT™ method, the basis of the standard ASTM D 6890 (Anon, 2007b), was shown to be reproducible and the results fully competitive or more reliable than those derived from ASTM D 613. Some results from the IQT™ are included in Table 1. For the IQT™, ID and CN are related by the following equation (Knothe *et al.*, 2003):

$$CN_{IQT} = 83.99 \times (ID - 1.512)^{-0.658} + 3.547 \qquad \text{[Eq. 1.1]}$$

In ASTM D 6890, only ignition delay times of 3.6–5.5 milliseconds, corresponding to 55.3 to 40.5 derived-CN (DCN), are covered since precision outside that range may be affected. However, the results for fatty compounds with the IQT™ are comparable to those obtained by other methods (Knothe *et al.*, 2003). Generally, the results of cetane testing for compounds with lower CNs, such as the more unsaturated fatty compounds, show better agreement over the various related literature references than the results for compounds with higher CNs. The reason is the non-linear relationship (Equation 1) between the ID and the CN. The non-linear relationship between the ignition delay time and the CN was observed previously (Allard *et al.*, 1996). Thus, small changes at shorter ignition delay times result in greater changes in CN than at longer ignition delay times. This would indicate a leveling-off effect on emissions—such as NOx discussed above—once a certain ignition delay time with corresponding CN has been reached, as the formation of certain species depend on the ignition delay time. However, for newer engines, this aspect must be modified.

1.3.2. Exhaust Emissions

Generally, four kinds of regulated exhaust emissions are analyzed when operating an engine. These species are particulate matter (PM), NOx, hydrocarbons (HC), and carbon monoxide (CO). Besides these regulated species, a host of other exhaust emissions are generated but they currently remain unregulated.

Biodiesel can lead to reductions of PM, HC and CO of 50% and more, with these results being summarized in a report by the United States Environmental Protection Agency (USEPA, 2002). However, more unregulated pollutants may be generated by the use of biodiesel, but without an increase in the total toxic emissions. Despite this effect of biodiesel operation on most regulated exhaust emissions species, biodiesel generally causes a slight increase (approximately 10%) of NOx exhaust emissions compared to petrodiesel. Since NOx exhaust emissions are precursors of ozone, a prime component of urban smog, this has led to considerable research efforts to identify the cause of this increase as well as to mitigate it. When blending biodiesel with petrodiesel, the effect of biodiesel on these blends is approximately linear to the blend level. Thus the common “B20” blend (20 vol% biodiesel in petrodiesel) displays reduced NOx increase but also less advantageous PM, HC and CO emissions. Also, the technology level of the engine has a strong effect on the levels of the exhaust emissions species (USEPA, 2002; McGeehan, 2004; Sharp *et al.*, 2000), as do engine load conditions (Krahl *et al.*, 2002, 2001).

During the combustion of fuels, it has been postulated that radicals react with atmospheric nitrogen to form NOx (Miller and Bowman, 1989). Otherwise, several causes have been postulated for the increase in NOx exhaust emissions when using biodiesel. One issue is the more widespread high-temperature distribution areas in the combustion chamber (Yuan *et al.*, 2005a), complemented by research postulating an increase in flame temperature due to the double bonds in biodiesel (Ban-Weiss *et al.*, 2006). Biodiesel also has a higher speed of sound and isentropic bulk modulus than petrodiesel, which can lead to changes in the fuel injection timing of diesel engines with resulting higher combustion pressures and temperatures, which in turn cause higher NOx exhaust emissions (Tat *et al.*, 2000). Other work discusses a similar influence of the bulk modulus of compressibility of biodiesel on NOx exhaust emissions (Boehman *et al.*, 2004). Changing the injection timing of the engine has been a method for reducing NOx exhaust emissions when using biodiesel.

Biodiesel in the United States successfully completed USEPA Tier II toxicity testing requirements for registering methyl soyate as a fuel or fuel additive under Title II, Section 211(b) of the Clean Air Acts (amended 1990) in a subchronic inhalation study designed in accordance with guidelines contained in 40 Code of Federal Regulations (CFR) 79, Subpart F (Finch *et al.*, 2002). Other health effects studies on exhaust emissions generated by the use of biodiesel have been conducted and the need for more research in this area has been discussed recently (Swanson *et al.*, 2007). It has been shown, however, that soot reduction when using biodiesel is connected to lower mutagenicity of the PM generated by biodiesel (Krahl *et al.*, 2001, 2002, 2003). This may be due to a lower content of polyaromatic hydrocarbons (Krahl *et al.*, 2002). Particle size plays a significant role in health effects of PM emissions, with small particles being especially problematic: biodiesel tended to cause more larger particles than petrodiesel under most load conditions (Krahl *et al.*, 2001). Other studies have also shown the favorable effect of biodiesel on PM and resulting health effects (Bagley *et al.*, 1998; Carraro *et al.*, 1997). Aldehydes, which are unregulated, tend to increase with biodiesel use (Krahl *et al.*, 2002).

Related to the discussion above, the effect of compound structure on exhaust emissions of biodiesel has been studied (McCormick *et al.*, 2001; Knothe *et al.*, 2006). Increasing unsaturation generally leads to an increase in NOx exhaust emissions, with saturated esters showing NOx exhaust emissions even slightly below the level of the petrodiesel reference fuel. The same effect was also reported for decreasing chain length in tests conducted with a 1991 model year engine (McCormick *et al.*, 2001) but hardly observed in tests with a 2003 model year engine (Knothe *et al.*, 2006). Biodiesel and its components reduced PM emissions more than neat hexadecane and dodecane, prime alkane components of “ultra-clean” petrodiesel fuels. The saturated species methyl palmitate and methyl laurate were especially effective, with reductions over 80% relative to the petrodiesel reference fuel (Knothe *et al.*, 2006). HC and CO emissions increased with shorter chain lengths. Furthermore, biodiesel and the neat esters tested in the 2003 model year engine almost met 2007 PM exhaust emissions standards of 0.01 g/hp h without any emissions control technologies.

The antioxidants butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), *tert*-butylhydroquinone (TBHQ), propyl gallate, ascorbyl palmitate and citric acid were evaluated for potential to reduce NOx emissions from a single cylinder, direct-injection, air-cooled, naturally aspirated Yanmar engine (Hess *et al.*, 2005). BHA and BHT reduced NOx emissions by 4.4 and 2.9%, respectively, but the other antioxidants evaluated did not exhibit any beneficial effects (see Table 1.2). Antioxidants may impede NOx formation by inhibiting the formation of combustion-derived radicals.

1.4. COLD FLOW PROPERTIES OF BIODIESEL

In spite of its many advantages, performance during cold weather will impact the year-round commercial viability of biodiesel in moderate temperature climates. Field trials have demonstrated that methyl esters of soybean oil fatty acids (SME) cause performance issues when ambient temperatures approach 0 °C. As overnight temperatures decrease into this range, saturated fatty acid methyl esters (FAME) within SME solidify and form crystals that plug or restrict flow through fuel lines and filters.

All diesel fuels eventually cause start-up and operability problems when subjected to sufficiently low temperatures. As the ambient temperature cools, high-molecular weight paraffins present in petrodiesel nucleate and form solid wax crystals which, suspended in liquid, are composed of short-chain *n*-alkanes and aromatics (Chandler *et al.*, 1992; Owen and Coley, 1990; Lewtas *et al.*, 1991; Brown *et al.*, 1989; Zielinski and Rossi, 1984). Left unattended overnight

TABLE 1.2. Effect of antioxidants on nitrogen oxides (NOx) exhaust emissions.[a]

Ratio	Antioxidant	Loading ppm	Change in NOx[b] %
B0	None	—	−6.6 ± 1.7
B20	BHA	1000	−4.4 ± 1.0
B20	BHT	1000	−2.9 ± 1.5
B20	Ascorbyl palmitate	500[c]	−1.3 ± 0.9
B20	Citric acid	1000	−0.7 ± 0.5
B20	Propyl gallate	1000	−0.4 ± 2.8
B20	TBHQ	1000	−0.3 ± 1.6
B20	α-tocopherol	1000	+0.3 ± 0.2

Source: Hess *et al.*, 2005.

[a] Ratio = blend ratio soybean oil fatty acid methyl esters (SME) in low-sulfur (≤500 ppm) No. 2 petrodiesel (LSD) where "B0" is 0% SME and "B20" contains 20 vol% SME; BHA = butylated hydroxyanisole; BHT = butylated hydroxytoluene; TBHQ = tert-butylhydroquinone.

[b] Relative to B20 blends without added antioxidant.

[c] 500 ppm used instead of 1000 ppm due to limited solubility of ascorbyl palmitate in B20.

in these conditions, growth and agglomeration of solid wax crystals in the fuel cause engine starvation or failure during start-up the next morning.

Cold weather performance of diesel fuels is determined by measuring the tendency of a fuel to solidify or gel at low temperature. Cloud point (CP) is defined as the temperature where crystals become visible ($d \geq 0.5$ μm) (Chandler *et al.*, 1992; Own and Conley, 1990; Westbrook, 2003; Nadkarni, 2000; Botros, 1997). At temperatures below CP, crystals continue to grow and agglomerate eventually causing operability problems (Chandler *et al.*, 1992; Lewtas *et al.*, 1991; Botros, 1997; Chandler and Zechman, 2000; Heraud and Pouligny, 1992; Brown and Gaskill, 1990; Coley, 1989; Brown *et al.*, 1988; Brown *et al.*, 1989; Zielinski and Rossi, 1984). Pour point (PP) is the temperature where agglomeration prevents free movement of fluid (Owen and Conley, 1990; Westbrook, 2003; Nadkarni, 2000; Botros, 1997). Both parameters may be measured easily and rapidly; however, CP generally underestimates the temperature limit to avoid start-up or operability issues while PP tends to be over-optimistic (Chandler *et al.*, 1992; Owen and Coley, 1990; Coley, 1989; Rickeard *et al.*, 1991; McMillan and Barry, 1983).

The cold filter plugging point (CFPP) test was developed to predict more accurately low-temperature limits. After the oil is cooled at a specified rate to the test temperature, a 20 mL volume is drawn through a 45 μm wire mesh filter screen under 0.0194 atm vacuum. The method is repeated in 1 °C increments and CFPP is recorded as the lowest temperature where oil safely passes through the filter within 60 s (Chandler *et al.*, 1992; Owen and Coley, 1990; Westbrook, 2003; Nadkarni, 2000). Although CFPP holds nearly world-wide acceptance as a standard test, in North America more stringent test conditions are necessary to correlate with performance in the field. Thus, the less userfriendly low-temperature flow test (LTFT) method was developed (Chandler *et al.*, 1992, Owen and Coley, 1990, Zielinski and Rossi, 1984; Brown *et al.*, 1988; McMillan and Barry, 1983; Chandler and Zechman, 2000). The oil is cooled at a rate of 1 °C/hr before 180 mL is drawn through a 17 μm wire mesh screen filter under 0.197 atm vacuum. Similar to CFPP, this method is repeated in 1 °C increments and LTFT is recorded as the lowest temperature where oil safely passes through the filter within 60 s (Chandler *et al.*, 1992, Owen and Coley, 1990, Westbrook, 2003, Rickeard *et al.*, 1991).

1.4.1. Effects of Biodiesel

Biodiesel made from feedstocks containing large concentrations of long-chain saturated fatty acids will have very poor cold flow properties. Less expensive feedstocks such as palm oil or tallow (see Table 1.3) may not be feasible in moderate temperature climates. In contrast, feedstocks with lower concentrations of long-chain saturated fatty acids yield biodiesel with more attractive cold flow properties. For example, biodiesel from canola, linseed, olive, rapeseed, and safflower oils have CP and PP close to or below 0 °C (Table 1.3).

Blending petrodiesel with SME significantly increases CP and PP at relatively low blend ratios (vol% SME) in No. 1 petrodiesel fuel and jet fuel (Dunn, 2001; Dunn and Bagby, 1995). For blends in No. 2 petrodiesel, increasing blend ratio increases CP and PP linearly ($R^2 = 0.99$ and 0.96). Blending petrodiesel with SME also increases CFPP and LTFT (Dunn and Bagby, 1995). Similar results were reported for blends with biodiesel derived from coconut oil, rapeseed oil, tallow and waste grease (see Table 1.4).

Nearly linear correlations for CFPP *versus* CP and LTFT *versus* CP were reported for neat biodiesel and its blends with petrodiesel (Dunn and Bagby, 1995, 1996; Dunn *et al.*, 1996). For LTFT, the correlation was essentially LTFT ~ CP, suggesting the labor- and time-intensive LTFT test could be spared by simply measuring CP. A major conclusion from these studies was that development of approaches to improve cold flow properties of biodiesel should focus on technologies that decrease CP.

Trace concentrations of contaminants are also known to influence cold flow properties of biodiesel. One study (Yu *et al.*, 1998) examined the effects of residual contaminants arising from refining and transesterification on cold flow properties of neat SME and its blends with No. 1 petrodiesel. Results showed that CP increases with increasing concentration of saturated monoacylglycerols and diacylglycerols. Unsaturated monoolein did not significantly affect CP or PP. Unsaponifiable matter increases CP and PP of SME at concentrations of 3 wt% but had no effect on a 20 vol% SME blend. More recent field data suggests that after long-term storage in cold weather monoacylglycerols and sterol glucosides may cause problems with insoluble matter buildup and plugged filters. Other contaminants arising from conversion processing that are known to influence cold flow properties include alcohol, free fatty acids, and triacylglycerols.

TABLE 1.3. Cold flow properties of biodiesel (B100) derived from various feedstock lipids and alcohols.[a]

Lipid	Alcohol	CP °C	PP °C	CFPP °C	LTFT °C
Canola oil	Methyl	1	–9		
Coconut oil	Ethyl	5	–3		
High oleic (HO) sunflower oil[b]	Methyl			–12	
Linseed oil	Methyl	0	–9		
Olive oil	Methyl	–2	–3	–6	
Palm oil	Methyl	13	16		
Rapeseed oil	Methyl	–2	–9	–8	
	Ethyl	–2	–15		
Safflower oil	Ethyl	–6	–6		
Soybean oil	Methyl	0	–2	–2	0
	Ethyl	1	–4		
	Isopropyl	–9	–12		
	n-Butyl	–3	–7		
	2-Butyl	–12	–15		
Soybean oil/tallow[c]	Methyl	2	1		
Tallow	Methyl	17	15	9	20
Tallow	Ethyl	15	12	8	13
Used cooking oil[d]	Methyl			–1	
Used hydrogenated soybean oil[e]	Ethyl	7	6		
Waste grease[f]	Ethyl	9	–3	0	9

Sources: Clark *et al.*, 1983; Dunn and Bagby, 1955; Foglia *et al.*, 1997; Fukuda *et al.*, 2001; González Gómez *et al.*, 2002; Kalligeros *et al.*, 2003; Lang *et al.*, 2001; Lee *et al.*, 1995; Masjuki *et al.*, 1993; Neto da Silva *et al.*, 2003; Peterson *et al.*, 2000; Peterson *et al.*, 1987; Wu *et al.*, 1998; Zhang and Van Gerpen. 1996.

[a] CP = cloud point; PP = pour point; CFPP = cold filter plugging point; LTFT = low-temperature flow test.

[b] Oleic acid content = 77.9 wt% before conversion to biodiesel.

[c] 4:1 v/v soybean oil methyl ester/tallow methyl ester.

[d] Total saturated fatty acid methyl ester content = 19.2 wt%.

[e] Hydrogenated to iodine value = 65 g I_2/100 g oil.

[f] Free fatty acids ~9 wt% before conversion to biodiesel.

1.4.2. Improving Cold Flow Properties, Operability and Performance of Biodiesel

Many approaches for improving the cold flow properties of biodiesel have been explored. These include blending with petrodiesel, transesterification with medium or branched-chain alcohols instead of methanol or ethanol, crystallization fractionation, and treatment with cold flow improver (CFI) additives.

1.4.2.1. Blends with Petrodiesel Cold flow properties of FAME and fatty acid ethyl esters of various feedstocks in blends with petrodiesel are summa-

TABLE 1.4. Cold flow properties of biodiesel/petrodiesel blends.[a]

Lipid	Alcohol	Grade	Ratio	CP °C	PP °C	CFPP °C	LTFT °C
None	—	No. 1	B0	–31	–46	–42	–27
Soybean oil	Methyl	No. 1	B10	–22	–42		
Soybean oil	Methyl	No. 1	B20	–17	–30	–27	–19
Soybean oil	Methyl	No. 1	B30	–14	–25	–20	–16
Soybean oil/tallow[b]	Methyl	No. 1	B20	–21	–29	–21	–18
Soybean oil/tallow[b]	Methyl	No. 1	B30	–13	–24	–18	–14
None	—	No. 2	B0	–16	–27	–18	–14
Coconut oil	Ethyl	No. 2	B20	–7	–15		
Rapeseed oil	Ethyl	No. 2	B20	–13	–15		
Soybean oil	Methyl	No. 2	B20	–14	–21	–14	–12
Soybean oil	Methyl	No. 2	B30	–10	–17	–12	–12
Soybean oil/tallow[b]	Methyl	No. 2	B20	–12	–20	–13	–10
Soybean oil/tallow[b]	Methyl	No. 2	B30	–10	–12	–11	–9
HO sunflower oil[c]	Methyl	No. 2	B30		–12		
Tallow	Methyl	No. 2	B20	–5	–9	–8	
Tallow	Ethyl	No. 2	B20	–3	–12	–10	1
Used hydrogenated soybean oil[d]	Ethyl	No. 2	B20	–9	–9		
Waste grease[e]	Ethyl	No. 2	B20	–12	–21	–12	–3

Sources: Anon., 2003a; Dunn and Bagby, 1995; Foglia *et al.*, 1997; Neto da Silva *et al.*, 2003; Peterson *et al.*, 2000; Wu *et al.*, 1998.

[a] Grade = petrodiesel grade according to ASTM fuel specification D 975; Ratio = blend ratio where 'B0' = 0 vol% biodiesel, 'B10' = 10%, 'B20' = 20% and 'B30' = 30%. See Table 1.3 for other abbreviations.

[b] 4:1 v/v soybean oil methyl ester/tallow methyl ester.

[c] Oleic acid content = 77.9 wt% before conversion to biodiesel.

[d] Hydrogenated to iodine value = 65 g I_2/100g oil).

[e] Free fatty acids ~9 wt% before conversion to biodiesel.

rized in Table 1.4. Properties of non-blended petrodiesel ("B0") are included for comparison and those for corresponding neat biodiesel ("B100") are in Table 1.3. An earlier study (Dunn and Bagby, 1995) reported that blends in No. 1 petrodiesel exhibit better CP, PP, CFPP and LTFT than blends in No. 2 petrodiesel largely because No. 1 petrodiesel generally has better cold flow properties than No. 2 petrodiesel. As discussed above, CP and PP increased nearly linearly with respect to increasing SME blend ratio. Although blends with 20–30 vol% SME in No. 2 petrodiesel did not greatly increase CFPP or LTFT, some exceptions were reported for LTFT of blends with tallow and waste grease ethyl esters. Blends in No. 1 petrodiesel had significant increases in CP, PP, CFPP and LTFT at blend ratios as low as 20 vol% SME. However, under some conditions blends with up to 30 vol% SME in No. 1 petrodiesel may be allowable (CFPP = –20 °C and LTFT = –16 °C as shown in Table 1.4).

As discussed above, CFPP and LTFT of biodiesel and its blends in petrodiesel demonstrate nearly linear correlation with respect to CP. Results from linear regression analyses yielded the following equations:

$$CFPP = 1.02(CP) - 2.9 \qquad \text{[Eq. 1.2]}$$

and

$$LTFT = 1.02(CP) - 0.4 \qquad \text{[Eq. 1.3]}$$

where $R^2 = 0.90$ and 0.95 and $\sigma_y = 2.5$ and 1.8, respectively (Dunn and Bagby, 1995). Statistical analysis indicated high probabilities ($P = 0.81$ and 0.78, respectively) that slope was unity for both equations. Analysis also yielded $P = 0.60$ favoring an intercept = 0 hypothesis for Equation 1.3, suggesting LTFT may be estimated reasonably accurately by measuring CP. This work also demonstrated that the key to developing effective approaches for improving cold flow properties and performance of biodiesel and biodiesel/petrodiesel blends is to identify ways to first significantly reduce CP.

1.4.2.2. Transesterification with Medium or Branched Chain Alcohols

Biodiesel made from conversion of oils or fats with medium (C_3—C_8) or branched chain alkyl alcohols generally possesses better cold flow properties than the corresponding FAME. For example, melting points (MP) for ethyl palmitate (19 °C) and stearate (31 °C) are significantly below those of their corresponding methyl esters (30 and 39.1 °C) (Lyde, 1990). Large or bulky alkyl headgroups disrupt spacing between individual molecules resulting in formation of nuclei with less stable packing during the early stages of crystallization.

Soybean oil fatty acid methyl, ethyl and *n*-butyl esters were reported to have CP = 0, 1 and −3 °C, respectively (Dunn and Bagby, 1995, Foglia *et al.*, 1997, Clark *et al.*, 1983). Similar decreases in CP with respect to increasing alkyl headgroup chainlength were reported for fatty acid alkyl esters of canola and linseed oils (Lang *et al.*, 2001). Transesterification of these oils with *n*-butanol decreased PP by 4–7 °C with respect to their corresponding methyl esters. Decreases in CP, PP, CFPP and LTFT of tallow alkyl esters with respect to corresponding methyl, ethyl, *n*-propyl and *n*-butyl head groups were also reported (Foglia *et al.*, 1997). Soybean oil fatty acid isopropyl and 2-butyl esters were reported to have CP = −9 and −12 °C and PP = −12 and −15 °C (Zhang and Van Gerpen, 1996; Lee *et al.*, 1995), compared with CP = 0 °C and PP = −2 °C for SME (Dunn and Bagby, 1995). Similar results were reported for CP, PP, CFPP and LTFT of tallow fatty acid isopropyl and isobutyl esters (Foglia *et al.*, 1997).

Transesterification of fats or oils with medium-chain alcohols may increase CN, a parameter that can influence ignition quality and exhaust emissions (Klopfenstein, 1985). On the other hand, increased branching in saturated hydrocarbon chains also decreases CN. Two studies comparing isopropyl esters of soybean oil fatty acids in blends with petrodiesel reported that these esters had similar performance and reduced exhaust emissions (Zhang and Van Gerpen, 1996; Chang *et al.*, 1996). Results showed that some emissions were further reduced when compared to analogous blends with SME (Chang *et al.*, 1996). Blends with *n*-butyl esters of soybean oil yielded performance and emission results that were also comparable to blends with SME (Clark *et al.*, 1983).

Disadvantages of this approach include increases in kinematic viscosity and overall fuel costs. Viscosity generally increases with the molecular weight of the hydrocarbon chain, though branching in alkyl headgroups may mitigate this effect. However, a major portion of the total fuel cost for biodiesel is the cost of acquiring feedstock and reactant alcohols. Thus, substituting higher alcohols for methanol or ethanol may significantly increase total fuel costs. One possible compromise may be to prepare mixtures of FAME or fatty acid ethyl esters with small portions of esters of higher alcohol.

1.4.2.3. Crystallization Fractionation (Winterization) Biodiesel made from most common feedstocks may be considered a pseudo-binary mixture of components categorized by a relatively large MP differential. Saturated long-chain FAME have very high MP (*e.g.*, 30 °C for methyl palmitate) while unsaturated and polyunsaturated FAME have very low MP (−21 °C for methyl oleate; −35 °C for methyl linoleate) (Lyde, 1990). This differential suggests that an effective approach for improving cold flow properties would be to reduce the total concentration of high-MP components by crystallization fractionation.

The traditional process consists of two stages, crystallization followed by separation. The crystallization stage consists of selective nucleation and crystal growth under controlled cooling and gentle agitation. Once well defined crystals are formed, the resulting slurry is transferred to the second stage for separation into solid and liquid fractions, typically by filtration or centrifugation (Illingworth, 2002; Kellens and Hendrix, 2000; O'Brien, 1998; Anderson, 1996; Krishnamurthy and Kellens, 1996; Rajah, 1996; Duff, 1991; Bailey, 1950). Product yield as defined by separation of high- and low-melting fractions depends greatly on maintaining control of both stages of the process (Anderson, 1996; Krishnamurthy and Kellens, 1996; Rajah, 1996; Duff, 1991).

Dry fractionation is defined as crystallization from a melt without dilution with solvent (O'Brien, 1998; Anderson, 1996; Bailey, 1950). This process is the simplest and least expensive process for separating high and low-MP fatty derivatives (Illingworth, 2002; Kellens and Hendrix, 2000; O'Brien, 1998; Anderson, 1996; Krishnamurthy and Kellens, 1996). It is also the most commonly practiced form of fat fractionation technologies currently in use (Illingworth, 2002; O'Brien, 1998).

Cold flow properties of liquid fractions obtained from dry fractionation of SME and FAME derived from tallow (TME) and used cooking oil (UCOME) are summarized in Table 1.5. These results showed that dry fractionation significantly improved cold flow properties in comparison with those of non-fractionated biodiesel (Table 1.3). Earlier reports (Dunn *et al.*, 1996; Dunn *et al.*, 1997; Dunn, 1998) demonstrated that application of dry fractionation to SME significantly reduces CP, PP, CFPP and LTFT of SME. These reductions required six steps where bath temperature of each step was decreased in 2 °C increments. Results in Table 1.5 also show that dry fractionation may reduce CP and LTFT of SME to temperatures below those reported for No. 2 petrodiesel (Table 1.4). Although total concentration of saturated FAME decreased to from 18.1 to 5.6 wt%, liquid yields were very small (≤33.4%) relative to mass of starting material (Dunn *et al.*, 1996, 1997).

Lee *et al.* (1996) applied step-wise crystallization fractionation to SME and reported similar results (Table 1.5). The liquid fraction had a total saturated FAME content = 5.5 wt% and crystallization onset temperature = –7.1 °C (determined by differential scanning calorimetry (DSC), compared to values of 15.6% and 3.7 °C before fractionation. Liquid product yield was also relatively low (25.5%).

González Gómez *et al.* (2002) applied crystallization fractionation to UCOME (Table 1.5). Following crystallization at a cooling rate = 0.1 °C/min, fractionation reduced CFPP from –1 to –5 °C and total saturated FAME content from 19.2 to 14 wt%. Again, liquid yields were low (25–30 wt%). Krishnamurthy and Kellens (1996) reported that application of crystallization fractionation to TME increases iodine value (IV) from 41 to 60 and reduces CP from 11 to –1 °C with liquid yields of 60–65%.

Crystallization fractionation of biodiesel modified by the use of crystallization modifiers and organic solvents was also investigated. Results from some of these studies are summarized in Table 1.5. Treating SME with crystallization modifiers commonly used in petrodiesel, such as PP-depressants (PPD) DFI-200 and Winterflow, increased liquid product yields to 80.0–87.0% and decreased CP and CFPP to temperatures below –10 °C (Dunn, 1998; Dunn *et al.*, 1997). Analogous to dry fractionation, fractionation using crystallization modifiers required six steps each with incrementally decreasing bath temperatures. Single-step crystallization fractionation from two organic solvents was investigated (Dunn *et al.*, 1997). Fractionation from hexane at –25 °C resulted in liquid product yields up to 78.4% and decreased CP to –10 °C. Fractionation from isopropanol at –15 °C resulted in yields up to 80.6 wt% and decreased CP to –9 °C.

Lee *et al.* (1996) also investigated crystallization fractionation of SME from several solvents. Fractionation from hexane in three sequential steps with a final bath temperature of –28.4 °C resulted in a liquid product yield of 77% and total saturated FAME content of 6.0 wt%. Crystallization onset temperature by DSC of the liquid fraction was –5.8 °C. Fractionation of SME from methanol solvent separated into two liquid layers as cooling temperatures approached –1.6 °C. Acetone did not reduce crystallization onset temperature of the liquid fraction, and chloroform failed to form crystals at temperatures below –25 °C. Hanna *et al.* (1996) studied fractionation of TME

TABLE 1.5. Cold flow properties of fractionated biodiesel.[a]

Biodiesel	Solvent	Modifier[b]	B/S g/g	Steps	T_{Bath} °C	Yield g/g	Sats. wt%	CP °C	PP °C	CFPP °C
SME	None	None	—	6	–10	0.334	6.3	–20	–21	–19
SME	None	None	—	11	–10	0.255	5.5	–7.1[c]		
UCOME[d]	None	None	—	1	–1	0.25–0.30	14			–5
SME	None	DFI-200, 2000 ppm	—	6	–10	0.801	9.8	–11		–12
SME	None	Winterflow, 2000 ppm	—	6	–10	0.870	9.3	–11		–11
SME	Hexane	None	0.284	1	–25	0.784	16.2	–10	–11	–10
SME	Hexane	None	0.217	3	–28.4	0.77	6.0	–5.8[c]		
SME[e]	Hexane	DFI-200, 2000 ppm	0.200	1	–34	0.992	13.5	–5	–12	
SME[e]	Hexane	Winterflow, 2000 ppm	0.200	1	–34	1.029	11.1	–5	–12	
SME	Isopropanol	None	0.228	1	–15	0.860	10.8	–9	–9	–9
SME[e]	Isopropanol	DFI-200, 2000 ppm	0.200	1	–20	0.952	12.8	–6	–9[f]	
SME[e]	Isopropanol	Winterflow, 2000 ppm	0.199	1	–20	0.989	13.3	–5	–9[f]	

Sources: Dunn, 1998; Dunn *et al.*, 1997; Lee *et al.*, 1996; González Gómez *et al.*, 2002.

[a] UCOME = used cooking oil methyl esters; B/S = biodiesel/solvent mass ratio; T_{Bath} = bath coolant temperature (final step); Yield = mass ratio liquid fraction to starting material; Sats = total concentration of saturated fatty acid methyl esters in liquid fraction (determined by GC). See Tables 1.2 and 1.3 for other abbreviations.

[b] Crystallization modifiers DFI-200 and Winterflow are pour point depressants (PPD) for petrodiesel, added before first fractionation step.

[c] Crystallization onset by differential scanning calorimetry (DSC).

[d] Total saturated FAME content = 19.2 wt% (before conversion of used cooking oil to biodiesel).

[e] Liquid fractions contained small quantities of residual solvent following evaporation.

[f] Results for samples fractionated at –15 °C.

from ethanol, petrodiesel and ethanol/petrodiesel solvents. Fractionation from ethanol/petrodiesel blends in five steps with a final bath temperature of –16 °C produced a liquid fraction with CP reduced to –5 °C.

Crystallization fractionation of biodiesel carries a number of disadvantages. Manipulating the FAME profile in SME affected kinematic viscosity, acid value (AV), specific gravity, IV, and the oxidation induction period (Dunn, 1998). Reducing total saturated FAME concentration had a profound impact on oxidative stability as determined from significant decreases in the oil stability index. Increasing the total unsaturated and polyunsaturated FAME concentration may increase ignition delay time as measured by CN, an effect that worsens performance and increases harmful exhaust emissions (Knothe *et al.*, 1997; Harrington, 1986; Knothe *et al.*, 1996). Fractionation will also increase fuel cost. Solvent-based fractionation will increase costs for safety, handling, and recovery of solvents (Illingworth, 2002; Kellens and Hendrix, 2000; O'Brien, 1998; Anderson, 1996; Krishnamurthy and Kellens, 1996; Rajah, 1996; Duff, 1991; Bailey, 1950). Separating and recycling crystallization modifiers or solvents and decontaminating collected fractions from residual solvent traces may also prove difficult. Finally, unless uses are developed for solid fraction(s) collected from the process, crystallization fractionation will make biodiesel production more costly.

1.4.2.4. Cold Flow Improver (CFI) Additives Performance and economic benefits of utilizing CFI additives to improve cold flow properties of petrodiesel have been recognized for more than 40 years. Many additives effective in modifying wax crystal nucleation, growth, or agglomeration mechanisms are reported in the scientific and patent literature. While exact chemical structures are proprietary, the most effective additives are generally composed of low molecular weight copolymers similar in melting point to *n*-alkanes found in petrodiesel. These additives include a variety of polymers such as ethylene vinyl acetate copolymers, fumarate vinyl acetate copolymers, alkenyl succinic amides, long-chain polyalkylacrylates, polymethacrylates, polyalkylmethacrylates, polyethylenes, chlorinated polyethylenes, copolymers of linear α-olefins with acrylic, vinylic and maleic compounds, copolymers containing esterified derivatives of maleic anhydride, styrene-maleate esters and vinyl acetate-maleate esters, secondary amines, random terpolymers of α-olefin, stearylacrylate and *N*-alkylmaleimide, copolymers of acrylate/methacrylate with maleic anhydride partially amidated with *n*-hexadecylamine, itaconate copolymers, polyethylene-polypropylene block copolymers, polyamides of linear or branched acids and copolymers of α-olefins, maleic anhydride copolymers, carboxy-containing interpolymers, styrene-maleic anhydride copolymers, polyoxyalkylene compounds, and copolymers with long chain alkyl groups from fatty alcohols as pendant groups (Chandler *et al.*, 1992; Owen and Coley, 1990; Lewtas *et al.*, 1991; Heraud and Pouligny, 1992; Brown and Gaskill, 1990; Machado and Lucas, 2002; Hipeaux *et al.*, 2000; Monkenbusch *et al.*, 2000; El-Gamal *et al.*, 1998; Davies *et al.*, 1994; Lal, 1994; Lal *et al.*, 1994; Böhmke and

Pennewiss, 1993; Lewtas and Block, 1993; Demmering *et al.*, 1992; Bormann *et al.*, 1991; Denis and Durand, 1991; Desai *et al.*, 1991; Müller *et al.*, 1991; Beiny *et al.*, 1990; Damin *et al.*, 1986.).

CFI additives mitigate the effect of wax crystals on fuel flow by modifying their shape, size, growth rate and degree of agglomeration. Their combined effect promotes formation of a very large number of smaller, more compact needle-shaped crystals. When trapped by fuel filters these crystals form a semi-permeable cake layer allowing some fuel flow through the filter (Chandler *et al.*, 1992; Owen and Coley, 1990; Lewtas *et al.*, 1991; Brown *et al.*, 1989; Zielinski and Rossi, 1984; Brown and Gaskill, 1990; Coley, 1989; Rickeard *et al.*, 1991; Damin *et al.*, 1986; Holder and Thorne, 1979). Some additives allow operation of diesel engines at temperatures as low as 10 °C below CP of the fuel (Brown *et al.*, 1989; Zielinski and Rossi, 1984; Botros, 1997; Richeard *et al.*, 1991.). Polymer-wax interactions are generally specific, so a particular additive may not perform equally well in all fuels.

Effects of six commercial petrodiesel CFI additives on SME and its blends with No. 1 and No. 2 petrodiesel were studied previously (Dunn and Bagby, 1996; Dunn *et al.*, 1996). Results from these studies are summarized in Table 1.6. These petrodiesel CFI additives decreased PP by up to 18–20 °C for B30 blends in No. 1 petrodiesel and B20 blends in No. 2 petrodiesel. Similarly, these additives decreased PP of neat SME ("B100") by as much as 6 °C. When applied to unblended petrodiesel ("B0"), these additives reduced PP by 7 °C for No. 1 petrodiesel and by 23 °C for No. 2 petrodiesel (Dunn *et al.*, 1996). These results suggested that mechanisms associated with crystalline growth and agglomeration in neat biodiesel were similar to those for petrodiesel (Dunn and Bagby, 1996; Dunn *et al.*, 1996).

Comparison of data in Tables 1.3, 1.4 and 1.6 demonstrates that increasing CFI additive loading (0 to 2000 ppm) decreases PP of SME and its blends in petrodiesel. Although reductions in PP tended to be proportionate to loading, some additives were more efficient than others. Additionally, effectiveness diminished with increasing blend ratio of SME in the blends, with respect to constant additive loading (Dunn *et al.*, 1996). The CFI additives listed in Table 1.6 were also effective in decreasing CFPP. Nylund and Aakko (2000) reported similar results when studying the effects of a CFI additive on cold flow properties of FAME from rapeseed oil (RME) blends in No. 2 petrodiesel. Biodiesel producers and sellers in the United States are presently treating their products with CFPP improvers during cooler weather.

In contrast to the PP data listed in Table 1.6, none of the CFI additives greatly affected CP of SME or its blends with No. 1 or No. 2 petrodiesel. In terms of wax crystallization, CFI additives designed for treating petrodiesel did not selectively modify crystal nucleation in biodiesel (Dunn *et al.*, 1996).

Regression analysis of CFPP and LTFT *versus* CP data sets combining results for biodiesel and biodiesel/petrodiesel blends with those for formulations treated with CFI additives yielded the following equations:

TABLE 1.6. Cold flow properties of SME and its blends in No. 1 and low-sulfur (500 ppm) No. 2 petrodiesel treated with commercial petrodiesel CFI additives.[a]

Ratio	Grade	Additive[b]	Loading, ppm	CP, °C	PP, °C
B100	—	DFI-100	1000	–2	–6
			2000	–1	—
B100	—	DFI-200	1000	–1	–8
			2000	–1	–16
B100	—	Hitec 672	1000	–2	–6
			2000	–2	—
B100	—	OS 110050	1000	–1	–7
			2000	–3	—
B100	—	Paramins	1000	0	–5
			2000	–1	—
B100	—	Winterflow	1000	0	–5
			2000	–1	–17
B30	No. 1	DFI-100	1000	–14	–49
B30	No. 1	DFI-200	1000	–21	–45
B30	No. 1	Hitech 672	1000	–13	–44
B30	No. 1	OS 110050	1000	–17	–46
B30	No. 1	Paramins	1000	–14	–29
B30	No. 1	Winterflow	1000	–19	–39
B20	No. 2	DFI-100	1000	–14	–26
B20	No. 2	DFI-200	1000	–14	–32
B20	No. 2	Hitech 672	1000	–14	–27
B20	No. 2	OS 110050	1000	–15	–18
			2000	—	–21
B20	No. 2	Paramins	1000	–14	–27
B20	No. 2	Winterflow	1000	–13	–39
			2000	—	–59

Sources: Dunn and Bagby, 1996; Dunn *et al.*, 1996, 1997.

[a] Ratio = blend ratios in petrodiesel as defined in Table 1.4; Grade = see Table 1.4; CFI = cold flow improver. See Tables 1.2 and 1.3 for other abbreviations.

[b] Vendors: Du Pont (DFI-100, DFI-200); Ethyl Corp. (Hitech 672); Exxon Chemical (Paramins); SVO/Lubrizol (OS 110050); Starreon Corp. (Winterflow).

$$CFPP = 1.03(CP) - 2.2 \qquad \text{[Eq. 1.4]}$$

and

$$LTFT = 0.81(CP) - 2.4 \qquad \text{[Eq. 1.5]}$$

where $R^2 = 0.82$ and 0.90 and $\sigma_y = 3.5$ and 4.0, respectively (Dunn and Bagby, 1996; Dunn *et al.*, 1996). Similar to Equations 1.2 and 1.3, Equations 1.4 and 1.5 exhibit a nearly linear correlation between CFPP and LTFT with respect to CP. Although scatter in the data resulted in relatively low R^2 coefficients, graphical evidence showed that generally decreasing CP is coupled with decreases in CFPP and LTFT. Statistical analysis showed $P = 0.743$ that slope was unity for Equation 1.4, though the slope of Equation 1.5 was decidedly not ($P < 0.0001$). Overall, results from this comparison of CFPP and LTFT data with corresponding CP data were consistent with those discussed above for biodiesel and biodiesel/petrodiesel blends. Addition of CFI additives did not alter the aforementioned conclusion that the most effective approaches for improving cold flow properties of biodiesel will be those that significantly decrease CP.

Chiu *et al.* (2004) investigated four commercial CFI additives at 0.1–2.0 wt% in SME and blends thereof in No. 1 and No. 2 petrodiesel (500 ppm S). In agreement with the studies discussed above, two additives significantly decreased PP of SME blends, but all four additives had little effect on CP, as can be seen from Tables 1.7 and 1.8. Also in agreement with a previous study (Dunn and Bagby, 1995) was the determination that PP changed in a linear fashion with blend composition, which is consistent with freezing point depression from the blending of miscible liquids. Lastly, the additive mixing procedure (addition of additives to SME either pre- or post-blending of SME with diesel fuels) did not appear to impact either CP or PP, as shown by Table 1.7.

Shrestha *et al.* (2005) conducted a study in which SME, mustard seed oil methyl and ethyl esters and used peanut oil methyl esters were blended (B0, B5 and B10) with No. 2 petrodiesel and treated with six commercial petrodiesel CFI additives. It was found that at 100, 200, and 300% of the specified loading rate, CP and PP were reduced by an average of 2.2 °C and 14.1 °C, respectively. Mustard seed oil ethyl esters exhibited the highest average reduction in CP and PP and SME exhibited the lowest, as shown by Table 1.9 for CP. Furthermore, a significant decrease in CP was noticed when additive concentration was increased from 100% of the specified loading rate to 200%; however, the difference between 200% and 300% was not significant. The authors conclude that the effect of fuel additive is not only different for different feedstocks but also some fuel additives worked better for a specific blend of biodiesel with No. 2 petrodiesel.

1.4.2.5. Development of CFI Additives for Treating Biodiesel

It was noted when comparing CFPP and LTFT with corresponding CP data (above) that the best approach for improving cold flow properties and performance of biodiesel would be to significantly decrease CP. Advances in the development of CP-depressants (CPD) specifically designed for biodiesel and blends thereof in ultra-low sulfur petrodiesel fuel (ULSD) will be required for additive strategies to be maximally effective in improving the low temperature operability of biodiesel fuel. Such strategies should entail the design of new materials whose molecular structures impart a greater degree of selectivity toward high melting point alkyl esters to allow for modification of the crystalline growth behavior of biodiesel.

TABLE 1.7. CP and PP of SME blended with low-sulfur (500 ppm) No. 2 petrodiesel treated with OS-110050 commercial petrodiesel CFI additive.[a]

OS 110050[b] wt%	Ratio vol%	Mix method 1[c]		Mix method 2[d]	
		CP, °C	PP, °C	CP, °C	PP, °C
0	B100	–4	–7	—	—
0	B40	–12	–15	—	—
0	B30	–12	–15	—	—
0	B20	–15	–21	—	—
0	B0	–18	–26	—	—
0.1	B100	–7	–12	—	—
0.1	B40	–12	–15	—	—
0.1	B30	–15	–21	—	—
0.1	B20	–15	–18	—	—
0.1	B0	–18	–29	—	—
0.2	B100	–7	–12	—	—
0.2	B40	–12	–18	—	—
0.2	B30	–12	–18	—	—
0.2	B20	–15	–21	—	—
0.2	B0	–15	–32	—	—
0.5	B100	–4	–7	—	—
0.5	B40	–15	–21	–15	–21
0.5	B30	–15	–23	–15	–23
0.5	B20	–15	–26	–12	–26
0.5	B0	–15	–32	—	—
0.75	B100	–7	–15	—	—
0.75	B40	–12	–26	—	—
0.75	B30	–15	–29	—	—
0.75	B20	–15	–29	—	—
0.75	B0	–18	–29	—	—
1.0	B100	–4	–7	—	—
1.0	B40	–15	–29	–15	–29
1.0	B30	–15	–32	–15	–29
1.0	B20	–15	–31	–15	–29
1.0	B0	–12	–32	—	—
2.0	B100	–7	–18	—	—
2.0	B40	–15	–18	–15	–26
2.0	B30	–15	–29	–15	–31
2.0	B20	–15	–31	–15	–26
2.0	B0	–12	–31	—	—

Source: Chiu *et al.*, 2004.

[a] Ratio = blend ratio in No. 2 petrodiesel where "B40" = 40 vol% SME, "B0" = 100% No. 2 petrodiesel and others are as defined in Table 1.4. See Tables 1.2, 1.3 and 1.6 for other abbreviations.

[b] 0.1 wt% = 1000 ppm.

[c] SME treated with OS-110050 before being blended with petrodiesel.

[d] SME blended with petrodiesel before being treated with OS-110050.

TABLE 1.8. CP and PP of SME and its blends in No. 1 petrodiesel treated with 0.1 wt% (1000 ppm) commercial CFI petrodiesel additives.[a]

Additive[b]	Ratio, vol%	CP, °C	PP, °C
None	B0	–1	–6
None	B10	–3	–12
None	B20	–5	–15
Bio Flow-875	B0	–1	–9
Bio Flow-875	B10	–3	–18
Bio Flow-875	B20	–5	–33
Bio Flow-870	B0	0	–18
Bio Flow-870	B10	–4	–24
Bio Flow-870	B20	–5	–30
Diesel Fuel Anti-Gel	B0	0	–15
Diesel Fuel Anti-Gel	B10	–4	–21
Diesel Fuel Anti-Gel	B20	–5	–24

Source: Chiu *et al.*, 2004.

[a] Ratio = blend ratio in No. 1 petrodiesel as defined in Tables 1.4 and 1.7. See Tables 1.2, 1.3 and 1.6 for other abbreviations.

[b] Vendors: Octel Starreon, LLC. (Bio Flow-870, Bio Flow-875); Dawn Chemical Corp. (Diesel Fuel Anti-Gel).

The first step in pursuit of this approach is to identify and test compounds for selectivity towards modifying nucleation and disrupting crystalline growth and agglomeration in biodiesel formulations. Analogous to petrodiesel CFI additives, compounds for treating biodiesel should possess some CPD characteristics. Soriano *et al.* (2006, 2005) investigated the utility of ozonized vegetable oil as a PPD for neat biodiesel. Ozonized vegetable oils (1.0–1.5 wt%) were effective in reducing the PP of biodiesel prepared from sunflower, soybean and rapeseed oils to –29, –11 and –31 °C, respectively, as shown in Table 1.10. In agreement with previously mentioned studies, CP was essentially unaffected. The lowest reduction in PP was observed in cases where the biodiesel and ozonized samples were prepared from the same vegetable oil. Furthermore, DSC and polarized light microscopy indicated that adding ozonized vegetable oil affects both nucleation and crystal growth of biodiesel. It was discovered that treatment of biodiesel with ozonized vegetable oil leads to formation of considerably smaller, more numerous crystals at subzero temperatures.

Two earlier studies (Kenar *et al.*, 2005; Knothe *et al.*, 2000) were conducted on the effects of compounds synthesized with hydrocarbon tail-group structures resembling those of FAME with attached bulky moieties. These studies examined novel fatty diesters made from reaction of diols with acids and diacids with 2-octanol in toluene solvent with *p*-toluene sulfonic acid catalyst and branched-chain esters of carbonic acid (carbonates) synthesized in nonyl alcohol with *n*-dibutyltin oxide catalyst. None of the synthesized compounds demonstrated effectiveness in decreasing CP or PP of SME.

TABLE 1.9. CP depression at manufacturer's recommended additive loading for biodiesel from various feedstocks and blend levels in low-sulfur (500 ppm) No. 2 petrodiesel.[a]

	MEE			MME			SME			UPEME		
Additive[b]	B5	B20	B100	B5	B20	B100	B5	B20	B100	B5	B20	B100
BioFlow 875	–2.0	0.0	–2.3	–1.5	–1.5	–1.3	–1.5	–1.0	–0.6	–1.0	–2.0	–1.7
Flozol 503	–0.5	–1.5	–0.1	–1.0	–1.5	–0.5	–1.0	–1.0	–1.3	–0.5	–1.0	–1.8
MCC P205	–3.0	–2.5	–6.3	–2.5	–2.0	–0.5	–1.7	–1.8	–1.3	–1.5	–1.5	–2.1
Arctic Express 0.25%	–3.5	–3.0	–6.4	–2.0	–2.5	–1.0	–0.3	0.0	–0.8	–2.5	–1.0	–2.3

Source: Shrestha *et al.*, 2005.

[a] MEE = mustard seed oil ethyl esters; MME = mustard seed oil methyl esters; UPEME = used peanut oil methyl esters; B5 = 5 vol% biodiesel in No. 2 petrodiesel blends; 'B20' and 'B100' are defined in Tables 1.4 and 1.6. See Tables 1.2 and 1.3 for other abbreviations.

[b] Vendors: Octel Starreon, LLC (Bioflow875); Lubrizol Corp. (Flozol 503); Midcontinental Chemical (MCC P205); Power Service (Arctic Express 0.25%).

TABLE 1.10. CP and PP of biodiesel derived from sunflower, soybean, palm and rapeseed oils blended with ozonized sunflower oil (OSFO).[a]

Fuel formulation	CP, °C	PP, °C
Neat SFME	1.0	–5.0
1.0% OSFO A[b] in SFME	0.0	–24.0
1.5% OSFO A in SFME	1.0	–25.0
1.0% OSFO B[b] in SFME	1.0	–29.0
1.5% OSFO B in SFME	1.0	–26.0
Neat SME	1.0	–2.0
1.0% OSFO A in SME	1.0	–9.0
1.5% OSFO A in SME	–1.0	–10.0
1.0% OSFO B in SME	2.0	–11.0
1.5% OSFO B in SME	1.0	–11.0
Neat PME	18.0	12.0
1.0% OSFO A in PME	13.0	11.0
1.5% OSFO A in PME	13.0	11.0
1.0% OSFO B in PME	13.0	11.0
1.5% OSFO B in PME	13.0	11.0
Neat RME	–4.0	–13.0
1.0% OSFO A in RME	–6.0	–30.0
1.5% OSFO A in RME	–4.0	–30.0
1.0% OSFO B in RME	–5.0	–30.0
1.5% OSFO B in RME	–5.0	–31.0

Source: Soriano *et al.*, 2006.

[a] SFME = sunflower oil methyl esters; PME = palm oil methyl esters; RME = rapeseed oil methyl esters. See Tables 1.2 and 1.3 for other abbreviations.

[b] OSFO A and OSFO B contain 0.183 and 0.206 g O_3/mL oil, respectively.

Two previous studies (Moser *et al.*, 2007, 2006) explored the effects of synthetic compounds with hydrocarbon tail-group structures resembling those of FAME with attached bulky moieties on the CP and PP of SME. These studies examined novel fatty ethers made from the reaction of various alcohols (C_2—C_{10}) with epoxidized alkyl oleates in the presence of sulfuric acid catalyst. Bulky esters (isopropyl and isobutyl) were chosen to further enhance the low temperature fluidity of the synthetic adducts produced. As the chain length of the ether moiety attached to the fatty backbone increased in length, a corresponding improvement in low temperature performance was noticed. Although the materials had improved low temperature properties over that of neat SME, none of the synthesized compounds demonstrated effectiveness in decreasing CP or PP when added to SME.

Two reports in the patent literature claim the invention of CFI additives specifically designed to improve the cold weather performance of biodiesel (Scherer and Souchik, 2001; Scherer *et al.*, 2001). Block copolymers of long-chain alkyl methacrylates and acrylates were effective as PPD and flow improvers for lubricant oils and biodiesel fuel additives. Another patent reported that methacrylate copolymers decrease CFPP of biologically-derived fuel oils and biodiesel fuels made from rapeseed oil (Auschra *et al.*, 1999).

Efforts have also been made to employ glycerol in synthesis of CFI agents. Two patents reported that glycerol co-products from biodiesel production can be reacted with isobutylene or isoamylene in the presence of a strong acid catalyst to produce glycerol ether derivatives (Noureddini, 2001, 2000). Adding the derivatives back to biodiesel was shown to improve fuel characteristics, though very large quantities (>1%) were generally required to significantly reduce CP.

1.5. OXIDATIVE STABILITY

The storage stability of a liquid fuel is defined by its relative resistance to physical and chemical changes brought about by interaction with its environment (Westbrook, 2003). Stability takes into account interactions of olefins, dienes and nitrogen-, sulfur- and oxygen-containing compounds that can lead to sediment formation and changes in color depending on type and quantity of unstable materials present. Cleanliness of the fuel with respect to the presence of water, particulate solids, fuel degradation products and microbial slimes also influences stability (Giles, 2003).

Fuel properties degrade during long-term storage by *i)* oxidation or autoxidation from contact with ambient air, *ii)* thermal or thermo-oxidative decomposition from excess heat, *iii)* hydrolysis from contact with water or moisture in tanks and fuel lines, and *iv)* microbial contamination from migration of dust particles or water droplets containing bacteria or fungi into the fuel (Westbrook, 2003, Giles, 2003). In terms of fuels derived from fatty compounds such as biodiesel, effects of oxidative degradation during storage on overall fuel quality have been identified as a major concern by fuel distributors, suppliers and consumers.

Biodiesel derived from oils or fats is typically a mixture of relatively high concentrations of long-chain monounsaturated and polyunsaturated compounds to promote more compatible cold flow properties. Thus, biodiesel such as SME is significantly more prone to oxidative degradation than petrodiesel. Unsaturated organic compounds are significantly more susceptible to autoxidation than saturated compounds. Autoxidation occurs at allylic methylene positions along the backbone of olefinic compounds progressing at different rates depending on number and location of allylic methylene positions (Frankel, 1998). With respect to long-chain fatty acid alkyl esters such as biodiesel, the polyunsaturated esters are particularly vulnerable to autoxidation because they contain more allylic methylene positions than monounsaturated esters. The relative rates of autoxidation of the “C_{18}” unsaturates given in the literature (Frankel, 1998, and references therein) clearly demonstrate this point: 1:41:98 for oleates:linoleates:linolenates.

Oxidative degradation during long-term storage may affect fuel quality of biodiesel and its blends with petrodiesel. Oxidation under accelerated conditions such as elevated temperatures or purging with dry air or oxygen affects kinematic viscosity, AV, and peroxide value (PV) (Dunn, 2002; Monyem *et al.*, 2000; Bondioli *et al.*, 1995; Thompson *et al.*, 1998; Du Plessis *et al.*, 1985, 1983). Increases in kinematic viscosity may indicate presence of high-molecular weight polymers while increases in AV generally indicate presence of secondary degradation products. Increases in PV may result in an increase in CN, a parameter that can affect ignition delay time (Clothier *et al.*, 1993; Van Gerpen, 1996). Factors known to influence oxidation of fatty derivatives include presence or exclusion of air, temperature, light, oxidation inhibitors (antioxidants), oxidation promoters (pro-oxidants) such as hydroperoxides and metal catalysts (Bondioli *et al.*, 1995; Du Plessis *et al.*, 1985; Knothe and Dunn, 2001; Canakci *et al.*, 1999; Graboski and McCormick, 1998; Knothe and Dunn, 1997). Consequently, a great deal of study has gone into developing test methods for monitoring and improving the oxidative stability of biodiesel.

An earlier study (Dunn, 2002) examined effects of oxidation under controlled accelerated conditions on fuel properties of SME. SME samples from four different sources with varying storage histories were oxidized at elevated temperatures with continuous stirring under a $0.5\,\text{cm}^3/\text{min}$ air purge. Antioxidants *tert*-butylhydroxyquinone (TBHQ) and α-tocopherol at 2000 ppm loadings retarded oxidative degradation of SME as determined by analysis of kinematic viscosity, AV, PV, specific gravity, CP, and PP results. It was shown that kinematic viscosity and AV had the best potential as parameters for timely and easy monitoring of biodiesel fuel quality during long-term storage.

1.5.1. Monitoring Oxidative Stability

Stavinoha and Howell (2000, 1999; Stavinoha, 1998) reviewed many standard tests and recommended modification of ASTM methods D 2274 (Oxidation Stability of Distillate Fuel Oil [Accelerated Method]), D 4625 (Diesel Storage Stability at 43 °C), or D 6468 (High Temperature Stability of Distillate Fuels). Method D 2274 showed poor precision and little correlation with field study data or with parameters utilized by the fats and oils industry (Westbrook, 2003; Giles, 2003; Monyem *et al.*, 2000). Bondioli *et al.* (2002) and Canakci *et al.* (1999) reported that D 2274 was not suitable for biodiesel because its degradation led to formation of soluble polymers that could not be efficiently isolated or quantified by washing and filtration. Although method D 4625 demonstrates good correlation with field study data, this method has a relatively long (4–16 week) test period that precludes it from being useful in monitoring oxidative stability of stored fuels (Westbrook, 2003; Giles, 2003; Monyem *et al.*, 2000; Stavinoha and Howell, 2000; Bondioli *et al.*, 2002). Method D 6468 was also problematic due to its inability to cope with difficult to isolate soluble polymers during degradation (Giles, 2003; Bondioli *et al.*, 2002).

The Biodiesel Stability (BIOSTAB) project, supported by the European Commission, was initiated in 2001 to establish clear criteria and analytical methods for the monitoring biodiesel fuel stability (Various, 2003; Prankl, 2002). The resulting unified method, EN 14112 (Anon., 2003c) established a means for measuring oxidative stability utilizing the Rancimat or oxidation stability instruments. This test method was essentially developed from standards employed in the fats and oils industry to measure isothermally the induction period for oxidation of fatty derivatives. At present, both biodiesel fuel standards ASTM D 6751 (Anon., 2007a) and EN 14214 (Anon., 2003b) include an oxidative stability specification based on measurement by method EN 14112.

In general, the test is based on analysis of the oil stability index (OSI) in accordance with American Oil Chemists' Society (AOCS) method Cd 12b-92 (Anon., 1999). An oil sample is placed in a glass test tube and held stationary in an electrically controlled block heater. The tube is capped and dry air is continuously purged at a constant flow rate through the sample. Effluent air containing volatile degradation products is then swept out of the test tube and transferred into a second test tube containing deionized water. Among the degradation products from thermo-oxidation of fatty compounds are volatile organic acids which are subsequently dissolved in the water. The conductivity in the water reservoir is continuously monitored by a probe with resultant data being recorded in 3 min (0.05 h) increments. OSI (the oxidation induction period) is the point where the second derivative of the conductivity *versus* time data curve equals zero. For analysis of biodiesel, block temperature must be set to 110 °C and sample mass is constant at 3 g for Rancimat and 5 g for the oxidative stability instrument. Biodiesel fuel specifications ASTM D 6751 and EN 14214 specify a minimum OSI = 3 h and 6 h, respectively (Anon., 2007a, 2003b).

As part of the aforementioned BIOSTAB framework, studies by Lacoste and Lagardere (2003) and Mittelbach and Schober (2003) applied analysis of OSI by Rancimat instrument to RME, TME, UCOME and FAME derived from sunflower oil. The former study also reported good correlations between OSI and AV, ester content and linolenic acid content. Bondioli *et al.* (Bondioli *et al.*, 2002) reported that OSI may be used to monitor degradation of biodiesel samples aged under storage conditions simulating ASTM method D 4625 (Diesel Storage Stability at 43 °C). Earlier applications of the Rancimat instrument to measure effects of aging on biodiesel were also reported by Du Plessis *et al.* (1985), Bondioli *et al.* (1995) and Mittelbach and Gangl (2001). Canakci *et al.* (1999) observed that conducting OSI measurements at 110 °C was not suitable for evaluating biodiesel derived from high IV feedstocks including SME. Biodiesel with IV > 110 tends to undergo very rapid thermo-oxidation under these conditions. Based on fuel tank temperature with normal return rates, this report recommended a more appropriate test temperature of 60 °C for SME. This result agreed with those reported in another study on the effects of block temperature on OSI of neat SME and its blends with JP-8 jet fuel

(Dunn and Knothe, 2003). That study also recommended block temperatures of 75-90 °C for SME/JP-8 jet fuel blends.

An earlier study (Dunn, 2005a) examined OSI analyses at 60 °C of SME from five separate sources by oxidative stability instrument. Samples had varying histories of storage and handling. Results showed that OSI was an effective means for monitoring oxidative stability of SME. This study also recommended utilizing a control or reference material such as methyl oleate to facilitate comparison of OSI analyses conducted periodically over a long period of time, such as the monitoring of biodiesel during storage. Finally, this work suggested that OSI was more sensitive than IV for detecting effects of oxidative degradation in its early stages when monitoring SME during storage.

Another work (Knothe and Dunn, 2003) investigated effects of fatty acid structure on OSI of SME. Despite having equivalent IV, OSI results at 70 °C reported for methyl petroselinate ($C_{18:1}$; $\Delta 6$) and vaccenate ($C_{18:1}$; $\Delta 11$) were significantly higher than for methyl oleate ($C_{18:1}$; $\Delta 9$). Besides position of the double bond, variations in alkyl headgroup chain length, hydrocarbon tailgroup chain length, and fatty acid or ester group functionality more significantly affected OSI than IV. Small quantities of unsaturated compounds containing bis-allylic carbon positions may have a disproportionately large effect on OSI compared to compounds containing just allylic carbon positions.

The IV is defined as an average total number of double bonds per mole in a mixture of fatty materials. It is not a good descriptor for correlating physical and chemical properties with fatty acid composition in biodiesel. For example, the IV does not provide any information on structural factors such as number of allylic or bis-allylic methylene groups or location of double bond(s) within the hydrocarbon chain. Knothe (2002) recommended alternative indices termed allylic position equivalents (APE) and *bis*-allylic position equivalent (BAPE) based on the total number of allylic and bis-allylic positions present in the fatty acid chains.

Thermal analytical techniques such as thermogravimetric analysis (TGA), conventional DSC and pressurized-DSC (P-DSC) have been extensively developed for studying oxidation reactions of many types of materials. Thermal analysis has advantages related to acceleration of rates of reaction at elevated temperatures and continuous purging with fresh dry air or oxygen. P-DSC has the added advantage of providing elevated pressures which increases the total number of moles of oxygen available for reaction. These techniques have been applied to the analysis of petrochemical and synthetic lubricants, biodegradable lubricants, aviation turbine oils and polymers (Sharma and Stipanovic, 2003; Gamelin *et al.*, 2002; Riga *et al.*, 1998; Yao, 1997; Zeman *et al.*, 1995; Patterson and Riga, 1993; Zeman *et al.*, 1993; Kaufman and Rhine, 1988; Zeman *et al.*, 1984; Walker and Tsang, 1980; Noel, 1972) as well as edible fats and oils, air-blown vegetable oils, epoxidized soybean oil, genetically modified soybean oil and alcohol-based fuels (Adhvaryu and Erhan, 2002; Kenar *et al.*, 2002; Tan *et al.*, 2002; Adhvaryu *et al.*, 2000; Kowalski *et al.*, 2000; Perez, 2000;

Litwinienko and Kasprzycka-Guttman, 1998; Litwinienko *et al.*, 1995; Kasprzycka-Guttman *et al.*, 1995; Kowalski, 1995; Hassel, 1976; Cross, 1970).

Perhaps the first study to examine oxidation of FAME was performed by Raemy *et al.* (1987). Results showed that increasing temperature or degree of unsaturation decreased induction period in isothermal DSC curves. Induction periods also demonstrated a direct correlation with results from analysis by Rancimat instrument. Several studies have reported on the use of non-isothermal (temperature-ramping) DSC and P-DSC to study (Litwinienko *et al.*, 2000; Litwinienko and Kasprzyska-Guttman, 2000; Litwinienko *et al.*, 1999) oxidation kinetics of C_{18} fatty acids and their ethyl esters and reported that increasing the degree of unsaturation increases reactivity by decreasing activation energies for oxidation.

Dunn (2000) demonstrated that increasing pressure from 1000 to 5000 kPa does not significantly affect oxidation onset temperature (OT) of SME from non-isothermal static mode (zero air-purge) P-DSC curves scanned at heating ramp rate (β) = 5 °C/min. A more recent work by Dunn (2006a) compared analysis of OT by non-isothermal P-DSC in static and dynamic (positive air-purge) modes, TGA and (conventional) DSC. Results from TGA analyses at β = 5 °C/min and under ambient pressure failed to detect measurable oxidation. On the other hand, results from dynamic mode P-DSC curves were consistently lower than those obtained from conventional DSC curves, with respect to constant β = 5 °C/min. This was attributed to the increased quantity of air (oxygen) present in the P-DSC cell (P = 2000 kPa) compared to air in the conventional DSC cell (ambient pressure). Increasing the quantity of oxygen available for reaction accelerated the oxidation component of the thermo-oxidative reaction mechanism resulting in a decrease in OT. Similar comparison of OT results from dynamic and static mode P-DSC showed that the positive air-purge further accelerates oxidation by replacing oxygen as it was consumed during the reaction. Thus, OT data from dynamic mode P-DSC were consistently lower than those from static mode P-DSC curves.

Similar to studies reported by Litwinienko and co-workers discussed above, a recent report (Dunn, 2006b) demonstrated that non-isothermal (conventional) DSC, static mode P-DSC and dynamic mode P-DSC may be employed to study kinetics of the oxidation of SME. OT results obtained at ambient pressure for DSC and P = 2000 kPa for P-DSC and with varying β = 1–20 °C/min were analyzed by the Ozawa-Flynn-Wall method to calculate activation energies and rate constants. This work concluded that rates of the oxidation reaction could be calculated at any temperature based on accurate measurement of kinetic parameters from analysis of non-isothermal dynamic mode P-DSC scans.

Many advances have been made in development of P-DSC and other thermal analysis techniques in the study of oxidation reactions in fatty derivatives such as biodiesel. Kinetic parameters and phase transitions associated with oxidative degradation may be rapidly and accurately determined. However, the applicability of P-DSC may be limited in analysis of fuel formulations since it does not allow direct measurement of effects of oxidation on kinematic viscosity, AV, PV and other important fuel properties (Stavinoha and Kline, 2001).

Other techniques to be investigated for analyzing effects of oxidation on fatty derivatives include monitoring PV, conjugated dienes, anisidine value, and carbonyls. Spectroscopic methods include electron spin resonance, infrared, fluorescence, chemiluminescence, and NMR (Shahidi and Wanasundara, 1998).

1.5.2. Improving Oxidative Stability of Biodiesel

A common strategy to combat autoxidation of biodiesel, aside from minimizing storage time, is the use of oxidation inhibitors (antioxidants). Derived from both natural and synthetic sources, antioxidants are diverse in structure and mode of action (metal chelators, free radical scavengers, etc.). In general, the biodiesel industry prefers synthetic antioxidants owing to their increased efficacy over natural antioxidants. Loadings (concentrations) are kept relatively low, 200–1000 ppm, to minimize effects on costs. Furthermore, synergism among antioxidants in the edible fats and oils industry is well documented (Frankel, 1998). Thus, many commercial antioxidant formulations are mixtures of two or more oxidation inhibitors.

Although there are numerous publications on the effect of natural and synthetic antioxidants on the stability of oils and fats used as food and feed, until recently relatively little publicly available information was available on the effect of antioxidants on the oxidative stability of biodiesel. One of the earliest studies reporting of the effects of antioxidants on biodiesel was that of Du Plessis *et al.* (1985), which examined storage stability of sunflower oil methyl esters (SFME) at various temperatures for 90 d. Effects of air temperature, presence of light, addition of TBHQ (see Figure 1.1) and contact with steel were evaluated by analysis of free fatty acid content, PV, kinematic viscosity, anisidine value, and induction period. Addition of TBHQ delayed oxidation of samples stored at moderate temperatures (≤30 °C). In contrast, under "unfavorable" (50 °C) conditions, TBHQ was ineffective.

Canacki *et al.* (1999) tested the influence of TBHQ on PV of SME during storage and found good improvement in stability. Simkovsky and Ecker (1999) investigated several antioxidants at relatively low loading (300 ppm) on the induction period of RME at different temperatures using the active oxygen method (AOM) but did not find significant improvement.

Working within the aforementioned "BIOSTAB" framework, Bondioli *et al.* (2003) studied the stability of RME under commercial storage conditions over a one year period using the Rancimat method (EN 14112, Anon., 2003c) with and without the addition of TBHQ and pyrogallol (Figure 1.1). Both additives, as can be seen in Table 1.11, imparted significant improvement in the oil stability index (OSI) compared with RME not treated with added antioxidant. This study also reported significant decreases in storage stability

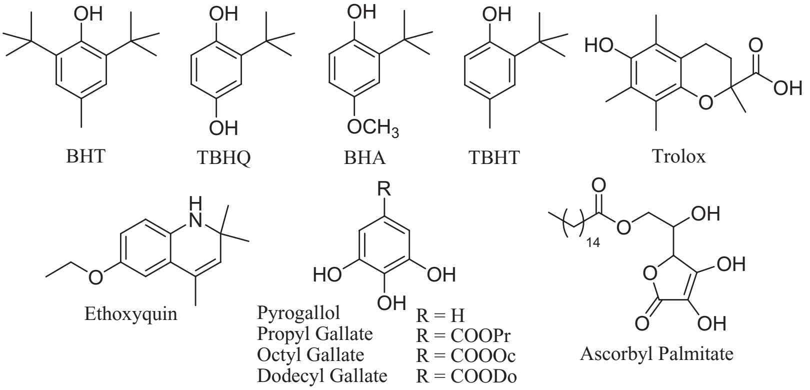

Figure 1.1. Selected Synthetic Antioxidants. BHT = Butylated hydroxytoluene; TBHQ = *tert*-butylhydroxyquinone; BHA = butylated hydroxyanisole; TBHT = *tert*-butyl hydroxytoluene; Trolox = 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid.

caused by removal of natural antioxidants (tocopherols) by distillation of RME. The authors conclude by suggesting, in part, that the minimum concentration of antioxidant be used for optimum effects since higher concentrations may have negative impacts on other parameters.

In 2003, Mittelbach and Schober, also working as part of the 'BIOSTAB' program, investigated the influence of ten commercially available synthetic antioxidants and ten mixtures of natural antioxidants on the OSI of undistilled and distilled RME, SFME, UCOME, and TME. The greatest enhancement in OSI was obtained from the synthetic antioxidants pyrogallol, propyl gallate, TBHQ, and butylated hydroxyanisole (BHA). These four antioxidants plus butylated hydroxytoluene (BHT), due to its widespread use in the food industry, were selected for further study at loadings from 100 to 1000 ppm. In agreement with results reported by Bondioli *et al.* (2003), undistilled biodiesel samples exhibited increased oxidative stability as measured by OSI than their distilled counterparts, with the exception of TME (2003). Furthermore, OSI of RME, UCOME, and TME could be improved significantly with pyrogallol, propyl gallate, and TBHQ, whereas BHT was not as effective.

Conversely, SFME exhibited relatively poor improvement in oxidative stability with the use of antioxidants, presumably due to the higher concentrations of linoleic acid methyl esters in sunflower oil in comparison to the other biodiesel samples evaluated by the authors. Therefore, a good correlation was found between the improvement in oxidative stability as measured by OSI when antioxidants are used and the fatty acid composition of the biodiesel sample (Mittelbach and Schober, 2003).

Schober and Mittelbach (2004) also investigated the impact of concentration of eleven synthetic phenolic antioxidants on oxidative stability of RME, UCOME and TME) by EN 14112 (Anon., 2003c) and on other relevant fuel

TABLE 1.11. Rancimat induction peroid (RIP = OSI) during a 12-month period of storage of RME with and without TBHQ and pyrogallol.[a]

			Monthly RIP [OSI], h							
Biodiesel	Antioxidant	Loading ppm	0	1	2	3	5	7	9	12
Distilled RME	None	—	4.16	4.21	4.23	4.25	4.11	4.02	4.01	3.89
Undistilled RME	None	—	9.20	8.84	8.35	7.65	7.37	7.22	7.08	6.83
Undistilled RME	TBHQ	400	36.00	35.85	35.00	34.17	33.05	33.18	33.73	32.77
Undistilled RME	Pyrogallol	250[b]	22.42	22.25	nd	22.25	22.33	21.82	21.54	20.85

Source: Bondioli *et al.*, 2003.

[a] OSI = oil stability index; nd = not determined. See Tables 1.2 and 1.10 for other abbreviations.

[b] 250 ppm used instead of 400 ppm due to limited solubility of pyrogallol in RME.

properties such as kinematic viscosity, density, carbon residue, CFPP, sulfated ash, and AV. At 1000 ppm, an improvement in oxidative stability was achieved for all antioxidants studied, as can be seen from Table 1.12. In particular, DTBHQ (di-tertbutylhydroquinone), Ionox 220, Vulkanox ZKF, Vulkanox BKF, and Baynox were able to improve significantly the OSI of biodiesel samples, even at lower concentrations. Variation of antioxidant loading from 100–1000 ppm showed that antioxidant efficacy varied depending on the type of biodiesel treated. For instance, the oxidative stability of RME at antioxidant loadings < 250 ppm could only be improved to a satisfactory level by Baynox. DTBHQ exhibited the strongest benefit on RME and UCOME, whereas Vulkanox BKF imparted highest OSI values for distilled UCOME and TME (see Table 1.12). Evaluation of the influence of antioxidants on other important biodiesel fuel parameters showed no negative impacts on kinematic viscosity, density, carbon residue, CFPP, and sulfated ash of the various biodiesel samples. In contrast, a noticeable increase in AV was observed at antioxidant levels of 1000 ppm. At lower antioxidant concentrations, the increase was much lower and AV remained within the prescribed EN 14214 limit of 0.50 mg KOH/g (Anon., 2003b). Lastly, the authors advise that to minimize the potential negative effect of antioxidants on other fuel properties that they be employed at the lowest possible useful loading, as also recommended by Bondioli *et al.* (2003).

TABLE 1.12. Effect of added synthetic antioxidant (1000 ppm) on OSI of RME, UCOME, Distilled-UCOME and Tallow methyl esters (TME).[a]

	OSI, h			
Antioxidant[b]	RME	UCOME	Distilled-UCOME	TME
None	4.56	7.50	2.03	4.74
DTBHQ	9.37	34.11	16.62	27.54
Ionox 220	8.62	21.89	19.77	45.73
Vulkanox ZKF	7.49	14.43	11.51	18.23
Vulkanox BKF	8.63	21.89	26.53	52.24
Baynox[c]	9.36	11.85	11.02	15.85
Ionox 103	8.35	11.10	7.09	10.86
Ionox 99	5.54	9.99	7.12	13.11
Ionox 75	5.72	9.65	7.46	13.71
Inol K65	6.00	9.83	8.21	13.12
MBP-K	5.67	8.89	5.71	12.03
MBM-K	4.97	8.16	4.35	9.41

Source: Schober and Mittelbach, 2004.

[a] DTBHQ = 2,5-di-*tert*-butylhydroquinone. See Tables 1.2, 1.5, 1.10 and 1.11 for other abbreviations.

[b] Vendors: Degussa Sant Celoni SA (Ionox 75, Ionox 99, Ionox 103, Ionox 220, Inol K65); Bayer AG (Vulkanox BFK, Vulkanox ZKF, MBP-K, MBM-K, Baynox); Fine Chemicals (DTBHQ).

[c] Loading = 5000 ppm to achieve effective antioxidant concentration of 1000 ppm (Baynox is 20% BHT in biodiesel).

Dunn (2005a) examined OSI of SME samples from five different sources with varying storage histories with and without added antioxidants. Both TBHQ and α-tocopherol increased OSI in comparison to untreated SME (see Table 1.13). TBHQ at 500 ppm exhibited greater efficacy than α-tocopherol at 1000 ppm at reducing oxidative degradation of biodiesel in all but one SME tested. Variations in OSI response of the various SME samples treated with antioxidants were likely due to aging and other effects sustained prior to acquisition and treatment with additives.

Liang *et al.* (2006) investigated the effect of natural and synthetic antioxidants on oxidative stability of crude and distilled palm oil FAME (PME). Crude palm oil contains minor components such as carotenes and α-tocopherols that upon transesterification, yields crude PME that exhibit superior oxidative stability (OSI > 25 h) compared to distilled PME (OSI ~ 3.5 h), which does not contain minor components. Liang and colleagues therefore endeavored to improve the oxidative stability of distilled PME so that it meets the minimum OSI = 6 h as specified in EN 14214 (Anon., 2003b). Natural (α-tocopherol) and synthetic (BHT and TBHQ) antioxidants were investigated in distilled PME. It was discovered that both natural and synthetic antioxidants exhibited beneficial effects on the oxidative stability of distilled PME

TABLE 1.13. Effect of TBHQ and α-tocopherol on OSI of SME.[a]

Ester	Antioxidant	Loading ppm	OSI[b] h	IV[c] g I_2/100 g oil
Methyl oleate	None	0	140 ± 3.5	84.7
SME-A	None	0	9.4 ± 0.25	133.4
	α-Tocopherol	1000	24 ± 1.0	
	TBHQ	500	54 ± 1.0	
SME-B	None	0	9.5 ± 0.22	120.4
	α-Tocopherol	1000	17.8 ± 0.53	
	TBHQ	500	20.2 ± 0.39	
SME-C	None	0	4.1 ± 0.59	130.7
	α-Tocopherol	1000	21 ± 4.3	
	TBHQ	500	17.2 ± 0.48	
SME-D	None	0	7.2 ± 0.30	134.5
	α-Tocopherol	1000	36.4 ± 0.30	
	TBHQ	500	146 ± 1.7	
SME-E	None	0	53 ± 1.3	130.3

Source: Dunn, 2005a.

SME from five different sources: SME-A, B and C were obtained from the ADEPT Group (Los Angeles, CA), SME-D from the National Biodiesel Board (Jefferson City, MO) and SME-E directly from its producer; Methyl oleate (99+%) was from Nu Chek Prep (Elysian, MN).

[a] IV = iodine value. See Table 1.2 for other abbreviations.

[b] OSI analyses by oxidative stability instrument: Block temperature = 60 °C, air flow rate = 150 mL/min.

[c] Calculated based on fatty acid composition determined by GC.

TABLE 1.14. Effect of natural and synthetic antioxidants on OSI of crude and distilled palm oil biodiesel (PME).[a]

		Dosage of Antioxidant, ppm			
Biodiesel	Mixture	α-Tocopherol	BHT	TBHQ	OSI h
Crude PME	654[b]	—	—	—	25.70
Distilled PME	0	—	—	—	3.52
Distilled PME	0	1000	—	—	6.17
Distilled PME	0	—	50	—	6.42
Distilled PME	0	—	—	50	8.85

Source: Liang *et al.*, 2006.

[a] See Tables 1.2, 1.10 and 1.11 for abbreviations.

[b] Mixture = α-Tocopherol (119 ppm)/α-tocotrienol (113 ppm)-tocotrienol (352 ppm)/δ-tocotrienol (70 ppm).

(see Table 1.14). In accordance with previously mentioned studies, synthetic antioxidants BHT and TBHQ were more effective than natural antioxidants as lower concentrations (17 times less) were necessary to achieve OSI > 6 h. Another study by Loh *et al.* (2006) investigated the effect of natural and synthetic antioxidants on oxidative stability of PME produced from used cooking oil. The order of increasing antioxidant effectiveness, determined by OSI, was found to be: α-tocopherol < BHT < TBHQ < BHA < PG.

Litwinienko *et al.* (1997) reported that non-isothermal (conventional) DSC and P-DSC analyses can evaluate antioxidant activity in linolenic ($C_{18:3}$) acid doped with phenolic antioxidants. Activation energies were inferred by applying the Ozawa-Flynn-Wall analytical method. Results showed that increasing BHT loading from 0.3 to 4.0 mM increased the activation energy of oxidation from 73.0 to 97.8 kJ/mol.

Stavinoha and Kline (2001) adapted ASTM method D 6186 (Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry [P-DSC]) for analyzing the oxidative stability of SME treated with antioxidants. This report concluded that isothermal P-DSC analysis is suitable for screening the effectiveness of antioxidants for treating biodiesel.

An earlier study (Stavinoha and Howell, 2000) examined the effects of TBHQ and α-tocopherol on oxidative stability of SME from four different sources by non-isothermal P-DSC in static (zero air-purge) mode. P-DSC curves were analyzed by measuring the OT where P = 2000 kPa, initial temperature = 25 °C, and β = 5 °C/min. Results for two of the SME samples showed that addition of 2000 ppm α-tocopherol increased OT by ~20 °C while addition of 2000 ppm TBHQ increased OT by ~30 °C. Addition of the same concentration of α-tocopherol and TBHQ to the other two SME samples increased OT by ~30 °C and ~40 °C, respectively. Interpretation of these results suggested TBHQ was more effective at increasing relative resistance to oxidation of SME than α-tocopherol, a conclusion that was in accordance with those by Mittelbach and Schober (2003) for the isothermal Rancimat method.

Although P-DSC results were consistent with corresponding OSI at 50 °C, no correlation for predicting OSI directly from OT results was evident (Dunn, 2000).

A recent study (Dunn, 2005b) evaluated the effectiveness of TBHQ, BHA, BHT, propyl gallate, and α-tocopherol in mixtures with SME by non-isothermal P-DSC analyses in static and dynamic (positive air-purge) modes. Antioxidant activity was interpreted from OT results derived from P-DSC curves conducted under P = 2000 kPa and at β = 5 °C/min. Synthetic antioxidants propyl gallate, BHT, and BHA were most effective and α-tocopherol least effective in terms of increasing OT with respect to untreated SME (see Table 1.15). Increasing antioxidant concentration showed sharp increases in OT for loadings up to 1000 ppm, followed by smaller increases in OT at higher loading levels. This study recommended BHA or TBHQ (concentrations up to 3000 ppm) for safeguarding biodiesel from effects of autoxidation during storage. BHT was also found to be suitable at relatively low concentrations (210 ppm). Propyl gallate showed some physical compatibility problems with SME during phase equilibrium studies and therefore may not be readily soluble in blends with petrodiesel at larger SME ratios. Although α-tocopherol exhibited good solubility in SME/No. 2 petrodiesel blends, it was significantly less effective than the synthetic antioxidants.

TABLE 1.15. Conventional DSC and pressurized-DSC (P-DSC) results showing effect of antioxidants on oxidation onset temperature (OT) of SME.[a]

Ester	Antioxidant	Loading ppm	Conventional DSC[b] OT, °C	Static mode[c] OT, °C	Dynamic mode[d] OT, °C
Methyl oleate	None	0	168 ± 3.9	159.2 ± 0.56	164 ± 2.4
SME	None	0	136 ± 2.0	126 ± 1.2	116 ± 1.4
SME	α-Tocopherol	500	—	134.2± 0.74	125.1 ± 0.31
		2000	143 ± 3.4	146.2 ± 0.37	128 ± 1.6
SME	TBHQ	500	—	139 ± 1.2	129 ± 1.1
		2000	167 ± 1.7	157.76 ± 0.078	137 ± 1.0
SME	BHA	500	—	146.3 ± 0.63	136.9 ± 0.16
		2000	—	161 ± 2.2	149.4 ± 0.24
SME	BHT	500	—	141 ± 1.7	138.52 ± 0.078
		2000	—	157.7 ± 0.46	151.3 ± 0.30
SME	Propyl gallate	500	—	142 ± 2.2	139.5 ± 0.75
		2000	—	161 ± 2.4	151.2 ± 0.84

Sources: Dunn, 2005b, 2006a.

Onset oxidation temperature (OT) from non-isothermal heating curve analyses as ramp rate (β) = 5 °C/min.

[a] See Tables 1.2 and 1.5 for abbreviations.

[b] Air-purge = 75 mL/min, cell pressure (P) = ambient, equilibration temperature = 25 °C.

[c] Zero air-purge (closed system), P = 2000 kPa (290 psig), equilibration temperature = 25 °C.

[d] Air-purge = 35 mL/min, P = 2000 kPa (290 psig), equilibrium temperature = 30 °C.

The effects of antioxidants on OT of SME by non-isothermal (conventional) DSC, static mode P-DSC, and dynamic mode P-DSC were investigated by Dunn (2006a), which is summarized in Table 1.15. Results from all three methods consistently showed that treating SME with antioxidants TBHQ and α-tocopherol increased OT with respect to untreated SME. Statistical comparison of P-DSC results with those from isothermal analysis of OSI at 60 °C was facilitated by calculation of the corresponding response factors (defined ratios of OT of the sample to that of methyl oleate, and of OSI of the sample to that of methyl oleate). Data for the sample and reference material (methyl oleate) were measured under the same experimental conditions. Results showed the highest degree of correlation ($P = 0.79$) between dynamic-mode P-DSC and isothermal OSI analyses.

1.6. VISCOSITY

Viscosity is the major reason why oils and fats are transesterified to biodiesel. The viscosity of vegetable oils is about an order of magnitude greater than that of petrodiesel while that of biodiesel is only slightly greater than that of petrodiesel. Kinematic viscosity is the form of viscosity prescribed in biodiesel standards. The ASTM fuel specification D 6751 (Anon., 2007a) requires the viscosity of biodiesel to be in the range of 1.9–6.0 mm^2/s at 40 °C while European specification EN 14214 (Anon., 2003b) prescribes a narrower range of 3.5–5.0 mm^2/s at 40 °C, which has the effect of excluding some oils or fats as sources of biodiesel. The kinematic viscosity of methyl soyate is typically in the range of 4.1–4.2 mm^2/s at 40 °C while that of the parent soybean oil is 32 mm^2/s at 37.8 °C. The kinematic viscosity of methyl esters of other vegetable oils is in a similar range of about 4.0–4.8 mm^2/s, including PME, SFME, and RME (canola oil methyl esters). Biodiesel from greases of used cooking oils tend to have higher viscosity, often above 5.0 mm^2/s due to their higher content of saturated or *trans* fatty acids. In comparison, the kinematic viscosity of petrodiesel fuels is typically in the range of 2.0–3.0 mm^2/s at 40 °C. Kinematic viscosity is typically determined with methods such as ASTM D 445 or ISO 3104 (Anon., 2003d). Viscosity is strongly temperature-dependent, increasing significantly with decreasing temperature.

The kinematic viscosity of alkyl esters or biodiesel and its components has been the subject of several studies (Krisnangkura *et al.*, 2006; Tate *et al.*, 2006; Knothe and Steidley, 2005a; Yuan *et al.*, 2005b; Kerschbaum and Rinke, 2004; Allen *et al.*, 1999; Tat and Van Gerpen, 1999; De Filippis *et al.*, 1995; Gouw *et al.*, 1966). The viscosity of a fatty acid ester depends on chain length as well as the number and nature of double bonds. The more CH_2 groups in the chain the higher the viscosity, the greater the number of *cis* double bonds, the lower the viscosity. Compounds with one *trans* double bond have nearly the same viscosity as the corresponding saturated compounds, thus *trans* double bonds impart higher viscosity than *cis* (Knothe and Steidley, 2005a). Consequently, the kinematic viscosity of biodiesel depends strongly on its fatty acid profile. Thus the kinematic viscosity at 40 °C of saturated methyl esters increases from 2.43 mm^2/s for methyl laurate to 3.30 mm^2/s for methyl myristate to 4.38 mm^2/s for methyl palmitate to 5.85 mm^2/s for methyl stearate. Increasing the size of the ester group has a similar effect. Thus ethyl oleate, propyl oleate and butyl oleate display kinematic viscosities of 4.78, 5.44 and 5.69 mm^2/s, respectively. Methyl oleate, on the other hand, has a kinematic viscosity at 40 °C of 4.51 mm^2/s while the its *trans* isomer methyl elaidate exhibits a value of 5.86 mm^2/s, virtually identical to that of methyl stearate. The polyunsaturated esters methyl linoleate and methyl linolenate have values of 3.65 mm^2/s and 3.14 mm^2/s, respectively. For sake of comparison, triolein has a kinematic viscosity at 40 °C of 32.94 mm^2/s. Methyl ricinoleate, the major component of castor oil methyl esters, which corresponds to methyl oleate with an OH group at C12 in the chain, has a kinematic viscosity at 40 °C of 15.44 mm^2/s.

1.7. LUBRICITY

The diesel engine has historically relied on petrodiesel components to lubricate parts such as fuel pumps and injectors. The advent of low-sulfur petrodiesel fuels and, more recently, ULSD ($\leq$15 ppm S) as required by regulations in the United States, Europe and elsewhere, has led to failure of such engine parts since these fuels possess poorer lubricity than the high sulfur fuels used previously. The reason is that the hydrodesulfurization process that eliminates the sulfur species from petrodiesel fuel also removes the polar oxygen- and nitrogen-containing species which had been responsible for this lubricity (Dimitrakis, 2003; Barbour *et al.*, 2000; Wei and Spikes, 1986). The poor lubricity of low-sulfur petrodiesel (Dimitrakis, 2003; Wei and Spikes, 1986; Wall *et al.*, 1999; Lacey and Westbrook, 1995; Tucker *et al.*, 1994; Wang and Reynolds, 1994; Nikanjam and Henderson, 1993; Lacey and Lestz, 1992a, 1992b) requires additives or blending with another fuel of sufficient lubricity.

Currently, the most common test method for assessing the lubricity of diesel fuel is the high-frequency reciprocating rig (HFRR) lubricity tester (standards are ASTM D 6079 and ISO 12156 (Anon., 2003e). During this test, usually carried out at 60 °C, a wear scar is generated on a steel ball by rubbing against a steel disk. The size of the wear scar correlates with the lubricity of the sample. The smaller the wear scar, the better the lubricity and vice versa. Lubricity specifications are not included in biodiesel standards. However, petrodiesel standards contain lubricity specifications, with a maximum wear scar of 460 µm prescribed in the European petrodiesel standard EN 590 and a maximum wear scar of 520 µm in the American standard ASTM D 975 (Anon., 2003a).

Biodiesel inherently possesses good lubricity (Lang *et al.*, 2001; Lacey and Westbrook, 1995; Drown *et al.*, 2001; Van Gerpen *et al.*, 1999; Galbraith and

TABLE 1.16. HFRR data (60 °C; duplicate determinations) of commercial biodiesel, petrodiesel, hydrocarbons and neat fatty compounds.

Material	Wear scar, µm	Material	Wear scar, µm
Biodiesel	129; 134	Hexadecane	572; 571
ULSD	651; 636	1-Hexadecene	475; 477

Neat fatty compounds

Material	Wear scar, µm	Material	Wear scar, µm
Methyl laurate	416; 408	Methyl 9,12-linolelaidate	175; 177
Methyl palmitate	357; 362	Methyl ricinoleate	191; 174
Methyl palmitoleate	246; 228	Linoleic acid	0; 0
Methyl stearate	322; *277*	Monoolein	139; 123
Oleic acid	0; 0	Diolein	186; 163
Methyl oleate	290; 342	Triolein	143; 154
Methyl linoleate	236; 219	Oleyl alcohol	301; 289
Methyl linolenate	183; 185	Ricinoleyl alcohol	148; 162

Source: Knothe and Steidley, 2005b.

Hertz, 1997; Waynick, 1997). As Table 1.16 demonstrates, commercial biodiesel displays better lubricity than its neat major components, fatty acid esters, and its parent vegetable oil (see entries with triolein). This observation has been described several times in the literature. However, in the neat form some minor components of biodiesel, especially monoacylglycerols, free fatty acids, and glycerol display lubricity equal to or better than commercial biodiesel (Knothe and Steidley, 2005b). Lubricity is also enhanced with increasing unsaturation of the fatty acid chain. When more than one lubricity-enhancing moiety is present in a molecule, for example, the two OH groups in monoacylglycerols and ricinoleyl alcohol or three OH groups in glycerol, then lubricity of the neat compound is even more improved. On the other hand, excellent lubricity of a neat compound does not necessarily translate into lubricity enhancement by this compound when used at additive level in a petrodiesel fuel with poor lubricity as exemplified by glycerol, whose poor solubility in petrodiesel negatively affects its lubricity enhancement capabilities.

Thus biodiesel is a better lubricity enhancer than its parent vegetable oil because of the presence of high-lubricity species, some of which, such as monoacylglycerols, can arise during biodiesel production. Biodiesel is required at levels such as 2% for lubricity enhancement in order to achieve a sufficient additive level of high-lubricity materials in petrodiesel. Table 1.17 gives data showing the effect of minor components of biodiesel on its lubricity.

Results related to those discussed above (Knothe and Steidley, 2005b) are available in the literature (Hu *et al.*, 2005; Hillion *et al.*, 1999). The results in these publications do not agree on all aspects, however, there is agreement that low-level "contaminants" significantly affect biodiesel lubricity and its low-level blends with petrodiesel.

TABLE 1.17. Effect of blending or additization on HFRR data (60 °C) of ultra-low sulfur petrodiesel fuel (ULSD). For data of the neat petrodiesel fuels, see Table 1.16.

Blend / additive w/ ULSD	Wear scar, µm
1% Biodiesel	292; 292
2% Biodiesel	281; 258
1% Methyl oleate	597; 515
2% Methyl oleate	384; 368
5% Methyl oleate	365; 359
10% Methyl oleate	289; 298
0.01% Oleic acid	234; 233
1% Monoolein	134; 161
1% Diolein	237; 251
1% Triolein	385; 370
2% Triolein	287; 314
1% Methyl linoleate	573; 573
2% Methyl linoleate	536; 551
1% Glycerol	641; 649
1% Methyl oleate, 0.01% monoolein	335; 303
1% Methyl oleate, 0.01% diolein	533; 485
1% Methyl linoleate, 0.01% linoleic acid	437; 413
1% Methyl linoleate, 0.01% glycerol	571; 580
1% Methyl linoleate, 0.01% monolinolein	301; 274
1% Methyl linoleate 0.01% dilinolein	527; 533

Source: Knothe and Steidley, 2005b.

1.8. CONCLUSIONS

Biodiesel is a renewable alternative fuel for combustion in compression ignition (diesel) powered trucks, automobiles and farm vehicles, and in many other applications. It is environmentally innocuous and safe to handle due to relatively high flash points. It has many fuel characteristics that are compatible to petrodiesel including combustible energy content, specific gravity, kinematic viscosity, and CN. Biodiesel has inherent lubricity characteristics that make it an ideal anti-wear additive when blended with ULSD (≤15 ppm S content) No. 2 petrodiesel. Combustion of biodiesel can significantly reduce exhaust emissions including HC, CO, PM, smoke opacity, sulfur oxides, and polycyclic aromatic hydrocarbons. Finally, almost no modification of modern diesel engines is necessary to adapt them for burning biodiesel or biodiesel/petrodiesel blends.

Despite its many advantages as a renewable alternative fuel, biodiesel presents a number of problems that must be resolved for it to be attractive for more widespread applications. These problems include improving relatively poor cold flow properties, monitoring and maintaining fuel quality against oxidative degradation during long-term storage, and reducing NOx levels in exhaust emissions.

The cold flow properties of biodiesel may cause issues when blended with petrodiesel during cooler months in moderate climates. SME begins to 'gel' or solidify very rapidly as its temperature approaches freezing (0 °C). This problem is more pronounced for biodiesel made from feedstock lipids possessing higher saturated fatty acid contents, such as palm oil and used cooking oils. Two promising approaches form improving cold flow properties include converting feedstock to biodiesel using medium or branched chain alcohols, and fractionation to reduce total saturated fatty acid content in biodiesel. Both of these approaches may be effective in decreasing CP, and they may also significantly increase costs of the final fuel product. Commercial CFI additives may be more economical. However, despite their effectiveness in depressing PP, these additives do not significantly reduce CP.

Maintaining fuel quality during long-term storage is a major concern for biodiesel producers, marketers and consumers. Again the most cost-effective means for improving oxidative stability of biodiesel is to treat it with antioxidants. Care must be exercised in cleaning tanks before filling them with biodiesel, and in paying attention to storage conditions such as temperature, purging out air with a nitrogen "blanket," and keeping the fuel away from direct lighting. Biodiesel stored over long periods should be monitored regularly for signs of degradation.

The use of additives to address a great number of fuel performance issues is ubiquitous in the biodiesel and petrodiesel industries. Unless the fuels themselves are enhanced through compositional modification, the employment of additives is likely to continue for the foreseeable future. As such, in spite of the impressive technological advances that have been made over the last 50 years or more in the field of fuel additives, a great deal of research remains to be accomplished to fully address technical deficiencies inherent in fuels, in particular the comparatively new arena of biodiesel and blends thereof in ULSD. With the conversion from low-sulfur (≤500 ppm) No. 2 petrodiesel to ULSD (≤15 ppm) in the U.S. in 2006, many additive treatment technologies that were previously successful with No. 2 petrodiesel may not yield similar results in ULSD. By extension, additives used for blends of SME/low-sulfur petrodiesel may not impart the same level of beneficial effect in blends of SME/ULSD, which once again emphasizes the need for continued research and development into the field of fuel additives.

1.9. ABBREVIATIONS

β	Ramp rate, °C/min
AV	Acid value, mg KOH/g oil
BHA	Butylated hydroxyanisole (*tert*-butyl-4-hydroxyanisole)
BHT	Butylated hydroxytoluene (2,6-di-*tert*-butyl-4-methylphenol)

CFI	Cold flow improver
CFPP	Cold filter plugging point, °C
CN	Cetane number
CO	Carbon monoxide
CP	Cloud point, °C
CPD	Cloud point-depressant
CVCA	Constant volume combustion apparatus
DSC	Differential scanning calorimetry
DTBHQ	Di-*tert*-butylhydroquinone
FAME	Fatty acid methyl esters
HC	Hydrocarbons
HFRR	High frequency reciprocating rig
ID	Ignition delay, ms
IQT	Ignition quality tester
IV	Iodine value, g I_2/100 g oil
LSD	Low-sulfur (≤500 ppm) petrodiesel
LTFT	Low-temperature flow test, °C
MP	Melting point, °C
NOx	Nitrogen oxides (emissions)
OSI	Oil stability index (induction period), h
OT	Oxidation onset temperature, °C
P-DSC	Pressurized-differential scanning calorimetry
PM	Particulate matter
PME	Palm oil fatty acid methyl esters
PP	Pour point, °C
PPD	Pour point-depressant
PV	Peroxide value, meq/kg
RME	Rapeseed oil fatty acid methyl esters
SME	Soybean oil fatty acid methyl esters
SFME	Sunflowerseed oil fatty acid methyl esters
TBHQ	*tert*-Butylhyroquinone
TGA	Thermogravimetric analysis
TME	Tallow fatty acid methyl esters
UCOME	Used cooking oil fatty acid methyl esters
ULSD	Ultra-low sulfur (≤15 ppm) petrodiesel

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