

Chapter 4

Biodiesel: An Alternative Diesel Fuel from Vegetable Oils or Animal Fats

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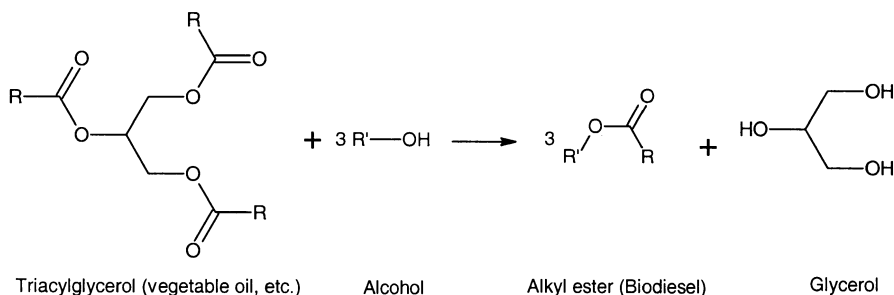
Introduction

Biodiesel is defined as “a fuel comprised of the mono-alkyl ester of long chain fatty acids derived from vegetable oils or animal fats” (1). Accordingly, biodiesel is derived from vegetable oils or animal fats by a transesterification reaction (Scheme 4.1), in which the oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. Methanol is the alcohol used most commonly to produce biodiesel as it is the least expensive alcohol in many countries.

Besides transesterification to alkyl esters, three other approaches—dilution with conventional, petroleum-based diesel fuel (DF), microemulsions (co-solvent blending), and pyrolysis—have been explored for utilizing vegetable oils as fuel (2). However, as the mono-alkyl esters of vegetable oils and animal fats—biodiesel—are the only approach that has found widespread use (and, accordingly, the vast majority of research papers deal with this approach), this article will focus on such mono-alkyl esters.

History and Overview

The use of vegetable oils as a DF is a concept nearly as old as the diesel engine itself. At the Paris World Exhibition in 1900, at the request of the French government, a diesel engine was demonstrated using a vegetable oil (peanut oil) as fuel



Scheme 4.1. The transesterification reaction.

(3) and was described in reports by Rudolf Diesel (4,5), the inventor of the engine that bears his name. Numerous papers were published until the late 1940s regarding the use of vegetable oils as fuel (3). The background in most cases was a rather modern one—namely, to provide an alternative source of energy. This was the case also in European countries with African colonies. Among those numerous reports are several articles (6–8) from Belgium and its former colony, the Belgian Congo, which are presumably the first to describe the use of what is today termed biodiesel as fuel (3). In that work, ethyl esters of palm oil were utilized, however, other oils and esters were described as suitable. During the age of inexpensive and easily accessible petroleum from approximately 1950 until the 1970s, hardly any reports on vegetable oil-based fuels were published. As a result of the energy crises of 1973 and later years, the interest in alternative fuels, among them vegetable oils was renewed. In 1980, the use of esters of sunflower oil as DF was reported (9). These authors explicitly pointed out that viscosity of the esters is significantly decreased compared to the parent vegetable oil, now being close to that of conventional DF. The lower viscosity nearly eliminated engine problems such as injector coking and deposits which are a problem with neat vegetable oils. Besides the energy security aspect, environmental concerns (with regulations and legislation arising therefrom) as well as utilization of excess agricultural commodities have become significant driving forces for the use of alternative fuels such as those derived from vegetable oils. Commercialization has occurred in numerous countries around the world with varying economic and legislative conditions. Standards have been or are being developed in Europe, the U.S. and elsewhere. Countless research papers on biodiesel as well as numerous reviews, book chapters, and general interest articles have been published.

Sources of Fuels

Biodiesel is obtained from various sources depending largely on the country and its climate. Accordingly, soybean oil is the vegetable oil most commonly used for biodiesel production in the U.S. Rapeseed oil (in low-erucic form canola oil) is the major feedstock in Europe, although it is also used in the Pacific Northwest of the U.S. Countries with tropical climate utilize tropical oils such as coconut and palm oil. Other common oils such as cottonseed, peanut (groundnut) and sunflower oils have been studied. Potential sources of biodiesel with some emphasis on developing countries were discussed in more detail (10). Less common or less studied vegetable oils that have been investigated as sources of biodiesel include *Cynara cardunculus* (Castillian thistle) (11), rubber seed oil (12), karanja (*Pongamia glabra*) and nahor (*Mesua ferrea* L.) oils (13), *Cuphea viscosissima* (14), and *Jatropha curcas* L. (15), tobacco seed oil (16) as well as other non-conventional oils (17). Various feedstocks for biodiesel were also explored in earlier times (3). Animal fats such as tallow have also been investigated. More recently, increasing emphasis has been placed on low-cost feedstocks such as used frying oils and soapstock. Microalgae were also suggested as a source of biodiesel (18).

Economics, Regulatory Issues, and Utilization

A major obstacle facing biodiesel commercialization is economics. The higher price of the feedstock compared to petroleum translates into a higher price for the resulting fuel. In the U.S. the price of a gallon (about 3.8 liters) of soybean oil is approximately \$1.40–\$1.50. Other feedstocks are even more expensive. After completion of fuel production, the price of a gallon of methyl soyate is even higher, approximately three to four times that of conventional DF. On the other hand, glycerol, which has numerous uses as a by-product of the transesterification process, may help offset some of the costs. Biodiesel with accompanying glycerol production has had a significant influence on glycerol prices in recent years (19).

Incentive-providing legislation and regulations regarding taxes, the environment and energy security offset the inherent economic disadvantage of biodiesel toward conventional DF. In some European countries such as Germany, biodiesel is not subject to the excise tax levied on petroleum-derived fuels. Since the total taxes on conventional fuels are so high, biodiesel becomes economically competitive with conventional DF if it is not subject to these taxes, causing biodiesel to be fairly widely available at filling stations for general use. However, beginning in 2003, tax incentives proportional to the level of biodiesel were applied in Germany to blends of biodiesel with conventional DF. In France, biodiesel is being promoted by approval of a 5% blend of biodiesel in conventional DF available at the pump and as 30% blend available to fleets of “urban vehicles.” In the U.S., environment and energy security-related issues have been the major driving forces apply, expressed in the Clean Air Act Amendments of 1990 and the Energy Policy Act (EPAAct) of 1992 as well as the Energy Conservation Reauthorization Act of 1998. Both neat biodiesel and “B20” (a blend of 80 vol% conventional DF with 20 vol% biodiesel) are recognized as alternative fuels in the U.S. under EPAAct criteria. Regulated fleets (government and other public fleets) can earn credits for using a certain amount of both neat biodiesel and B20. Therefore, in the U.S. biodiesel has been mainly promoted for use in regulations-affected and niche markets (regulated fleets, urban bus fleets, marine and mining markets). In developing countries, especially those that produce significant amounts of tropical oils, the main incentive for using biodiesel is to become independent of petroleum imports.

A major development which will likely serve to additionally promote the use of biodiesel is upcoming mandates prescribing the use of low-sulfur conventional DF. Removal of the sulfur-containing components from conventional DF causes the lubricity of the conventional DF to be significantly reduced or even eliminated. Inherent lubricity of the fuel is important for the functioning of engine components such as fuel pumps and injectors. Adding biodiesel in low amounts (1–2%) to low-sulfur conventional DF restores the lubricity. An advantage of biodiesel in that case is its inherent fuel value, which is not necessarily the case with lubricity additives.

Agricultural policies play a role in the production of biodiesel. In the U.S., the goal is to find a significant use of excess soybean oil and provide price support for

that commodity. Increased demand for soybean oil as a result of biodiesel production could increase soybean oil prices by up to 14% (20). The 2002 Farm Bill contains an energy title which provides for payments to biofuels producers who purchase agricultural commodities for that purpose. In countries of the European Community, set-aside land taken out of crop production for food use may be used for growing crops for nonfood uses. Affected farmers would still receive the general set-aside premium, providing an additional incentive to grow crops for nonfood uses.

Biodiesel production has increased significantly over the past few years and is likely to increase further (21, 22). According to some estimates, the capacity for biodiesel production in Europe in 2003 was approximately as high as 2.5 to 2.7 million metric tons (22). More than 90% of this capacity is in Europe with the U.S. accounting for the rest. Numerous biodiesel plants are under construction or in planning stages with accompanying significant increases in production.

According to a life-cycle analysis of biodiesel (23) in the U.S., biodiesel is competitive with other alternative fuels such as compressed natural gas (CNG) and methanol in the urban transit bus market. An advantage of biodiesel is its near full compatibility with existing fuel distribution and use infrastructure. No engine modifications (with the exception of some seals and gaskets) are required to commercial diesel engines and storage is similar to conventional DF. This advantage can offset the higher price of the biodiesel fuel in comparison to other alternative fuels which may require significant and expensive infrastructure changes. On the other hand, life-cycle assessments should be carried out individually for each source as the results can vary significantly and the methods used also have great influence (24).

With the exception of nitrogen oxides (NO_x), the use of biodiesel reduces exhaust emissions compared to conventional petroleum-based DF. Due to its lack of sulfur, biodiesel does not cause SO_2 emissions. The lower emissions make biodiesel attractive for use in urban bus fleets and other niche markets such as mining and marine engines. Besides environmental and health reasons with accompanying regulations, focusing on the use of biodiesel in niche markets is additionally attractive because not enough feedstocks are available to supply the whole diesel market with biodiesel.

Cetane Numbers and the Suitability of Fatty Compounds as Diesel Fuel

A scale conceptually similar to the familiar octane scale used for gasoline (petrol), the cetane number (CN), exists for describing the ignition quality of conventional DF or its components. The CN is determined by standards such as ASTM D613. The CN of a DF is determined by the ignition delay time, that is, the time that passes between injection of the fuel into the cylinder and onset of ignition. The shorter the ignition delay time, the higher the CN and vice versa. Generally, a com-

pound that has a high octane number tends to have a low CN and vice versa. Thus, 2,2,4-trimethylpentane (*iso*-octane), a short, branched alkane, is the high-quality standard (a primary reference fuel; PRF) for the octane scale (and also gives it its name) of gasoline with an octane number of 100 while *n*-heptane is the low-quality PRF with an octane number of 0 (25). For the cetane scale, a long straight-chain hydrocarbon, hexadecane ($C_{16}H_{34}$; trivial name cetane, giving the cetane scale its name) is the high-quality standard and has been assigned a CN of 100. At the other end of the scale, a highly branched compound, 2,2,4,4,6,8,8-heptamethylnonane (HMN, also $C_{16}H_{34}$), a compound with poor ignition quality in a diesel engine, has been assigned a CN of 15. Thus branching and chain length influence CN with CN decreasing with decreasing chain length and increasing branching. Aromatic compounds occur in significant amounts in conventional DF and have low CN but their CN increase with increasing size of *n*-alkyl side chains (26,27). The cetane scale is arbitrary and compounds with CN >100 (although the cetane scale does not provide for compounds with CN >100) or CN <15 have been identified.

The cetane scale demonstrates the suitability of fatty compounds as alternative DF. The structure of the long, unbranched chains of fatty acids (FA) is similar to those of *n*-alkanes which yield good conventional DF. CN of fatty compounds and alkyl esters of vegetable oils and animal fats are presented in [Tables 4.1](#) and [4.2](#).

However, besides ignition quality as expressed by the cetane scale, several other properties determine the overall quality of any DF. Especially heat of combustion, pour point (PP), cloud point (CP), viscosity, oxidative stability and lubricity are of importance.

General Comparison of Fuels from Vegetable Oils and Animal Fats

Some relevant properties of the most common FA occurring in vegetable oils and animal fats as well as some of their esters are listed in Table 4.1. Besides these FA, numerous other FA occur in vegetable oils and animal fats, but their amounts usually are considerably lower. Properties of esters of oils and fats are given in Table 4.2.

The most common derivatives of TG (or FA) for fuels are methyl esters. These are formed by transesterification of the TG with methanol in the presence of usually a basic catalyst to give the methyl ester and glycerol (see Scheme 4.1). Other alcohols have been used to generate esters such as the ethyl, propyl, and butyl esters. As discussed above, the suitability of fats and oils as DF results from their molecular structure and high energy content. Long, saturated, unbranched hydrocarbon chains as they are found in fatty compounds are especially suitable for conventional DF as shown by the CN scale. CN generally increase with increasing chain length (28). Other observations (29) are (i) that double bonds decrease CN (therefore, the number of double bonds should be small rather than large), (ii) that a double bond, if present, should be positioned near either end of the molecule, and (iii) no aromatic compounds should be present. However, branching in the ester

moiety (*iso*-propyl esters, etc.) does not negatively influence CN of fatty compounds (30). The combustion of the glyceryl moiety of triacylglycerols could lead to the formation of acrolein and this in turn to the formation of aromatics (29), although no acrolein was found in precombustion of triacylglycerols (31). This may be one reason why fatty esters of vegetable oils perform better in a diesel engine than oils containing the TG (29).

The above statements on CN correlate with the values given in [Tables 4.1 and 4.2](#). The CN of mixtures are influenced by the nature of their components. Fuel components with higher CN impart these higher CN to the biodiesel fuel.

It is occasionally emphasized that biodiesel is an oxygenated fuel, implying its oxygen content plays a role in making fatty compounds suitable as DF by “cleaner” burning. The responsibility for this suitability rests, however, mainly with the hydrocarbon portion which is similar to conventional DF. Furthermore, the oxygen in fatty compounds may be removed from the combustion process by decarboxylation, which yields incombustible carbon dioxide (CO₂), as precombustion (31), pyrolysis and thermal decomposition studies discussed below imply. Also, pure unoxxygenated hydrocarbons, like cetane, have CN higher than biodiesel.

The CN of esters correlate well with boiling points (28). Quantitative correlations and comparisons to numerous other physical properties of fatty esters confirmed that the boiling point gives the best approximation of CN (32).

ASTM D613 is used in determining CN. For vegetable oil-derived materials, an alternative scale utilized a constant-volume combustion apparatus (CVCA) (33). The amount of material needed for CN determination was reduced significantly with this bomb and it also allows studying materials with high melting points (mp) that cannot be measured by ASTM D613. Estimated cetane numbers (ECN) were determined on a revised scale permitting values greater than 100. In this case, the ECN of methyl stearate is 159 and that of methyl arachidate (20:0) is 196 (33). The ECN of other esters were methyl laurate 54, methyl myristate 72, methyl palmitate 91, and methyl oleate 80. The ECN of the TG trilaurin and trimyristin exceeded 100, while in another series of experiments the ECN of tripalmitin was 89, tristearin 95, triolein 45, trilinolein 32, and trilinolenin 23. The term “Lipid Combustion Quality Number” with an accompanying scale was suggested instead of CN to provide for values in excess of CN 100 (33).

Often the “cetane index” of a fuel is published and should not be confused with CN. This is an ASTM-approved alternative method for a “non-engine” predictive equation of CN for petroleum distillates (34). Equations for predicting CN are usually not applicable to nonconventional DF such as biodiesel or other lipid materials (35). Cetane indices are not given here. Methods for estimating the cetane indices of esters of FA and vegetable oils were presented (36,37).

Besides CN, gross heat of combustion (HG) is another property of fatty compounds that is essential in proving the suitability of these materials as DF as the heat content of vegetable oils is nearly 90% that of DF2 (38–41). The heats of

TABLE 4.1Properties of Fatty Acids and Esters of Relevance to Biodiesel^a

Trivial (Systematic) name; Acronym ^b	m.p. (°C)	b.p. (°C)	Cetane no.	Kinematic viscosity (40°C; mm ² /s = cSt)	HG (kg-cal/mole)
Lauric (Dodecanoic); 12:0	44	131 ¹			
Methyl ester	5	266 ⁷⁶⁶	61.4 (99.1)	1.95 ^c ; 2.38	1940
Ethyl ester	−1.8fr	163 ²⁵		2.88 ^c	2098
Myristic (Tetradecanoic); 14:0	58	250.5 ¹⁰⁰			
Methyl ester	18.5	295 ⁷⁵¹	66.2 (96.5)	2.69 ^c , 3.23	2254
Ethyl ester	12.3	295	66.9 (99.3)		2406
Palmitic (Hexadecanoic); 16:0	63	350			
Methyl ester	30.5	415–4418 ⁷⁴⁷	74.5 (93.6)	3.60 ^c ; 4.32	2550
Ethyl ester	19.3/24	191 ¹⁰	85.9		2717
Propyl ester	20.4	190 ¹²	93.1		
<i>Is</i> -propyl ester	13–14	160 ²	85.0 82.6		
Stearic (Octadecanoic); 18:0	71	360 ^d	61.7		
Methyl ester	39	442–3 ⁷⁴⁷	86.9 (92.1)	4.74 ^c , 5.61	2859
Ethyl ester	31–33.4	199 ¹⁰	101		3012
Propyl ester			76.8; 97.7		
<i>Is</i> -propyl ester			69.9; 90.9 96.5		

Palmitoleic (9(Z)-Hexadecenoic); 16:1					
Methyl ester			51.0		2521
Oleic (9(Z)-Octadecenoic); 18:1	16	286 ¹⁰⁰	46.1		
Methyl ester	-20	218.520	55; 59.3	3.73 ⁱ ; 4.45	
Ethyl ester		216–2217 ¹⁵¹	53.9; 67.8	5.50 (25°) ^c	
Propyl ester			55.7; 58.8		
Iso-propyl ester			86.6		
Linoleic (9Z,12Z-Octadecadienoic); 18:2	-5	229–230 ¹⁶	31.4		
Methyl ester	-35	215 ²⁰	42.2; 38.2	3.05 ^c ; 3.654	2794
Ethyl ester		270–275 ¹⁸⁰	37.1; 39.6		
Propyl ester			40.6; 44.0		
Linolenic (9Z,12Z,15Z-Octadecatrienoic); 18:3	-11	230–232 ¹⁷	20.4		
Methyl ester	-57/–52	109 ^{0.018}	20.6; 22.7	2.65 ^c ; 3.27	2750
Ethyl ester		174 ^{2.5}	26.7		
Propyl ester			26.8		
Erucic (13Z-Docosenoic); 22:1	33–34	265 ¹⁵			
Methyl ester		22–222 ⁵		5.91 ^c ; 7.21 ⁱ	3454
Ethyl ester		229–230 ⁵			

^aMelting points (m.p.) and boiling points (b.p.) obtained from References 42 and 309. Superscripts denote pressure (mm HG) at which the boiling point was determined. Heats of combustion obtained from References 40 and 42. Cetane numbers obtained from References 28, 30, and 180. Number in parentheses indicates purity (%) of the material used in CN determinations in Reference 28. Kinematic viscosity values from Reference 310. Dynamic viscosity values from Reference 313.

^bThe numbers denote the number of carbons and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond.

^cDynamic viscosity values, see footnote a.

TABLE 4.2

Fuel-Related Physical Properties of Esters of Oils and Fats

Oil or fat; ester	Cetane number	HG high/low (kJ/kg)	Kinematic viscosity (mm ² /s)	Cloud point (°C)	Pour point (°C)	Flash point ^a (°C)	Reference
Coconut Ethyl	67.4	38158	3.08	5	−3	190	223
Corn Methyl	65	38480 (lower)	4.52	−3.4	−3	111	312
Cottonseed Methyl	51.2	—	6.8 (21°)	—	−4	110	313
Palm Ethyl	56.2	39070 (h)	4.50 (37.8°C)	8	6	—	314
Rapeseed (low-erucic; canola) Methyl	53.7	38850 (h/l)	4.96	CFPP: −6			315
Methyl	47.9	39870 (h)	4.76	−3	−9	166	314
Ethyl	67.4	40663	6.02	1	−12	170	223
Safflower Methyl	49.8	40060	—	—	−6	180/149	316

Soybean							
Methyl	49.6	39823/37372	4.18 (40°C)	−1.1	−3.9	190.6	317
Methyl	55.9	39753	4.27	1	0	185	223
<i>iso</i> -Propyl				−9	−12		218
Sunflower							
Methyl	58	38472	4.39	1.5	3	110	312
Tallow							
Methyl	61.8	39961/37531	4.99 (40°C)	15.6	12.8	187.8	317
<i>iso</i> -Propyl			7.10	8	0		220
Hydrogenated soybean							
Ethyl	65.1	40093	5.54	7	6	174	223
Yellow grease							
Methyl	62.6	39817/37144	5.16	—	—	—	318

^aSome flash points are very low. These may be typographical errors in the references or the materials may have contained residual alcohols.

^bDynamic viscosity.

combustion of fatty esters and triacylglycerols (40) as well as fatty alcohols (41) were determined and shown to be within the same range. Heats of combustion range from about 1,700 kg-cal/mole to about 3,500 kg-cal/mole for C_{12} – C_{22} FA and esters, increasing with chain length (40,42). For purposes of comparison, the literature value (42) for the heat of combustion of hexadecane (cetane), the high CN standard for conventional DF, is 2559.1 kg-cal/mole (at 20°C), which is in the same range.

Other important fuel properties are viscosity and those related to low temperatures. This is shown by the data in [Tables 4.1](#) and [4.2](#), which list the mp (and boiling points) of neat fatty compounds as well as the viscosities of neat fatty compounds and methyl esters of some oils and fats. The viscosity of vegetable oils is approximately one order of magnitude greater than that of conventional DF. The high viscosity with resulting poor atomization in the combustion chamber was identified early as a major cause of engine problems such as nozzle coking, deposits, etc. (9,40,43–46). Therefore, neat vegetable oils have been largely abandoned as alternative DF. However, as the data show, the viscosity of the alkyl esters is close to that of conventional DF. Accordingly, the ranges for kinematic viscosity in biodiesel standards are 1.9–6.0 mm²/s (ASTM D6751) and 3.5–5.0 mm²/s (EN 14214).

FA methyl esters have higher CP and PP than their parent oils and fats and conventional DF. This is important for engine operation in cooler environments. The CP is defined as the temperature at which the fuel becomes cloudy due to formation of crystals which can clog fuel filters and supply lines. The PP is the lowest temperature at which the fuel will flow. It is recommended by engine manufacturers that the CP be below the temperature of use and not more than 6°C above the PP. A more detailed discussion of low temperature of esters from vegetable oils and animal fats can be found below.

Numerous reports exist showing that fuel economies of certain biodiesel blends and conventional DF are virtually identical. In numerous on-the-road tests, primarily with urban bus fleets, vehicles running on blends of biodiesel with conventional DF (usually 80 vol% conventional DF and 20% biodiesel) required only about 2–5% more of the blended fuel than of the conventional fuel. No significant engine problems were reported.

The methyl and ethyl esters of soybean oil generally compared well with DF2 with the exception of gum formation which leads to problems with fuel filter plugging (45). Another study reports that methyl esters of rapeseed and high-linoleic safflower oils formed equal and lesser amounts of deposits than a DF standard while the methyl ester of high-oleic safflower oil formed more deposits (47). Soybean methyl and ethyl esters were evaluated by 200-h EMA (Engine Manufacturers Association) engine tests and compared to DF2. Engine performance with soybean esters differed little from that with DF. In that work, also a slight power loss was observed, together with an increase in fuel consumption due to the lower heating values of the esters. The emissions for the two fuels were sim-

ilar, with the exception of NO_x which are higher for the esters as discussed above. Engine wear and fuel-injection system tests showed no abnormal characteristics for any of the fuels. Although deposit amounts in the engine were comparable, the methyl ester showed greater varnish and carbon deposits on the pistons. Operating DI engines with neat soybean oil esters under certain conditions produced lubricating oil dilution which was not observed with an IDI engine (50).

Vegetable oil-based fuels possess inherent lubricity. This is significant because environmental concerns and resulting future regulations dictate the use of conventional DF with low sulfur levels. Conventional DF serves as its own lubricant within the fuel system. At low sulfur levels, that ability is lost. Even at low blend levels (additive levels, approximately ≤ 2 wt%), biodiesel could serve not only as a fuel component but as a lubricity-improving additive. Methyl soyate was a more effective lubricant than soybean oil at equal treatment rates but a soybean oil-based additive was even more effective (49). For the conventional DF with poorest inherent lubricity, 1% or slightly higher treatments rates with soybean oil were necessary to meet specifications.

Biodiesel is readily biodegradable, which contrasts with conventional DF. This was shown by the CO_2 evolution method in an aquatic system (50). Conventional DF degraded faster in the presence of biodiesel. Another advantage of esters from vegetable oils and animal fats as fuels is their higher flashpoint which makes them safer to handle and store than conventional DF.

Due to its solvent properties (see above), ester fuels are not compatible with some polymers used in fuel system components such as seals and gaskets of conventional DF. Accordingly, it has been reported that Teflon[®] and other fluoroelastomers are least affected by biodiesel and its blends with conventional DF while nitrile rubber, nylon 6/6 and high-density polypropylene showed less resistance (51). It was reported in the same study that copper-containing metals are severely corroded by biodiesel and its blends and also showed gum formation. Steel and aluminum did not show gum formation but caused high acid numbers which could cause corrosion. Storage stability is discussed below.

Biodiesel Standards

As mentioned above, some biodiesel standards have been established, including in the U.S. and Europe. While similar in many aspects, they also contain some notable differences as briefly discussed here and elsewhere in this chapter.

The iodine value (IV) has been included in the European standard and is based on rapeseed oil as biodiesel feedstock. The maximum IV in EN 14214 is 120, which would largely exclude soybean oil and some other common vegetable oils (neat vegetable oils and their methyl esters have nearly identical IV) as biodiesel feedstock. However, the use of the IV is not without problems (52), including the fact that it does not adequately reflect that a specific IV can arise from a nearly infinite number of FA profiles. Biodiesel from vegetable oils with high amounts of

saturates (low IV) will have a higher CN while the low-temperature properties are poor. Biodiesel from vegetable oils with high amounts of unsaturates (high IV) will have low CN while the low-temperature properties are better. Thus, CN and low-temperature properties run counter to each other and this must affect IV for biodiesel standards. The IV also does not take into consideration structural factors of fatty compounds as discussed above where the CN depend on double bond position, etc. It was suggested that it appears better to limit the amount of higher unsaturated FA (e.g., linolenic acid) than to limit the degree of unsaturation by means of the IV (53). In the standard EN 14214, the amount of linolenic acid is now limited to 12%, which may be difficult to reconcile with an IV limit of 120. Soybean oil, rapeseed oil, and canola oil (low-erucic rapeseed oil) have very similar 18:3 FA content, which is the most problematic in the formation of engine deposits through polymerization. However, linseed oil methyl ester (high 18:3 content and IV) satisfactorily completed 1000 h of testing in a DI engine while neat linseed oil caused the engine to fail (54). In a study on prepared ester fuels of medium to high iodine values, no significant differences in engine performance and deposits were observed and no limit for the IV could be given (55). EN 14214 calls for a maximum of 12% C18:3 in biodiesel, which would permit soybean oil as feedstock. A major difference therefore affecting feedstocks and their IV is the C18:2 content. Additionally, EN 14214 limits the amount of FA with ≥ 4 double bonds to 1%, which would mainly appear to affect biodiesel from animal sources (fish oils).

Since most esters have higher CN than neat vegetable oils and conventional DF, the esters could accommodate higher CN than the minimum of 40 given in the ASTM standard for conventional DF. For example, the lowest reported CN for methyl soyate is 46.2. The minimum CN in the European standard is higher.

The European biodiesel standard EN 14214 includes the cold-filter plugging point (CFPP) that pertains to the low-temperature flow properties of biodiesel. This low-temperature property test is used in Europe, South America, and the Pacific rim. Each European country can determine the limit for CFPP individually depending on the time of year. In North America, a more stringent test, the Low-Temperature Flow Test (LTFT), is used and specified by ASTM D4539. Although the LTFT is more useful in evaluating low-temperature flow properties, ASTM D6751 requires only specification of CP for certification without a limit being given in the standard due to varying climate conditions in the U.S.

Combustion and Emissions

Conventional DF and vegetable oil-derived fuels generate similar types of compounds in exhaust emissions. This is another indication of the suitability of fatty compounds as DF because there presumably exist similarities in their combustion behavior.

Emissions from any engine are the result of the preceding combustion within in the engine. The combustion process, in relation to the properties of the fuel, and its (in)completeness are responsible for any problems associated with the use of

any fuel, such as formation of deposits. Ideally, the products of complete combustion of hydrocarbons are CO_2 and water. Combustion in a diesel engine occurs mainly through a diffusion flame and thus is incomplete (56). This causes the formation of partially oxidized materials such as carbon monoxide (CO), other oxygenated species (aldehydes, etc.), and hydrocarbons.

In the case of biodiesel, liberation of CO_2 (decarboxylation), as discussed above, can occur besides combustion formation of CO_2 from the hydrocarbon portions of biodiesel. The formation of incombustible CO_2 shows that oxygenated compounds as combustion enhancers need to be chosen judiciously since the combustion-enhancing properties depend on the nature of the oxygen (bonding, etc.) in these compounds. Therefore, the higher oxygen content of biodiesel does not necessarily imply improved combustion compared to conventional DF as oxygen may be removed from the combustion process by decarboxylation. CO_2 , however, may contribute to combustion in other ways.

Exhaust emissions observed in the combustion of conventional DF and biodiesel are smoke, which is a mixture of fuel and lubricating oil particles in unburned, partially burned or cracked states (57), particulates [particulate matter (PM)], polyaromatic hydrocarbons (PAH), hydrocarbons, CO, and oxides of nitrogen (NO_x , also referred to as nitrous oxides, or nitrogen oxides). Sulfur-containing emissions are not formed from neat biodiesel due to its lack of sulfur. Rapeseed contains low amounts of sulfur but in variations such as canola, erucic acid and sulfur content are further reduced (58). The rapeseed oil mentioned in European publications on alternative fuels usually refers to canola-type oil.

The composition of particulate matter has been studied for conventional DF. Particulates are soot that has collected high molecular weight hydrocarbons (and sulfates in the case of conventional DF) (57,59). Thus, particulates from conventional DF have a high carbon to hydrogen ratio. Soot particles consist of spherules (somewhat spherical species) arranged in irregular clusters or chains (57). The size of particulates is of concern because smaller species (diameters less than 10 μm) can be inhaled deeply into the lungs. Therefore, the size distribution of particulate matter may be of greater significance than its mass.

PAH are compounds composed of fused aromatic rings that may carry alkyl substituents such as a methyl group. They are of concern because many of them are known carcinogens.

Hydrocarbons represent a broad category of compounds including hydrocarbons and oxygenated species such as aldehydes, ketones, ethers, etc. Although some of these emissions such as aldehydes are unregulated (not limited by legislation), many of these species such as formaldehyde are ozone precursors.

As precursors of ozone, which in turn is a major component of urban smog, NO_x exhaust emissions are of particular concern. Accordingly, both NO_x exhaust emissions and ozone in ambient air are subject to environmental regulations. NO_x species arise by the reaction of nitrogen and oxygen from air at an early stage in the combustion process (56,60). NO_x emissions are difficult to control because

such techniques may increase other emissions or fuel consumption. Soot can be reduced by higher injection pressures and higher air swirl levels but this enhanced combustion increases NO_x (59). The trade-off between particulates and NO_x as a result of changes in engine design or operational parameters is a general problem (59).

Neat vegetable oils give satisfactory engine performance and power output, often equal to or even slightly better than conventional DF. However, vegetable oils cause engine problems. This was recognized in the early stages of renewed interest in vegetable oil-based alternative DF. Studies on sunflower oil as fuel noted coking of injector nozzles, sticking piston rings, crankcase oil dilution, lubricating oil contamination, and other problems (9,44). These problems were confirmed and studied by other authors (61–68). A test for external detection of coking tendencies of vegetable oils was reported (69). The causes of these problems were attributed to the polymerization of TG *via* their double bonds which leads to formation of engine deposits as well as low volatility and high viscosity with resulting poor atomization patterns. For blends of vegetable oils and conventional DF, it was postulated that carbon buildup was a result of a polymerization growth process on preferred metallic surfaces (70). The engine problems have caused neat vegetable oils to be largely abandoned as alternative DF and have led to the research on the aforementioned four solutions (2).

The Transesterification Process

Several reviews on transesterification are available (71–74). The most commonly prepared esters are methyl esters, which is largely a result of methanol being the least expensive alcohol.

Alkali catalysis (sodium or potassium hydroxide or alkoxides) is a much more rapid process than acid catalysis in the transesterification reaction (75–77). For the transesterification to give maximum yield, the alcohol should be free of moisture and the free FA content of the vegetable should be less than 0.5% (76). At 32°C, transesterification was 99% complete in 4 h when using an alkaline catalyst (NaOH or NaOMe). At 60°C and an alcohol:oil molar ratio of at least 6:1 and with fully refined oils, the reaction was complete in 1 h to give methyl, ethyl, or butyl esters. The reaction parameters investigated were molar ratio of alcohol to vegetable oil, type of catalyst (alkaline vs. acidic), temperature, reaction time, degree of refinement of the vegetable oil, and effect of the presence of moisture and free FA. Although the crude oils could be transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils.

Another paper reports on the use of both NaOH and KOH in the transesterification of rapeseed oil (78). Recent work on producing biodiesel from waste frying oils employed KOH. With the reaction conducted at ambient pressure and temperature, conversion rates of 80 to 90% were achieved within 5 min, even when stoichiometric amounts of methanol were employed (79). In two steps, the ester yields

are 99%. It was concluded that even a free FA content of up to 3% in the feedstock did not affect the process negatively and phosphatides up to 300 ppm phosphorus were acceptable. The product met the quality requirements for Austrian and European biodiesel without further treatment. In a study similar to previous work on the transesterification of soybean oil (75–76), it was concluded that KOH is preferable to NaOH in the transesterification of safflower oil of Turkish origin (80). The optimal conditions were given as 1 wt% KOH at $69 \pm 1^\circ\text{C}$ with a 7:1 alcohol:vegetable oil molar ratio to give 97.7% methyl ester yield in 18 min.

Transesterification is a reversible reaction. The transesterification of soybean oil with methanol or 1-butanol was reported to proceed with pseudo-first-order or second-order kinetics, depending on the molar ratio of alcohol to soybean oil (30:1 pseudo-first order, 6:1 second order; NaOBu catalyst) while the reverse reaction was second order (81). The methanolysis of sunflower oil at a molar ratio of methanol:sunflower oil = 3:1 was reported to begin with second-order kinetics but then the rate decreased to formation of glycerol (82). The originally reported kinetics (81) were reinvestigated (82–85) and differences were found. A shunt reaction originally proposed (81) as part of the forward reaction was shown to be unlikely, that second-order kinetics are not followed and that miscibility phenomena play a significant role (82–85). The addition of co-solvents such as tetrahydrofuran (THF) or methyl *tert*-butyl ether (MTBE) to the methanolysis reaction was reported to accelerate the methanolysis of vegetable oils as a result of solubilizing methanol in the oil and to a rate comparable to that of the faster butanolysis (83,85). Other possibilities for accelerating the transesterification appear to be microwave (86) and ultrasonic (87) irradiation. Factorial experiment design and surface response methodology have been applied to different production systems (88). A continuous pilot plant-scale process for producing methyl esters with conversion rates greater than 98% was reported (84) as well as a discontinuous two-stage process with a total methanol:acyl ratio of 4:3 (89). The kinetics of noncatalyzed alcoholysis of soybean oil were also investigated (90).

The transesterification of beef tallow was studied with regard to effects of mixing (91), catalyst, free FA and water as well as solubilities of different alcohols in the fat (92). Water had the greatest undesirable effect (93).

With increasing emphasis on utilizing low-cost sources of biodiesel, the question of the quality of these sources is of utmost importance. The low-cost sources such as restaurant greases and soapstock are of lower quality than refined vegetable oils. A major problem associated with them is the high content of free FA, which, as indicated above, the feedstock should contain a minimum of. Thus the processing of high-free FA feedstocks requires some changes to the overall production process. A two-step alkali-catalyzed transesterification was reported for high-free FA feedstocks (94). Pretreatment of the free FA by acid-catalyzed esterification prior to converting the triacylglycerols by alkali-catalyzed transesterification is an effective method for producing biodiesel from high-free FA feedstocks (95). A pilot plant based on this process was described (96). For the production of

biodiesel from soapstock, all ester bonds were hydrolyzed by alkali catalysis and the resulting FA sodium salts converted to methyl esters by acid catalysis (97). This procedure was also taken to the small pilot scale (98). Relatedly, acid oil was converted to biodiesel (99). More aspects are given below.

Other Transesterification Processes

Besides the methods discussed here, other catalysts have been applied in transesterification reactions (100). Some recently studied variations of the above methods as applied to biodiesel preparation are briefly discussed here.

Enzymatic transesterification methods are receiving attention for producing esters suitable as biodiesel. Advantages of enzymatic reactions can be specificity, mild reaction conditions, reduced product isolation problems and reduced waste (101), although they are more expensive. Lipases from *Pseudomonas fluorescens* as well as two immobilized enzymes from *Mucor miehei* and a *Candida* sp. with petroleum ether as solvent yielded methyl and ethyl esters of sunflower oil (102). The lipase from *Mucor miehei* was most efficient in yielding esters of primary alcohols while the lipase from *Candida antarctica* was most efficient for yielding branched esters from secondary alcohols (103). Some other reports on enzymatic production of esters mainly for fuel purposes include ethanolysis of sunflower oil with a solvent-free, immobilized 1,3-specific *Mucor miehei* lipase (104); a variety of enzymes used for producing different materials (105) with dependence on the presence of solvent (106) as well as stepwise addition of methanol (106,107); the synthesis of esters of restaurant greases (108–110); stepwise use of immobilized *Candida antarctica* lipase (111) modified later for continuous use (112), methyl acetate as an acyl acceptor (113); use of *Rhizopus oryzae* lipase in a water-containing system without an organic solvent (114); and in the methanolysis of vegetable oils contained in waste activated bleaching earth (115).

Supercritical technology has also been employed for transesterification (116–119). Alkylguanidines attached to modified polystyrene or siliceous MCM-41, encapsulated in the supercages of zeolite Y or entrapped in SiO₂ sol-gel matrices were used as transesterification catalysts (120).

Various alkaline-earth metal compounds such as calcium oxide, calcium methoxide and barium hydroxide were used as heterogeneous catalysts for producing rapeseed oil methyl esters (121) as was calcium carbonate (122). Diorganotin (IV) compounds were studied as catalysts for the methanolysis of tripalmitin (123).

Methyl and ethyl esters of palm and coconut oils were produced by alcoholysis of raw or refined oils using boiler ashes, H₂SO₄ and KOH as catalysts (124). Fuel yields >90% were obtained using alcohols with low moisture content and EtOH-H₂O azeotrope.

One-step *in situ* processes in which the alcohol acts as extraction solvent for the oil-containing material and as esterifying reagent have been reported. Sunflower seed oils were transesterified *in situ* using macerated seeds with methanol in the pres-

ence of H_2SO_4 (125). Higher yields were reported than from transesterification of the extracted oils although seed moisture reduced the yield of methyl esters. The CP of the *in situ* prepared esters appeared slightly lower than those prepared by conventional methods. In a related study, best yields were achieved with a 300:1 molar ratio methanol: oil (126). Similarly, macerated soybeans were treated with methanol, ethanol, *n*-propanol and *n*-butanol to give the corresponding esters (127), although due to the insolubility of soybean oil in methanol, conversion was low in that case.

The synthesis of methyl or ethyl esters with 90% yield by reacting palm and coconut oil from the press cake and oil mill and refinery waste with methanol or ethanol in the presence of easily available catalysts such as ashes of the waste of these two oilseeds (fibers, shell, and husk), lime, zeolites, etc., was reported (128). Similarly, the methanolysis of vegetable oils was catalyzed by ashes from the combustion of plant wastes such as coconut shells or fibers of a palm tree that contain K_2CO_3 or Na_2CO_3 as catalyst (129). Thus the methanolysis of palm oil by refluxing 2 h with MeOH in the presence of coconut shell ash gave 96–98% methyl esters containing only 0.8–1.0% soap. The ethanolysis of vegetable oils over the readily accessible ash catalysts gave lower yields and less pure esters than the methanolysis.

Several catalysts (CaO , K_2CO_3 , Na_2CO_3 , Fe_2O_3 , NaOMe , NaAlO_2 , Zn , Cu , Sn , Pb , ZnO , and an anion exchange resin) were tested for catalytic activity in the reaction of low-erucic rapeseed oil with MeOH (130). The best catalyst was CaO on MgO . At 200°C and 68 atm, the anion exchange resin produced substantial amounts of fatty methyl esters and straight-chain hydrocarbons.

The transesterification reaction is also the subject of numerous patents. A transesterification process permitting the recovery of all by-products such as glycerol and FA has been described (131). Some patent procedures were briefly reviewed (132). The procedures used in the proprietary literature generally resemble those published in journals.

Analysis of Transesterification Products

Potential contaminants of biodiesel include unreacted triacylglycerides; residual alcohol and catalyst may be present as well as intermediate mono- and diacylglycerides and glycerol co-product. Various methods have been investigated for analyzing biodiesel accordingly (133).

Glycerol mixtures were analyzed by TLC-FID (thin-layer chromatography/flame ionization detection) (134), which was also used in the studies on the variables affecting the yields of fatty esters from transesterified vegetable oils (76). The TLC-FID method has been abandoned (134–135). Gas chromatography (GC) is the most commonly used method for detailed analysis of transesterification and biodiesel. Analysis of reaction mixtures by capillary GC determining esters, mono-, di- and triacylglycerols was carried out in one run (136). Free glycerol was deter-

mined in transesterified vegetable oils (137–138). Besides analyzing esters for sterols (139–141), which are often minor components in vegetable oils, and different glycerides (142–143), the previous GC method (136) was extended to include analysis of glycerol (144). In both papers (136,144), the hydroxy groups were derivatized by silylation with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide. The GC method simultaneously analyzing for glycerol, methyl esters, and the various acylglycerols (144) forms the basis of standards such as ASTM D6584 and EN 14105. Simultaneous analysis of methanol and glycerol was also described (145) as was a sole determination of methanol (146). Flame-ionization detectors (FID) were usually employed although use of a mass selective detector was reported (138,145).

Other authors, using GC to determine the conversion of TG to methyl esters, gave a correlation between the bound glycerol content determined by TLC/FID and the acyl conversion determined by GC (135). Glycerol was also analyzed by high-performance liquid chromatography (HPLC) using pulsed amperometric detection, which offers the advantage of higher sensitivity compared to refractometry and being suitable for detection of small amounts for which GC may not be suitable (147). An enzymatic method for glycerol analysis was reported (148). An enzyme-based analysis method for glycerol is now commercially available (149).

Several other studies have been performed using HPLC analyses. The first HPLC-related report (150) used density detection to analyze for the various glycerides and methyl esters as classes of compounds in order to determine the conversion of transesterification reactions. An evaporative light scattering detector (ELSD) was employed for analyzing the product, glycerides, and free FA from an enzymatic transesterification (151). Atmospheric pressure chemical ionization mass spectrometry was more suitable as a detection method for reversed-phase HPLC than ELSD and UV (152). Several LC-GC methods were also reported including methods for analyzing for sterols (140,141,153). High-performance size exclusion chromatography was applied in the ethanolysis of rapeseed oil (154) or methanolysis of palm oil (155). Other analyses include the determination of biodiesel in conventional DF by silica cartridge chromatography (156).

Spectroscopic methods applied to the analysis of transesterification and biodiesel are nuclear magnetic resonance (NMR) and near-infrared (NIR) spectroscopies. In ^1H -NMR spectrometry, the protons of the methylene group adjacent to the ester moiety in triacylglycerols and the protons in the alcohol moiety of the methyl esters were used to monitor the methanolysis of rapeseed oil (157). For determining conversion and kinetics by ^{13}C -NMR, the unchanging signal of the terminal CH_3 groups as well as the signals of the glyceridic moieties in the triacylglycerols (158) were used. NIR peaks at 4428 cm^{-1} and especially 6005 cm^{-1} which distinguish methyl esters and triacylglycerols can be used for monitoring transesterification and assessing biodiesel fuel quality by an inductive method (159). The use of a fiber-optic probe for acquiring the spectra renders the method rapid and easy. NIR and ^1H -NMR results can be correlated (160).

Viscosity was used for determining the methyl ester content based on a transesterification mixture (161). The results agreed well with GC. The method is reportedly more rapid than GC and therefore especially suitable for process control.

IR spectroscopy (carbonyl absorption at 1750 cm^{-1}) with (162) and without (163) a fiber-optic probe was used to assess the amount of biodiesel in lubricating oil. The problem is important because biodiesel can cause dilution of lubricating oil, ultimately resulting in engine failure.

With the increased use of biodiesel blends, the determination of blend levels of biodiesel has recently received more attention. Methods that have been employed include NIR and NMR spectroscopy (164), ester number (165), IR spectroscopy (165) and silica cartridge chromatography (166). A European standard, EN 14078, utilizing the carbonyl absorption in the IR range is being developed. An interesting problem involves the in-vehicle detection of biodiesel blends in order to adjust relevant engine functions to the blend level. For this purpose, sensors have been developed (167,168).

Emissions from Ester Fuels (Biodiesel)

Generally, most exhaust emissions observed when using conventional DF are reduced when using biodiesel. NO_x emissions, however, are an exception. In an early paper reporting emissions with methyl and ethyl soyate as fuel (45), it was found that CO and hydrocarbons were reduced but NO_x emissions were produced consistently at a higher level than with the conventional DF. The differences in exhaust gas temperatures corresponded with the differences in NO_x levels. Similar results were obtained from a study on the emissions of rapeseed oil methyl ester (169). NO_x emissions were slightly increased, while hydrocarbon, CO, particulate and PAH emissions were in ranges similar to the DF reference. Alkyl esters emitted less aldehydes than the corresponding neat rapeseed oil. Unrefined rapeseed oil methyl ester emitted slightly more aldehydes than the refined ester, while the opposite held for PAH emissions. A 31% increase in aldehyde and ketone emissions was reported when using rapeseed oil methyl ester as fuel, mainly due to increased acrolein and formaldehyde, while hydrocarbons and PAH were significantly reduced, NO_x increased slightly, and CO was nearly unchanged (170). Another study on agricultural tractors found that aldehydes increased by 20% with CO and NO_x similar to those from conventional DF (171). The general trend on reduced emissions except NO_x was confirmed by later studies (172), although some studies report little changes in NO_x (173,174). Little differences compared to conventional DF were also reported for formaldehyde emissions when using soy methyl ester (174). It was suggested that the average slight rise in NO_x exhaust emissions when using biodiesel can be at least partially traced to isentropic bulk modulus and speed of sound of fatty esters, which are higher than for conventional DF (175). This means that the fuel is less compressible (due to the larger mole-

cules) which in turn causes early injection timing leading to higher combustion temperatures and pressures responsible for the rise in NO_x exhaust emissions. High temperatures are known to increase the formation of NO_x in fuel combustion (60). However, the structure of the FA chains was found to have a significant impact on emissions. Increasing the number of double bonds increased NO_x exhaust emissions (176). This could not be explained by the known trade-off between NO_x and particulate emissions, also indicating that NO_x formation when using biodiesel is not driven thermally. Particulate emissions were essentially constant if $\text{CN} > 45$ and density < 0.89 (176). NO_x exhaust emissions can be reduced by retarded injection timing (177) and comparing at the same start of combustion led to lower NO_x exhaust emissions than from conventional DF.

Various compounds such as alkyl nitrates and peroxides are used as cetane-enhancing additives in conventional DF (27). NO_x exhaust emissions reportedly are lowered by increasing the CN of conventional DF (178). Thus, an approach utilizing cetane improvers with biodiesel to lower NO_x exhaust emissions appears feasible. It was reported (179) that in a turbulence combustion chamber and at an intake air temperature of 105°C , 8% hexyl nitrate in vegetable oils (cottonseed, rape, palm) was necessary to exhibit the same ignition delay as conventional DF. Recently, some oxygenated compounds were identified as cetane improvers for fatty esters (180) which apparently had selective effects on fatty compounds depending on the kind of alkyl ester and nature of the FA chain. This may offer the possibility of tailoring the cetane improver to the predominant fatty compound in a specific biodiesel fuel. In a comparative study (181) of exhaust emissions at various injection timings of conventional DF, B20, B20 with a peroxide cetane improver and other DF, it was observed that retarded timing reduced NO_x and increased particulate matter for all settings. The fuel blend with cetane improver had the lowest PM emissions of all fuels. NO_x emissions for the additized blend were slightly lower than for the unadditized blend. Furthermore, cetane improvers derived from fatty compounds have been reported (182–185).

A study on PAH emissions (186), in which the influence of various engine parameters was also explored, found that these emissions from sunflower ethyl ester were situated between DF and the corresponding neat vegetable oil. Reduced PAH emissions may correlate with the reduced carcinogenicity of particulates when using rapeseed methyl ester as fuel (187). With the same ester fuel in DI engines, particulate matter showed large amounts of volatile and extractable compounds adsorbed on the soot, which caused the PM emissions to be higher than with conventional DF, although the soot itself was reduced (171). While total particulate matter was lower for methyl soyate than for conventional DF, an oxidation catalytic converter (OCC) reduced those emissions by 50–80% (188). Greater reductions in mutagenicity were observed for the biodiesel fuel when using the OCC. Other authors (189) reported similar results when using a catalytic converter. However, conflicting results were obtained when using a ceramic trap. These and additional authors (190) also found that exhaust emissions from biodiesel fuel,

both rapeseed and soybean oil methyl esters, had reduced environmental impact and mutagenicity compared to conventional DF. Emissions from low-sulfur conventional DF was also reported to be in the range of those from biodiesel, thus high sulfur content as well as high engine speeds and loads were associated with increased mutagenicity of diesel exhaust particles (190). In another study (191), the emitted mass of PM from rapeseed methyl ester fuel was higher compared to that from conventional DF but mutagenicity again was reduced. In the U.S., biodiesel is the only alternative fuel that has completed Tier 2 Health Effects Testing required by the Clean Air Act Amendments of 1990 (192).

In a DI engine, sunflower methyl ester produced equal hydrocarbon emissions but less smoke than a 75:25 blend of sunflower oil with DF (193). A diesel oxidation catalyst (DOC) in conjunction with soy methyl ester was reported to be a possible emissions reduction technology for underground mines (194). Soy methyl esters reportedly were more sensitive toward changes in engine parameters than conventional DF (195).

Precombustion phase studies of methyl, ethyl, *n*-propyl, and *n*-butyl fatty esters in a reactor simulating conditions in a diesel engine showed that various species such as branched and straight-chain alkanes, alkenes, cyclic hydrocarbons, aldehydes, ketones, esters, substituted benzenes as well as other compounds can arise at this stage (196). Aromatic compounds, which possess low CN, were observed more frequently for unsaturated fatty compounds. This observation may constitute a possible partial explanation for the differing CN of fatty compounds and may correlate with emissions studies.

Cold Flow Properties

All DF are susceptible to start-up and operability problems when subjected to cold temperatures. As ambient temperature decreases below saturation temperature(s) of high-molecular weight paraffins (C_{18} – C_{30} *n*-alkanes) present in conventional DF, these paraffins nucleate to form crystals suspended in a liquid phase composed of shorter-chain *n*-alkanes and aromatics (197–201). Leaving the fuel unattended in cold temperatures overnight can cause start-up and operability problems the next morning.

The tendency of DF to solidify at low temperatures may be quantified by the following parameters: CP, PP, cold filter plugging point (CFPP) and low temperature flow test (LTFT). The CP is defined as the temperature where crystalline growth becomes visible in the form of a hazy or cloudy suspension of small solid crystals ~ 0.5 μm in diameter (197,198,202–204). As temperatures decrease below the CP larger crystals interlock and form agglomerates that restrict or cut off flow through fuel lines and filters (197,198,200,201,204–209). The temperature where sufficient agglomeration prevents free pouring of fluid is determined by measuring PP (199,202–204). In terms of predicting tendency of crystals to cause start-up or operability problems after cooling overnight, the CP tends to be over-cautious and

the PP tends to be over-optimistic (197,199,205). Therefore, low temperature filterability tests (CFPP and LTFT) were developed based on results from cold weather operability field studies (197,199,201,205,207–210). Both parameters are measured by cooling a sample under controlled conditions then drawing a specified volume through a wire mesh filter screen within 60 sec. Conditions for measuring CFPP are volume = 20 mL, vacuum force = 0.0194 atm and mesh size = 45 μm . Corresponding conditions for LTFT are 180 mL, 0.197 atm and 17 μm (197, 199,202,203,211). The CFPP serves as the standard low temperature operability parameter for most of the world while the more stringent and less user-friendly LTFT is the standard for North America.

Thermal analytical methods such as sub-ambient differential scanning calorimetry (DSC) have also been applied in analysis of conventional DF (206,212–216). DSC has advantages including relatively small sample sizes (<20 mg) and applicability to samples that are solid at room temperature. Most importantly, cold flow properties may be directly correlated to crystallization onset temperature (TCO) and mp.

Biodiesel made from feedstocks containing larger amounts of high-mp long-chain saturated FA tends to have relatively poor cold flow properties (see [Tables 4.1 and 4.2](#)). For example, tallow contains 23.7–27.6 wt% palmitic acid (C_{16}) and 18.4–25.0 % stearic acid (C_{18}) (217,218), compounds whose corresponding methyl esters have mp = 30 and 39.1°C, respectively (219). As a consequence, tallow methyl esters have a relatively high CP (15–17°C) (220). In contrast, feedstocks with relatively low concentrations of saturated long-chain FA generally yield biodiesel with much lower CP and PP. Thus, linseed, olive, rapeseed, safflower and soybean oils are examples whose biodiesel product has CP near or below 0°C (47,80,221–223). Nevertheless, comparison with No. 2 conventional DF (CP = –16°C; PP = –27°C (224) suggests that biodiesel from most common feedstocks will have less reliable operability during cold weather.

Previous studies (224–226) reported a nearly linear correlation between low-temperature filterability (CFPP and LTFT) and CP of soybean oil methyl esters and its blends with conventional DF. Results showed that a 1°C decrease in CP reduced CFPP or LTFT by 1°C (224). This work concluded that efforts to improve cold flow properties of biodiesel should emphasize development of approaches that significantly decrease CP. This conclusion was applicable to neat biodiesel and its blends with conventional DF and was later reported to apply to blends treated with commercial DF cold flow improver additives (226).

Analyses of methyl esters of soybean oil, tallow, admixtures thereof and winterized soybean oil methyl esters showed that CP, PP and other cold flow properties could be accurately correlated to parameters inferred from sub-ambient DSC analyses (227). The temperature of maximal heat flow for freezing peaks yielded the most accurate correlations with respect to CP, PP and CFPP; LTFT was most accurately correlated to freezing point. Onset temperature (TCO) yielded good correlations for predicting PP, CFPP and LTFT. Although parameters from analysis of

cooling curves were found to be more reliable than those from heating curves, other studies (217,218,228) successfully correlated CP of the soybean oil, tallow and waste grease alkyl esters to results from analysis of DSC heating curves.

Approaches investigated or under investigation to address improvement of cold flow properties of biodiesel include the following: blending with conventional DF, cold flow improver additives, branched-chain esters and fractionation/winterization. Blending of esters is the simplest method for improving cold flow operability and will be discussed in the next section.

Studies of commercial DF cold flow improver additives as modifiers for biodiesel revealed these additives were very effective in reducing PP and CFPP (225,226,229–232). These additives depressed PP by up to 18°C for 20 vol% blends of soybean oil methyl esters in No. 2 conventional DF (226). Increasing additive loading (concentration) resulted in nearly linear reductions in PP, though some additives were more effective than others (225,226). These results demonstrated that additives may be used to ease biodiesel pumping operations during cooler weather. Some additives depressed CFPP, demonstrating they had greater selectivity for modifying wax crystallization of biodiesel than simple PP depressants (197,199–201,207,208,233,234). None of the additives demonstrated sufficient selectivity to significantly affect nucleation in neat or blended biodiesel, resulting in little effect on CP or LTFT (224–226). Thus, additives designed primarily to modify wax crystallization in conventional DF also demonstrated some degree of selectivity for modifying crystal nucleation mechanisms prevalent in biodiesel.

The use of fatty compound-derived materials with bulky moieties in the chain at additive levels is another approach (235). The background is that the bulky moieties would destroy the harmony of the solids which are usually oriented in one direction. However, these materials had only slight influence on the CP and PP. Efforts to employ glycerol yielded as co-product from biodiesel production in synthesis of agents that effectively improve cold flow properties of biodiesel were also studied (236). Glycerol ether derivatives from reaction with isobutylene or isoamylene in the presence of strong acid catalyst were shown to improve cold flow properties of in blends with biodiesel.

Transesterification of oils or fats with medium chain-length (C_3 – C_8) or branched-chain alkyl alcohols is known to improve the cold flow properties of biodiesel. Large or bulky headgroups disrupt spacing between individual molecules in the crystal lamellae causing rotational disorder in the hydrocarbon tailgroup chains, resulting in formation of crystal nuclei with less stable chain packing. Transition to a more stable form eventuates at lower temperatures (237).

Comparison of data in [Table 4.1](#) illustrates many examples of the effects of chain-length and branching in the alkyl moiety of the ester “headgroup” on the melting properties of esters. Consistent with the first part of this comparison, biodiesel made from canola, linseed and soybean oil shows decreases in both CP and PP with increasing alkyl chain-length from methyl to *n*-butyl (220,222,224,238). Similar

decreases in CFPP and LTFT for tallow alkyl esters were also reported (220). Consistent with the second part of the comparison of data in [Table 4.1](#), biodiesel made from soybean oil showed decreases in TCO (measured by DSC) of 7–11°C for isopropyl esters and 12–14°C for 2-butyl esters relative to methyl esters (218). Other studies (224,239) showed significant decreases in CP and PP for branched-chain alkyl esters of soybean oil. Although decreases in CP and PP were reported for isopropyl and isobutyl esters of tallow, CFPP and LTFT only decreased slightly (220).

Crystallization fractionation is the separation of components of fatty derivatives based on differences in MP (240–247). The physical nature of biodiesel suggests that this technique may be a useful for improving cold flow properties by reducing total concentration of high-mp saturated esters. Traditional crystallization fractionation features two process stages—nucleation and crystalline growth under carefully controlled conditions followed by separation of fractions by filtration or centrifugation. Cooling rate and agitation in the crystallizer must be controlled to reduce the rate of entrainment of liquid inside crystal agglomerates (240–245, 247,248). Efficient separation of solid from low-mp unsaturated esters (liquid) yields fractions with significantly altered physical properties (242–244).

Dry fractionation, sometimes referred to as winterization, is the simplest and least costly technique for separating high- and low-mp fatty derivatives (240–244). Bench-scale dry fractionation studies on soybean oil methyl esters indicated that CP and PP may be decreased to –16°C, a temperature close to LTFT of No. 2 conventional DF (226,228). Although fractionation reduced total concentration of saturated methyl ester (C_{16} and C_{18}) to <6 wt%, yields of liquid fractions were very low at only 25–30% relative to starting material. Cooling times were typically overnight (~16 h) and multiple crystallization steps were necessary to significantly impact CP. Similar fractionation of tallow methyl esters (IV = 41; CP = 11°C) resulted in yields of 60–65% liquid fraction characterized by IV = 60 and CP = –1°C (244). Fractionation of waste cooling oil methyl esters was reported to decrease CFPP by 2–4°C (249). Addition of commercial DF cold flow improver additives improved separation efficiency of to 80–87% liquid fraction but still required multiple crystallization steps to reduce CP to –10°C (250).

Solvent fractionation was also applied to separation of alkyl esters. Soybean oil methyl esters have been successfully fractionated from acetone, isopropanol and hexane solvents. In isopropanol, one 5-h crystallization step at –15°C was necessary to reduce CP to –8°C (250). Liquid fraction yields were in the range improved to 77–86% (226,250). Other solvents that have been applied to partial separation of alkyl esters include methanol, Skellysolve B and ether (246).

Trace contaminants of biodiesel as they could remain after refining and transesterification affected the cold flow properties of methyl soyate and blends thereof with No. 1 conventional DF (251). Mono- and diglycerides did not influence the PP of the esters, but the CP increased with increasing amounts of saturated mono- or diglycerides. Even low concentrations of 0.1 wt% saturated mono- or diglycerides raised the CP. Monoolein did not affect CP and PP. Unsaponifiable material

at concentrations as low as 3% raised the T_{CO} , CP and PP of soybean oil methyl esters but had virtually no effect on a 20% blend in No. 1 conventional DF.

Storage Stability

In terms of handling and storage safety, biodiesel compares favorably with conventional DF. The reason is the significantly higher flashpoint of vegetable oils and their methyl esters. However, due to the content of unsaturated fatty compounds, storage stability can be an issue when using biodiesel. The more conjugated or methylene-interrupted double bonds in a fatty molecule, the more susceptible the material is to oxidation and degradation.

Generally, storage stability is defined by the relative resistance of liquid fuels to physical and chemical changes resulting from interaction with the environment (202). 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 that depend 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 can also influence stability (252).

Degradation in fuel properties during long-term storage occurs primarily by the following mechanisms: (i) oxidation (autooxidation) from contact with air; (ii) thermal or thermal-oxidative decomposition from excess heat; (iii) hydrolysis from contact with water or moisture in tanks and fuel lines; and (iv) microbial contamination from the migration of dust particles or water droplets containing bacteria or fungi into the fuel (202,252). A book on oxidation of fatty compounds has been published (253).

Numerous studies usually relating to the first two aforementioned mechanisms have been carried out regarding stability of biodiesel (254–272). Summarily, these studies have shown that storage stability of biodiesel is affected by factors such as presence of air, heat, traces of metal (including influence of metal storage containers), peroxides, light, structural features of the compounds themselves as well as degree of refining. High temperature, presence of light, presence of air and presence of metals, copper being especially effective (257), usually accelerate oxidation of fatty compounds and their ultimate degradation. Antioxidants such as tocopherols (which occur naturally in vegetable oils), TBHQ (*tert*-butyl hydroquinone), BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), pyrogallol and propyl gallate were investigated and shown to often have beneficial effects of increasing storage stability. Methods that were used for investigating storage stability include peroxide value, acid value, viscometry, oxidative stability index (OSI) which is closely related to the Rancimat, and other procedures. Acid value and viscosity were shown to be especially appropriate methods (258). Methods such as ASTM D2274 for testing the oxidative stability of conventional DF were found to be inappropriate for biodiesel (265). Sometimes contradictory results are reported, also in regard to the effectiveness of specific additives affecting oxida-

tion. They may be due to different reaction conditions and other parameters, including feedstock quality, employed by different researchers.

An oxidative stability parameter has not been included in the ASTM standard D6751. Several properties in the European standards EN 14214 and EN 14213 are a result of concerns regarding oxidative stability. In the years 1998–2002, the BIOSTAB project in Europe involving research groups in several countries carried out related experiments. Some results were summarized in several publications (254–256,261). In the standards EN 14213 and EN 14214, a parameter on oxidative stability was added as a result. This parameter prescribes the use of the standard EN 14112 (Rancimat) for determining the oxidative stability. At 110°C, the minimum induction time for biodiesel as transportation fuel (EN 14214) is prescribed as 6 h and for heating purposes the time is 4 h.

Other studies (257–258,260) evaluated oxidation induction periods by running OSI analyses in accordance with standard methods such as AOCS Cd 12b-92 modified for lower temperatures. Milder reaction conditions were necessary because many biodiesel samples contained high concentrations of more readily oxidizable polyunsaturated FA esters.

Thermal analytical techniques such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been applied in the analysis of oxidation of petroleum-based and synthetic lubricants (273–279). These studies generally showed that DSC analysis under pressure (P-DSC) increases the total number of moles of oxygen present in the cell accelerating oxidation at lower temperatures. Cross (280) and Hassel (281) were among the first to apply DSC and P-DSC in analysis of edible fats and oils. Results from these studies together with later work (282) showed good correlations between isothermal induction periods measured by P-DSC (in minutes) and OSI (in hours or days).

Perhaps the first study to examine oxidation of FA methyl esters was performed by Raemy *et al.* (283). Results from that study showed that increasing temperature or degree of unsaturation decreased induction period as measured by conventional DSC. Results showed a direct correlation with those from the Rancimat test, with respect to 6–12% variation. P-DSC analysis was also identified as an efficient means for screening the activity of antioxidants with respect to type and concentration in biodiesel (284).

Although most of the DSC and P-DSC studies cited above featured isothermal analysis of oxidation induction period, non-isothermal (heat-ramping) thermal analyses may provide a more rapid means for evaluating resistance to oxidation. Several studies have reported on the use of non-isothermal DSC and P-DSC in analysis of fatty derivatives. With respect to biodiesel, Litwinienko and co-workers (285–287) studied oxidation kinetics of unsaturated C₁₈ FA and their ethyl esters. Non-isothermal DSC and P-DSC analyses were applied in screening phenolic antioxidants in methyl soyate (259) and linolenic acid (288). Finally, induction period results showed a good correlation between non-isothermal P-DSC scans and those from analysis of OSI (259).

Other parameters that can be seen as relating to oxidative stability include content of FA ≥ 3 double bonds limited to 1% in both EN 14213 or EN 14214. Contained only in EN 14214 and not in EN 14213 is a provision that linolenic acid be limited to a maximum of 12%. The IV is limited in EN 14213 to a maximum of 130 and in EN 14214 to a maximum of 120. However, structure indices termed “*bis*-allylic position equivalents” and “allylic position equivalents” probably better reflect the tendency of a fatty compound to oxidize than the iodine value (257, 289).

Blending of Esters

The most common application of esters (usually methyl esters; “biodiesel”) of vegetable oil in the U.S. is blends of conventional DF with these esters. The most common ratio is 80% vol% conventional DF and 20% vegetable oil ester (also termed “B20,” indicating the 20% level of biodiesel). There have been numerous reports that significant emission reductions are achieved with these blends. Methyl soyate can also be blended with jet fuels JP-5 and JP-8 (290). Winterization or use of additives improves the low-temperature properties of those blends.

No engine problems were reported in larger-scale tests with, for example, urban bus fleets running on B20. Fuel economy was comparable to DF2, with the consumption of biodiesel blend being only 2–5% higher than that of conventional DF. Another advantage of biodiesel blends is the simplicity of fuel preparation which only requires mixing of the components. Ester blends were reported to be stable. For example, a blend of 20 vol% peanut oil with 80% DF did not separate at room temperature over a period of 3 mon (291).

A few examples from the literature demonstrate the suitability of blends of esters with conventional DF in terms of fuel properties. In transient emission tests on an IDI engine for mining applications (194), the soybean methyl ester used had a CN of 54.7, viscosity 3.05 mm²/s at 40°C, and a CP of –2°C. The DF2 used had CN 43.2, viscosity 2.37 mm²/s at 40°C and a CP of –21°C. A 70: 30 DF2: soybean methyl ester blend had CN 49.1, viscosity 2.84 mm²/s at 40°C, and a CP of –17°C. The blend had 4% less power and 4% higher fuel consumption than the DF2, while the neat esters had 9% less power and 13% higher fuel consumption than DF2. Emissions of CO and hydrocarbons as well as other materials were reduced. NO_x emissions were not increased here, although higher NO_x emissions have been reported for blends (DI engines) (169, 173).

Irregularities compared to other ester blends were observed when using blends of the isopropyl ester of soybean oil with conventional DF (239). Deposits were formed on the injector tips. This was attributed to the isopropyl ester containing 5.2 mol% monoglyceride which was difficult to separate from the isopropyl ester. However, in another report (292), the isopropyl and methyl esters of soybean oil performed well in blends with conventional DF. CO and unburned hydrocarbon emissions were reduced as were particulates by 28% when using the isopropyl

ester (25% reduction with the methyl ester); however, NO_x emissions increased a maximum of 12% for a 1:1 isopropyl soyate/DF blend.

Ester Fuels from Animal Fats and Waste Oils

Animal Fats. The animal fat most commonly studied for potential biodiesel use is tallow. Tallow contains a high amount of saturated FA (Table 4.2) and its mp is above ambient temperature. Blends of tallow esters (methyl, ethyl, and butyl) with conventional DF were studied (293). Smoke emissions were reduced with the esters, particularly the butyl ester. Other features such as torque, power, and thermal efficiency did not deviate from conventional DF by more than 3% in any case. Specific fuel consumption was higher for the neat esters but only 1.8% higher for a 50:50 blend of butyl tallowate with conventional DF. A study on beef tallow and an inedible yellow grease both neat and a 1:1 (weight ratio) blend of tallow with DF in short-term engine tests with DI and IDI engines was carried out (294). The deposits were softer than those formed with reference to cottonseed oil but still excessive. In a 200-h EMA test the deposits caused ring sticking and cylinder wear. Thus, animal fats, like vegetable oils, are not suitable for long-term use unless modified.

Other researchers blended methyl tallowate with 35 vol% ethanol to achieve the viscosity of conventional DF and the fuel properties were closely related to that of No. 2 DF (295). In an investigation of blends of DF2 with methyl tallowate and ethanol (296), an 80:13:7 blend of DF2:methyl tallowate:ethanol reduced emissions the most without a significant drop in engine power output. The same authors determined numerous physical properties of blends of DF with methyl tallowate, methyl soyate and ethanol and found them to be similar to the pertinent properties of DF2.

Waste Vegetable Oils. The use of vegetable oils as frying oils produces significant amounts of used oils which may also present a disposal problem. A major incentive for the use of waste oils is their lower price. Acid catalyzed-processes for biodiesel production from waste oils is economically competitive with the alkali-catalyzed processes applied to virgin vegetable oils (297). Used vegetable oils usually contain some degradation products of vegetable oils and foreign material. A potential operational problem of biodiesel from waste oils is their less favorable cold flow properties due to higher amounts of saturated fatty compounds. The production of biodiesel from such sources is briefly discussed above. However, in analyses of used vegetable oils it was reported (298) that the differences between used and unused fats are not very great and in most cases simple heating and removal by filtration of solid particles suffices for subsequent transesterification. The CN of a used frying oil methyl ester was given as 49 (299), thus comparing well with other materials, but little demand could be covered by this source. Biodiesel in form of esters from waste cooking oils was tested and it was reported that emissions were favorable (300). Used canola oil (only purified by filtration) was blended with DF2 (301). Fuel property tests, engine performance tests and

exhaust emission values gave promising results. Filtered frying oil was transesterified under both acidic and basic conditions with different alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-ethoxyethanol) (301). The formation of methyl esters with base catalysis (KOH) gave the best yields. The methyl, ethyl, and 1-butyl esters obtained here performed well in short-term engine tests on a laboratory high-speed diesel engine. However, during heating of frying oil, chemical changes such as formation of polymers can occur. In a study on heated rapeseed (canola) oil as a source of biodiesel, heating caused the amount of polymers to increase up to 15% in rapeseed oil but only 5% in the methyl esters (302). Dimeric and trimeric triacylglycerols in the starting oil were mainly converted into monomeric and dimeric FA methyl esters. The monomeric and dimeric species negatively influenced fuel properties. Thus, after 6 h heating Conradson carbon residue and after 16 h viscosity exceeded biodiesel specifications. The amount of polymers in waste oil was taken as an indicator for its suitability in biodiesel production. Viscosity and Conradson carbon residue were taken as good indicators for the existence of higher dimer levels.

Waste olive oil without any further derivatization was also studied in blends with conventional DF and these blends were found to be suitable as fuel (303). Used, underivatized sunflower oil was also studied (304). Methyl esters of waste olive oil were reported to be a suitable fuel (305). Waste palm oil was transesterified with ethanol to biodiesel (306) and tested in a water-cooled furnace (307). Waste oil was thermally cracked to obtain a fuel suitable for use in a diesel engine (308). As discussed above, the FA in soapstock, a by-product of vegetable oil refining consisting mainly of water, acylglycerols, phosphoglycerols and free FA with a total FA content of 25–30%, were also converted into biodiesel and the fuel found to be competitive with biodiesel from other sources (97,98).

Summary and Outlook

The use of vegetable oil-based DF, particularly in the form of esters (“biodiesel”), will probably continue to increase. Numerous reports in the popular and lay scientific press discuss this topic and new biodiesel plants are constantly being constructed. Further refinement of existing standards is likely as well as development of standards in more countries around the world. Although vegetable oil-based fuels cannot replace all petroleum-based DF, they play an important role among the alternative fuels and contribute to the goal of energy independence and security.

References

1. ASTM standard D6751 “Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels,” American Society for Testing and Materials, West Conshohocken, PA, 2003.
2. Schwab, A.W., M.O. Bagby, and B. Freedman, Preparation and Properties of Diesel Fuels from Vegetable Oils, *Fuel* 66: 1372–1378 (1987).

3. Knothe, G., Historical Perspectives on Vegetable Oil-Based Diesel Fuels, *inform 12*: 1103–1107 (2001).
4. Diesel, R., The Diesel Oil-Engine, *Engineering* 93: 395–406 (1912).
5. Diesel, R., The Diesel Oil-Engine and Its Industrial Importance Particularly for Great Britain, *Proc. Inst. Mech. Eng.*, pp. 179–280 (1912).
6. Chavanne, C.G., Belgian Patent 422,877, Aug. 31, 1937.
7. van den Abeele, M., Palm Oil as Raw Material for the Production of a Heavy Motor Fuel, *Bull. Agr. Congo Belge* 33: 3–90 (1942).
8. Chavanne, G., Sur un Mode d'Utilisation Possible de l'Huile de Palme à la Fabrication d'un Carburant Lourd (A Method of Possible Utilization of Palm Oil for the Manufacture of a Heavy Fuel), *Bull. Soc. Chim.* 10: 52–58 (1943).
9. Bruwer, J.J.; B. van D. Boshoff, F.J.C. Hugo, L.M. du Plessis, J. Fuls, C. Hawkins, A.N. van der Walt, and A. Engelbrecht, Sunflower Seed Oil as an Extender for Diesel Fuel in Agricultural Tractors, paper presented at the 1980 Symposium, South African Institute of Agricultural Engineers.
10. Shay, E.G., Diesel Fuel from Vegetable Oils: Status and Opportunity, *Biomass Bioenergy*, 4: 227–242 (1993).
11. Encinar, J.M., J.F. González, E. Sabio, M.J. and Ramiro, Preparation and Properties of Biodiesel from *Cynara cardunculus* L. Oil, *Ind. Eng. Chem. Res.* 38: 2927–2931 (1999).
12. Ikwuagwu, O.E., I.C. Ononogbu, and O.U. Njoku, Production of Biodiesel Using Rubber [*Hevea brasiliensis* (Kunth. Muell.)] Seed Oil, *Industr. Crops Prod.* 12: 57–62 (2000).
13. De, B.K., and D.K. Bhattacharyya, Biodiesel from Minor Vegetable Oils like Karanja Oil and Nahor Oil, *Fett/Lipid* 101: 404–406 (1999).
14. Geller, D.P., J.W. Goodrum, and S.J. Knapp, Fuel Properties of Oil from Genetically Altered *Cuphea viscosissima*, *Industr. Crops Prod.* 9: 85–91 (1999).
15. Foidl, N., G. Foidl, M. Sanchez, M. Mittelbach, and S. Hackel, *Jatropha curcas* L. as a Source for the Production of Biofuel in Nicaragua, *Bioresour. Technol.* 58: 77–82 (1996).
16. Giannelos, P.N., F. Zannikos, S. Stournas, E. Lois, and G. Anastopoulos, Tobacco Seed Oil as Alternative Diesel Fuel: Physical and Chemical Properties, *Industr. Crops. Prods.* 16: 1–9 (2002).
17. Munavu, R.M., and D. Odhiambo, Physicochemical Characterization of Nonconventional Vegetable Oils for Fuel in Kenya, *Kenya J. Sci. Technol.* 5: 45–52 (1984).
18. Nagle, N., and P. Lemke, Production of Methyl Ester Fuel from Microalgae, *Appl. Biochem. Biotechnol.* 24–25: 355–361 (1990).
19. de Guzman, D., Global Glycerine Prices Pressured on Market Fundamentals, *Chemical Market Reporter* February 3, 2003 (Vol. 263, No. 5), p. 12.
20. Raneses, A.R., L.K. Glaser, J.M. Price, and J. A. Duffield, Potential Biodiesel Markets and Their Economic Effects on the Agricultural Sector of the United States, *Industr. Crops Prods.* 9: 151–162 (1999).
21. Knothe, G., Current Perspectives on Biodiesel, *inform 13*: 900–903 (2002).
22. de Guzman, D., European Biodiesel Capacities Surge on EU Directives, *Chemical Market Reporter* June 30, 2003 (Vol. 263, No. 5), p. 12.
23. Ahouissoussi, N.B.C., and Wetzstein, M.E., in *Industrial Uses of Agricultural Materials*, published by the Economic Research Service, U.S. Department of Agriculture, September 1995, p. 35–41.

24. Zemanek, G., and G.A. Reinhardt, Notes on Life-Cycle Assessment of Vegetable Oils, *Fett/Lipid* 101: 321–327 (1999).
25. Hochhauser, A.M., Gasoline and Other Motor Fuels, in *Kirk-Othmer, Encyclopedia of Chemical Technology* (Kroschwitz, J.I., and Howe-Grant, M., eds.), 4th edn, Vol. 12, John Wiley & Sons, New York, pp. 341–388 (1994).
26. Puckett, A.D., and B.H. Caudle, Ignition Qualities of Hydrocarbons in the Diesel Fuel Boiling Range, *U.S. Bur. Mines, Inform. Circ.* No. 7474 (1948).
27. Clothier, P.Q.E., B.D. Aguda, A. Moise, and H. Pritchard, How Do Diesel-fuel Ignition Improvers Work? *Chem. Soc. Rev.* 22: 101–108 (1993).
28. Klopfenstein, W.E., Effect of Molecular Weights of Fatty Acid Esters on Cetane Numbers as Diesel Fuels, *J. Am. Oil Chem. Soc.* 62: 1029–1031 (1985).
29. Harrington, K.J., Chemical and Physical Properties of Vegetable Oil Esters and Their Effect on Diesel Fuel Performance, *Biomass* 9: 1–17 (1986).
30. Knothe, G. A.C. Matheaus, and T.W. Ryan III, Cetane Numbers of Branched and Straight-Chain Fatty Esters Determined in an Ignition Quality Tester, *Fuel* 82: 971–975 (2003).
31. Knothe, G., M.O. Bagby, T.W. Ryan, III, T.J. Callahan, and H. G. Wheeler, Vegetable Oils as Alternative Diesel Fuels: Degradation of Pure Triglycerides During the Precombustion Phase in a Reactor Simulating a Diesel Engine, *SAE Technical Paper Series, No. 920194*, also in *Alternative Fuels for CI and SI Engines*, SAE Publication No. SP-900, SAE, Warrendale, PA, pp. 37–63 (1992).
32. Freedman, B., and M.O. Bagby, Predicting Cetane Numbers of *n*-Alcohols and Methyl Esters from Their Physical Properties, *J. Am. Oil Chem. Soc.* 67: 565–571 (1990).
33. Freedman, B., M.O. Bagby, T.J. Callahan, and T.W. Ryan, III, Cetane Numbers of Fatty Esters, Fatty Alcohols and Triglycerides Determined in a Constant Volume Combustion Bomb, *SAE Techn. Paper Series* No. 900343 (1990).
34. Pande, S.G., and D.R. Hardy, A Practical Evaluation of Published Cetane Indices, *Fuel* 69: 437–442 (1990).
35. Ladommatos, N., and J. Goacher, Equations for Predicting the Cetane Number of Diesel Fuels from Their Physical Properties, *Fuel* 74: 1083–1093 (1995).
36. Klopfenstein, W.E., Estimation of Cetane Index for Esters of Fatty Acids, *J. Am. Oil Chem. Soc.* 59: 531–533 (1982).
37. Krisnangkura, K., A Simple Method for Estimation of Cetane Index of Vegetable Oil Methyl Esters, *J. Am. Oil Chem. Soc.* 63: 552–553 (1986).
38. Batel, W., M. Graef, G.-J. Mejer, R. Möller, R., and F. Schoedder, Plant Oils for Fuel and Energy Supplies, *Grundl. Landtechnik*, 30: 40–51 (1980).
39. Goering, C.E., A.W. Schwab, M.J. Daugherty, E.H. Pryde, and A.J. Heakin, Fuel Properties of Eleven Vegetable Oils, *Trans. ASAE* 25: 1472–1477, 1483 (1982).
40. Freedman, B., and M.O. Bagby, Heats of Combustion of Fatty Esters and Triglycerides, *J. Am. Oil Chem. Soc.* 66: 1601–1605 (1989).
41. Freedman, B., M.O. Bagby, and H. Khoury, Correlation of Heats of Combustion with Empirical Formulas for Fatty Alcohols, *J. Am. Oil Chem. Soc.* 66: 595–596 (1989).
42. Weast, R.C., Astle, M.J., and Beyer, W.H., *Handbook of Chemistry and Physics*, 66th edn., CRC Press, Boca Raton, FL, pp. D-272–D-278 (1985–1986).
43. Schmidt, A.W., Motorische Untersuchungen mit Dieselmotoren (Engine Investigations with Diesel Fuels), *Automobiltechn. Z.* 36: 212–214 (1933).

44. Bruwer, J.J., B. van D. Boshoff, F.J.C. Hugo, J. Fuls, C. Hawkins, A.N. van der Walt, A. Engelbrecht, and L.M. du Plessis, The Utilization of Sunflower Seed Oil as a Renewable Fuel for Diesel Engines, paper presented at the 1980 National Energy Symposium, American Society of Agricultural Engineers, p. 11.
45. Clark, S.J., L. Wagner, M.D. Schrock, and P.G. Piennaar, Methyl and Ethyl Soybean Esters as Renewable Fuels for Diesel Engines, *J. Am. Oil Chem. Soc.* **61**: 1632–1638 (1984).
46. Ryan, T.W., III, L.G. Dodge, and T.J. Callahan, The Effects of Vegetable Oil Properties on Injection and Combustion in Two Different Diesel Engines, *J. Am. Oil Chem. Soc.* **61**: 1610–1619 (1984).
47. Peterson, C.L., R.A. Korus, P.G. Mora, and J.P. Madsen, Fumigation with Propane and Transesterification Effects on Injector Coking with Vegetable Oil Fuels, *Trans. ASAE* **30**: 28–35 (1987).
48. Siekmann, R.W., and G.H. Pischinger, Evaluation of Lubricating Oil Contaminated with Small Amounts of Soybean Oil Ester in Comparison with Normal Diesel Oil Operation, *Proc. Vegetable Oil Diesel Fuel, Seminar III*, Agricultural Reviews and Manuals, U.S. Department of Agriculture, Agricultural Research Service, Peoria, IL, pp. 163–168 (1983).
49. Van Gerpen, J.H., S. Soylu, and M.E. Tat, Evaluation of the Lubricity of Soybean Oil-Based Additives in Diesel Fuel, *Proc. 1999 ASAE/CSAE-SCGR Annual Intern. Meeting*, Paper No. 996134 (1999).
50. Zhang, X., C. Peterson, D. Reece, R. Haws, and G. Möller, Biodegradability of Biodiesel in the Aquatic Environment, *Trans. ASAE* **41**: 1423–1430 (1998).
51. Bessee, G.B., and J.P. Fey, Compatibility of Elastomers and Metals in Biodiesel Fuel Blends, *Soc. Automot. Eng., [Spec. Publ.]*, SP-1274, 221–232 (1997).
52. Knothe, G., Structure Indices in Fatty Acid Chemistry. How Relevant is the Iodine Value? *J. Am. Oil Chem. Soc.* **79**: 847–854 (2002).
53. Mittelbach, M., Analytical Aspects and Quality Criteria for Biodiesel Derived from Vegetable Oils, *Liq. Fuels, Lubr. Addit. Biomass, Proc. Altern. Energy Conf.* (Dale, B.E., ed.), American Society of Agricultural Engineers, St. Joseph, MI, pp. 151–156 (1994).
54. Andrews, A.S., and G.R. Quick, Fuel Substitution in Agriculture, *Energy Agric.* **3**: 323–332 (1984).
55. Prankl, H., and M. Wörgetter, Influence of the Iodine Number of Biodiesel to the Engine Performance, *Proc. Third Liquid Fuel Conference: Liquid Fuels and Industrial Products from Renewable Resources* (J.S. Cundiff, E.E. Gavett, C. Hansen, C. Peterson, M.A. Sanderson, H. Shapouri, D.L. VanDyne, eds.), ASAE, St. Joseph, MI, pp. 191–196 (1996).
56. Lilly, L.R.C., *Diesel Engine Reference Book*, 1st edn, Butterworths, London, 1980.
57. Ricardo Consulting Engineers, Exhaust Smoke, Measurement and Regulation and Exhaust Emissions, in *Diesel Engine Reference Book* (B. Challen and R. Baranescu, eds.), 2nd edn, Society of Automotive Engineers, Warrendale, PA (1998).
58. Eskin, N.A.M., B.E. McDonald, R. Przybylski, L.J. Malcolmson, R. Scarth, T. Mag, K. Ward, and D. Adolph, Canola Oil, in *Bailey's Industrial Oil and Fat Products* (Y.H. Hui, ed.), 5th edn, Vol. 5, Wiley-Interscience, New York, pp. 1–95, (1996).
59. Van Gerpen, J. and R. Reitz, Diesel Combustion and Fuels, in *Diesel Engine Reference Book* (B. Challen, and R. Baranescu, eds.), Society of Automotive Engineers, Warrendale, PA, pp. 89–104 (1998).

60. Glassman, I., *Combustion*, 3rd edn, Academic Press, San Diego, 1996.
61. Cruz, J.M., A.S. Ogunlowo, W.J. Chancellor, and J.R. Goss, Vegetable Oils as Fuels for Diesel Engines, *Resour. Conserv.* 6: 69–74 (1981).
62. Bacon, D.M., F. Brear, I.D. Moncrieff, and K.L. Walker, The Use of Vegetable Oils in Straight and Modified Form as Diesel Engine Fuels, in *Beyond the Energy Crisis* (R.A. Fazzolare, and C.B. Smith, eds), Vol. 3, Pergamon Press, Oxford, England, pp. 1525–1533 (1981).
63. Bettis, B.L., C.L. Peterson, D.L. Auld, D.J. Driscoll, and E.D. Peterson, Fuel Characteristics of Vegetable Oil from Oilseed Crops in the Pacific Northwest, *Agron. J.* 74: 335–339 (1982).
64. Peterson, C.L., G.L. Wagner, and D.L. Auld, Winter Rape Oil Fuel for Diesel Engines: Recovery and Utilization, *Trans. ASAE* 26: 322–327, 332 (1983).
65. Pryor, R.W., M.A. Hanna, J.L. Schinstock, and L.L. Bashford, Soybean Oil Fuel in a Small Diesel Engine, *Trans. ASAE* 26: 333–337 (1983).
66. Korus, R.A., T.L. Mousetis, and L. Lloyd, Polymerization of Vegetable Oils, *ASAE Publ.* 4–82 (Vegetable Oil Fuels): 218–223 (1982).
67. Darcey, C.L., W.A. LePori, C.M. Yarbrough, and C.R. Engler, Lubricating Oil Contamination from Plant Oil Fuels, *Trans. ASAE*, 26: 1626–1632 (1983).
68. Vellguth, G., Emissions When Using Alternative Fuels in Tractor Diesel Engines, *Grundl. Landtechnik* 32: 177–186 (1982).
69. Clevenger, M.D., M.O. Bagby, C.E. Goering, A.W. Schwab, and L.D. Savage, Developing an Accelerated Test of Coking Tendencies of Alternative Fuels, *Trans. ASAE* 31: 381–388 (1988).
70. Pestes, M.N., and J. Stanislaw, Piston Ring Deposits When Using Vegetable Oil as a Fuel, *J. Test. Eval.* 12: 61–68 (1984).
71. Gutsche, B., Technology of Methyl Ester Production—Application for Biodiesel Production, *Fett/Lipid* 99: 418–427 (1997).
72. Schuchardt, U., R. Sercheli, and R.M. Vargas, Transesterification of Vegetable Oils: A Review, *J. Braz. Chem. Soc.* 9: 199–210 (1998).
73. Ma, F., and M. Hanna, Biodiesel Production: A Review, *Bioresour. Technol.* 70: 1–15 (1999).
74. H. Fukuda, A. Kondo, H. Noda, Biodiesel Fuel Production by Transesterification of Oils, *J. Biosci. Bioeng.* 92: 405–416 (2001).
75. Freedman, B., and E.H. Pryde, Fatty Esters from Vegetable Oils for Use as a Diesel Fuel, *ASAE Publ.* 4–82 (Veg. Oil Fuels): 117–122 (1982).
76. Freedman, B., E.H. Pryde, and T.L. Mounts, Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils, *J. Am. Oil Chem. Soc.* 61: 1638–1643 (1984).
77. Canakci, M., and J. Van Gerpen, Biodiesel Production via Acid Catalysis, *Trans. ASAE* 42: 1203–1210 (1999).
78. Mittelbach, M., M. Wörgetter, J. Pernkopf, and H. Junek, Diesel Fuel Derived from Vegetable Oils: Preparation and Use of Rape Oil Methyl Ester, *Energy Agric.* 2: 369–384 (1983).
79. Ahn, E., M. Koncar, M. Mittelbach, and R. Marr, A Low-Waste Process for the Production of Biodiesel, *Sep. Sci. Technol.* 30: 2021–2033 (1995).
80. Isigigür, A., F. Karaosmanoglu, and H.A. Aksoy, Methyl Ester from Safflower Seed Oil of Turkish Origin as a Biofuel for Diesel Engines, *Appl. Biochem. Biotechnol.* 45–46: 103–122 (1994).

81. Freedman, B., R.O. Butterfield, and E.H. Pryde, Transesterification Kinetics of Soybean Oil, *J. Am. Oil Chem. Soc.* 63: 1375–1380 (1986).
82. Mittelbach, M., and B. Trathnigg, Kinetics of Alkaline Catalyzed Methanolysis of Sunflower Oil, *J. Am. Oil Chem. Soc.* 92: 145–148 (1990).
83. Boocock, D.G.B., S.K. Konar, V. Mao, V., and H. Sidi, Fast One-Phase Oil-Rich Processes for the Preparation of Vegetable Oil Methyl Esters, *Biomass Bioenergy* 11: 43–50 (1996).
84. Noureddini, H., and D. Zhu, Kinetics of Transesterification of Soybean Oil, *J. Am. Oil Chem. Soc.* 74: 1457–1463 (1997).
85. Boocock, D.G.B., S.K. Konar, V. Mao, C. Lee, and S. Buligan, Fast Formation of High-Purity Methyl Esters from Vegetable Oils, *J. Am. Oil Chem. Soc.* 75: 1167–1172 (1998).
86. Breccia, A., B. Esposito, G. Breccia Fratadocchi, and A. Fini, Reaction Between Methanol and Commercial Seed Oils Under Microwave Irradiation, *J. Microwave Power Electromagn. Energy* 34: 3–8 (1999).
87. Stavarache, C., M. Vinatoru, R. Nishimura, and Y. Maeda, Conversion of Vegetable Oil to Biodiesel Using Ultrasonic Irradiation, *Chem. Lett.* 32: 716–717 (2003).
88. Vicente, G., A. Coteron, M. Martinez, and J. Aracil, Application of the Factorial Design of Experiments and Response Methodology to Optimize Biodiesel Production, *Ind. Crops Prod.* 8: 29–35 (1998).
89. Cvengros, J., and F. Povazanec, Production and Treatment of Rapeseed Oil Methyl Esters as Alternative Fuels for Diesel Engines, *Bioresour. Technol.* 55: 145–152 (1996).
90. Dasari, M.A., M.J. Goff, and G.J. Suppes, Noncatalytic Alcoholysis Kinetics of Soybean Oil, *J. Am. Oil Chem. Soc.* 80: 189–192 (2003).
91. Ma, F., L.D. Clements, and M.A. Hanna, The Effect of Mixing on Transesterification of Beef Tallow, *Bioresour. Technol.* 69: 289–293 (1999).
92. Ma, F., L.D. Clements, and M.A. Hanna, Biodiesel Fuel from Animal Fat, Ancillary Studies on Transesterification from Beef Tallow, *Ind. Eng. Chem. Res.* 37: 3768–3771 (1998).
93. Ma, F., L.D. Clements, and M.A. Hanna, The Effects of Catalyst, Free Fatty Acids, and Water on Transesterification of Beef Tallow, *Trans. ASAE* 41: 1261–1264 (1998).
94. Dorado, M.P., E. Ballesteros, J.A. de Almeida, C. Schellert, H.P. Löhrllein, and R. Krause, An Alkali-Catalyzed Transesterification Process for High Free Fatty Acid Waste Oils, *Trans. ASAE* 45: 525–529 (2002).
95. Canakci, M., and J. Van Gerpen, Biodiesel Production from Oils and Fats with High Free Fatty Acids, *Trans. ASAE* 44: 1429–1436 (2001).
96. Canakci, and J. Van Gerpen, A Pilot Plant to Produce Biodiesel from High Free Fatty Acid Feedstocks, *Trans. ASAE* 46: 945–954 (2003).
97. Haas, M.J., S. Bloomer, and K. Scott, Simple, High-Efficiency Synthesis of Fatty Acid Methyl Esters from Soapstock, *J. Am. Oil Chem. Soc.* 77: 373–379 (2000).
98. Haas, M.J., K.M. Scott, T.L. Alleman, and R.L. McCormick, Engine Performance of Biodiesel Fuel Prepared from Soybean Soapstock: A High Quality Renewable Fuel Produced from a Waste Feedstock, *Energy Fuels* 15: 1207–1212 (2001).
99. Haas, M.J., P.J. Michalski, S. Runyon, A. Nunez, and K.M. Scott, Production of FAME from Acid Oil, a By-product of Vegetable Oil Refining, *J. Am. Oil Chem. Soc.* 80: 97–102 (2003).

100. Kaufmann, H.P., F. Grandel, and B. Grothues, Interesterification in Fats. I. Theoretical and Background—Hydrogenation, *Fette Seifen Anstrichm.* 60: 919–930 (1958).
101. Posorske, L.H., Industrial-Scale Application of Enzymes to the Fats and Oil Industry, *J. Am. Oil Chem. Soc.* 61: 1758–1760 (1984).
102. Mittelbach, M., Lipase Catalyzed Alcoholysis of Sunflower Oil, *J. Am. Oil Chem. Soc.* 67: 168–170 (1990).
103. Nelson, L.A., T.A. Foglia, W.N. Marmer, Lipase-Catalyzed Production of Biodiesel, *J. Am. Oil Chem. Soc.* 73: 1191–1195 (1996).
104. Selmi, B., and D. Thomas, Immobilized Lipase-Catalyzed Ethanolysis of Sunflower Oil in a Solvent-Free Medium, *J. Am. Oil Chem. Soc.* 75: 691–695 (1998).
105. Linko, Y.-Y., M. Lämäsä, X. Wu, E. Uosukainen, J. Seppälä, and P. Linko. Biodegradable Products by Lipase Biocatalysis, *J. Biotechnol.* 66: 41–50 (1998).
106. Soumanou, M.M., and U.T. Bornscheuer, Lipase-Catalyzed Alcoholysis of Vegetable Oils, *Eur. J. Lipid Sci. Technol.* 105: 656–660 (2003).
107. Bélafi-Bakó, K., F. Kovács, L. Gubicza, and J. Hancsók, Enzymatic Biodiesel Production from Sunflower Oil by *Candida antarctica* Lipase in a Solvent-Free System, *Biocatal. Biotransform.* 20: 437–439 (2002).
108. Wu, W.H., T.A. Foglia, W.N. Marmer, and J.G. Phillips, Optimizing Production of Ethyl Esters of Grease Using 95% Ethanol by Response Surface Methodology, *J. Am. Oil Chem. Soc.* 76: 517–521 (1999).
109. Hsu, A.-F., K. Jones, T.A. Foglia, and W.N. Marmer, Immobilized Lipase-Catalyzed Production of Alkyl Esters of Restaurant Grease as Biodiesel, *Biotechnol. Appl. Biochem.* 36: 181–186 (2002).
110. Hsu, A.-F., K.C. Jones, T.A. Foglia, and W.N. Marmer, Optimization of Alkyl Ester Production from Grease Using a Phyllosilicate Sol-Gel Immobilized Lipase, *Biotechnol. Lett.* 25: 1713–1716 (2003).
111. Shimada, Y., Y. Watanabe, T. Samukawa, A. Sugihara, H. Noda, H. Fukuda, and Y. Tominaga, Y., Conversion of Vegetable Oil to Biodiesel Using Immobilized *Candida antarctica* Lipase, *J. Am. Oil Chem. Soc.* 76: 789–793 (1999).
112. Watanabe, Y., Y. Shimada, A. Sugihara, H. Noda, H. Fukuda, and Y. Tominaga, Continuous Production of Biodiesel Fuel from Vegetable Oil Using Immobilized *Candida antarctica* Lipase, *J. Am. Oil Chem. Soc.* 77: 355–360 (2000).
113. Xu, Y., W. Du, D. Liu, and J. Zeng, A Novel Enzymatic Route for Biodiesel Production from Renewable Oils in a Solvent-Free Medium, *Biotechnol. Lett.* 25: 1239–1241 (2003).
114. Kaieda, M., T. Samukawa, T. Matsumoto, K. Ban, A. Kondo, Y. Shimada, H. Noda, F. Nomoto, K. Ohtsuka, E. Izumoto, and H. Fukuda, Biodiesel Fuel Production from Plant Oil Catalyzed by *Rhizopus oryzae* Lipase in a Water-Containing System Without an Organic Solvent, *J. Bioscience Bioeng.* 88: 627–631 (1999).
115. Lara Pizarro, A.V., and E.Y. Park, Lipase-Catalyzed Production of Biodiesel Fuel from Vegetable Oils Contained in Waste Activated Bleaching Earth, *Process Biochem.* 38: 1077–1082 (2003).
116. Kusdiana, D., and S. Saka, Kinetics of Transesterification in Rapeseed Oil to Biodiesel Fuel as Treated in Supercritical Methanol, *Fuel* 80: 693–698 (2001).
117. Demirbas, A., Biodiesel from Vegetable Oils via Transesterification in Supercritical Methanol, *Energy Convers. Managem.* 43: 2349–2356 (2002).

118. Demirbas, A., Biodiesel Fuels from Vegetable Oils *via* Catalytic and Non-Catalytic Supercritical Alcohol Tranesterifications and Other Methods: A Survey, *Energy Conv. Managem.* 44: 2093–2109 (2003).
119. Warabi, Y., D. Kusdiana, and S. Saka, Reactivity of Triglycerides and Fatty Acids of Rapeseed Oil in Supercritical Alcohols, *Bioresour. Technol.* 91: 283–297 (2004).
120. Sercheli, R., R.M. Vargas, and U. Schuchardt, Alkylguanidine-Catalyzed Heterogeneous Transesterification of Soybean Oil, *J. Am. Oil Chem. Soc.* 76: 1207–1210 (1999).
121. Gryglewicz, S., Rapeseed Oil Methyl Esters Preparation Using Heterogeneous Catalysts, *Bioresour. Technol.* 70: 249–253 (1999).
122. Suppes, G.J., K. Bockwinkel, S. Lucas, J.B. Botts, M.H. Mason, and J.A. Heppert, Calcium Carbonate Catalyzed Alcoholysis of Fats and Oils, *J. Am. Oil Chem. Soc.* 78: 139–145 (2001).
123. Yean, C.H., and V.G. Kumar Das, Studies on the Transesterification of Glycerides: I. The Methanolysis of Tripalmitin Catalysed by Diorganotin (IV) Compounds, *J. Appl. Organomet. Chem.* 14: 304–315 (2000).
124. Graille, J., P. Lozano, D. Pioch, and P. Geneste, Pilot Trials on the Alcoholysis of Vegetable Oils with Natural Catalysts to Produce Diesel Fuels, *Oleagineux* 41: 457–464 (1986).
125. Harrington, K.J., and C. D’Arcy-Evans, A Comparison of Conventional and *in situ* Methods of Transesterification of Seed Oil from a Series of Sunflower Cultivars, *J. Am. Oil Chem. Soc.* 62: 1009–1013 (1985).
126. Siler-Marinkovic, S., and A. Tomasevic, Transesterification of Sunflower Oil *in situ*, *Fuel* 77: 1389–1391 (1998).
127. Kildiran, G., S.Ö. Yücel, and S. Türkay, *In-situ* Alcoholysis of Soybean Oil, *J. Am. Oil Chem. Soc.* 73: 225–228 (1996).
128. Graille, J., P. Lozano, D. Pioch, P. Geneste, and A. Guida, Methyl or Ethyl Esters as Substitute Diesel Fuels, *Oleagineux* 37: 421–424 (1982).
129. Graille, J., P. Lozano, D. Pioch, and P. Geneste, Alcoholysis Tests of Vegetable Oils with Natural Catalysts for the Production of Diesel Fuels, *Oleagineux* 40: 271–276 (1985).
130. Peterson, G.R., and W.P. Scarrah, Rapeseed Oil Transesterification by Heterogeneous Catalysis, *J. Am. Oil Chem. Soc.* 61: 1593–1597 (1984).
131. Stage, H, Principle of the New ATT-Process for Converting Vegetable Oils to Diesel Fuels, *Fett Wiss. Technol.* 90: 28–32 (1988).
132. Knothe, G., R.O. Dunn, and M.O. Bagby, Biodiesel: The Use of Vegetable Oils and Their Derivatives as Alternative Diesel Fuels, in *ACS Symposium Series 666: Fuels and Chemicals from Biomass* (B.C. Saha and J. Woodward, eds), American Chemical Society, Washington, DC, pp. 172–208 (1997).
133. Knothe, G., Analytical Methods Used in the Production and Fuel Quality Assessment of Biodiesel, *Trans. ASAE* 44: 193–200 (2001).
134. Freedman, B., E.H. Pryde, and W.F. Kwolek, Thin-Layer Chromatography/Flame Ionization Analysis of Transesterified Vegetable Oils, *J. Am. Oil Chem. Soc.* 61: 1215–1220 (1986).
135. Cvengros, J., and Z. Cvengrovová, Z, Quality Control of Rapeseed Oil Methyl Esters by Determination of Acyl Conversion, *J. Am. Oil Chem. Soc.* 71: 1349–1352 (1994).

136. Freedman, B., W.F. Kwolek, and E.H. Pryde, Quantitation in the Analysis of Transesterified Soybean Oil by Capillary Gas Chromatography, *J. Am. Oil Chem. Soc.* 63: 1370–1375 (1986).
137. Bondioli, P., C. Mariani, A. Lanzani, E. Fedeli, and S. Veronese, Vegetable Oil Derivatives as Diesel Fuel Substitutes. Analytical Aspects. Note 2: Determination of Free Glycerol, *Riv. Ital. Sostanze Grasse* 69: 7–9 (1992).
138. Mittelbach, M., Diesel Fuel Derived from Vegetable Oils, V [1]: Gas Chromatographic Determination of Free Glycerol in Transesterified Vegetable Oils, *Chromatographia* 37: 623–626 (1993).
139. Plank, C., and E. Lorbeer, Analysis of Free and Esterified Sterols in Vegetable Oil Methyl Esters by Capillary GC, *J. High Resolut. Chromatogr.* 16: 483–487 (1993).
140. Plank, C., and E. Lorbeer, Minor Components in Vegetable Oil Methyl Esters I: Sterols in Rape Seed Oil Methyl Ester, *Fett Wiss. Technol.* 96: 379–386 (1994).
141. Plank, C., and E. Lorbeer, On-line Liquid Chromatography–Gas Chromatography for the Analysis of Free and Esterified Sterols in Vegetable Oil Methyl Esters Used as Diesel Fuel Substitutes, *J. Chromatogr. A* 683: 95–104 (1994).
142. Mariani, C., P. Bondioli, S. Venturini, and E. Fedeli, Vegetable Oil Derivatives as Diesel Fuel Substitutes. Analytical Aspects. Note 1: Determination of Methyl Esters, Mono-, Di-, and Triglycerides, *Riv. Ital. Sostanze Grasse* 68: 549–551 (1991).
143. Plank, C., and E. Lorbeer, Quality Control of Vegetable Oil Methyl Esters Used as Diesel Fuel Substitutes: Quantitative Determination of Mono-, Di-, and Triglycerides by Capillary GC, *J. High Resolut. Chromatogr.* 15: 609–612 (1992).
144. Plank, C., and E. Lorbeer, Simultaneous Determination of Glycerol, and Mono-, Di-, and Triglycerides in Vegetable Oil Methyl Esters by Capillary Gas Chromatography, *J. Chromatogr. A* 697: 461–468 (1995).
145. Mittelbach, M., G. Roth, A. Bergmann, Simultaneous Gas Chromatographic Determination of Methanol and Free Glycerol in Biodiesel, *Chromatographia* 42: 431–434 (1996).
146. Bondioli, P., C. Mariani, E. Fedeli, A.M. Gomez, and S. Veronese, Vegetable Oil Derivatives as Diesel Fuel Substitutes. Analytical Aspects. Note 3: Determination of Methanol, *Riv. Ital. Sostanze Grasse* 69: 467–469 (1992).
147. Lozano, P., N. Chirat, J. Graille, and D. Pioch, Measurement of Free Glycerol in Biofuels, *Fresenius' J. Anal. Chem.* 354: 319–322 (1996).
148. Bailer, J., and K. de Hueber, Determination of Saponifiable Glycerol in “Bio-Diesel,” *Fresenius' J. Anal. Chem.* 340: 186 (1991).
149. Anon., Enzymatic Determination of Free and Total Glycerine in Biodiesel, *Chemical Market Reporter* (Vol. 263, No. 21), May 26, 2003, p. 12.
150. Trathnigg, B., and M. Mittelbach, Analysis of Triglyceride Methanolysis Mixtures Using Isocratic HPLC with Density Detection, *J. Liquid Chromatogr.* 13: 95–105 (1990).
151. Foglia, T.A., and K.C. Jones, Quantitation of Neutral Lipid Mixtures Using High-Performance Liquid Chromatography with Light Scattering Detection, *J. Liq. Chromatogr. Relat. Technol.* 20: 1829–1838 (1997).
152. Holcapek, M., P. Jandera, J. Fischer, and B. Prokes, Analytical Monitoring of the Production of Biodiesel by High-Performance Liquid Chromatography with Various Detection Methods, *J. Chromatogr. A* 858: 13–31 (1999).

153. Lechner, M., C. Bauer-Plank, and E. Lorbeer, Determination of Acylglycerols in Vegetable Oil Methyl Esters by On-Line Normal Phase LC-GC, *J. High Resolut. Chromatogr.* 20: 581–585 (1997).
154. Fillières, R., B. Benjelloun-Mlayah, and M. Delmas, Ethanolysis of Rapeseed Oil: Quantitation of Ethyl Esters, Mono-, Di-, and Triglycerides by High-Performance Size-Exclusion Chromatography, *J. Am. Oil Chem. Soc.* 72: 427–432 (1995).
155. Darnoko, D., M. Cheyan, and E.G. Perkins, Analysis of Vegetable Oil Transesterification Products by Gel Permeation Chromatography, *J. Liq. Chromatogr. Rel. Technol.* 23: 2327–2335 (2000).
156. Bondioli, P., A. Lanzani, E. Fedeli, M. Sala, and S. Veronese, Vegetable Oil Derivatives as Diesel Fuel Substitutes. Analytical Aspects. Note 4: Determination of Biodiesel and Diesel Fuel in Mixture, *Riv. Ital. Sostanze Grasse* 71: 287–289 (1994).
157. Gelbard, G., O. Brès, R.M. Vargas, F. Vielfaure, and U.F. Schuchardt, ¹H Nuclear Magnetic Resonance Determination of the Yield of the Transesterification of Rapeseed Oil with Methanol, *J. Am. Oil Chem. Soc.* 72: 1239–1241 (1995).
158. Dimmig, T., W. Radig, C. Knoll, and C. Dittmar, ¹³C-NMR Spectroscopic Determination of the Conversion and Reaction Kinetics of Transesterification of Triglycerides to Methyl Esters, *Chem. Tech. (Leipzig)* 51: 326–329 (1999).
159. Knothe, G., Rapid Monitoring of Transesterification and Assessing Biodiesel Fuel Quality by Near-Infrared Spectroscopy Using a Fiber-Optic Probe, *J. Am. Oil Chem. Soc.* 77: 489–493 (1999).
160. Knothe, G., Monitoring a Progressing Transesterification Reaction by Fiber-Optic Near Infrared Spectroscopy with Correlation to ¹H Nuclear Magnetic Resonance Spectroscopy, *J. Am. Oil Chem. Soc.* 76: 795–800 (2000).
161. De Filippis, P., C. Giavarini, M. Scarsella, and M. Sorrentino, Transesterification Processes for Vegetable Oils: A Simple Control Method of Methyl Ester Content, *J. Am. Oil Chem. Soc.* 72: 1399–1404 (1995).
162. Sadeghi-Jorabchi, H., V.M.E. Wood, F. Jeffery, A. Bruster-Davies, N. Loh, and D. Coombs, Estimation of Bio-Diesel in Lubricating Oil Using Fourier Transform Infrared Spectroscopy Combined with a Mid-Infrared Fibre Optic Probe, *Spectrosc. Eur.* 6: 16, 18, 20–1 (1994).
163. Siekmann, R.W., G.H. Pischinger, D. Blackman, and L.D. Carvalho, The Influence of Lubricant Contamination by Methyl Esters of Plant Oils on Oxidation Stability and Life, *ASAE Publ.* 4–82 (Veg. Oil Fuels): 117–122 (1982).
164. Knothe, G., Determining the Blend Level of Mixtures of Biodiesel with Conventional Diesel Fuel by Fiber-Optic NIR Spectroscopy and ¹H-NMR Spectroscopy, *J. Am. Oil Chem. Soc.* 78: 1025–1028 (2001).
165. Bírová, A., E. Svajdlénka, J. Cvengros, and V. Dostálková, Determination of the Mass Fraction of Methyl Esters in Mixed Fuels, *Eur. J. Lipid Sci. Technol.* 104: 271–277 (2002).
166. Bondioli, P., and L. Della Bella, The Evaluation of Biodiesel Quality in Commercial Blends with Diesel Fuel, *Riv. Ital. Sostanze Grasse* 80: 173–176 (2003).
167. Tat, M.E. and J.H. Van Gerpen, Biodiesel Blend Detection with a Fuel Composition Sensor, *Appl. Eng. Agricult.* 19: 125–131 (2003).
168. Munack, A., J. Krahel, and H. Speckmann, A Fuel Sensor for Biodiesel, Fossil Diesel Fuel, and Their Blends, *ASAE Paper No.* 02–6081 (2002).

169. Mittelbach, M., P. Tritthart, H. Junek, Diesel Fuel Derived from Vegetable Oils, II: Emission Tests Using Rape Oil Methyl Ester, *Energy Agric.* 4: 207–215 (1985).
170. Krah, J., G. Vellguth, A. Munack, K. Stalder, and M. Bahadir, Emissions and Environmental Effects When Using Rape Oil Fuels in Agriculture, *Motortechn. Z.* 57: 24–31 (1996).
171. Krah, J., G. Vellguth, A. Munack, K. Stalder, and M. Bahadir, Exhaust Gas Emissions and Environmental Effects by Use of Rape Seed Oil Based Fuels in Agricultural Tractors, *SAE Tech. Pap. Ser.* 961847, Society of Automotive Engineers, Warrendale, PA (1996).
172. Ali, Y., M.A. Hanna, and L.I. Leviticus, Emissions and Power Characteristics of Diesel Engines on Methyl Soyate and Diesel Fuel Blends, *Bioresour. Technol.* 52: 185–195 (1995).
173. Last, R.J., M. Krüger, and M. Dürnholtz, Emissions and Performance Characteristics of a 4–Stroke, Direct Injected Diesel Engine Fueled with Blends of Biodiesel and Low Sulfur Diesel Fuel, *Soc. Automot. Eng. [Spec. Publ.]*, SP-1093, 9–21 (1995).
174. McDonald, J.F., D.L. Purcell, B.T. McClure, and D.B. Kittelson, Emissions Characteristics of Soy Methyl Ester Fuels in an IDI Compression Ignition Engine, *Soc. Automot. Eng. [Spec. Publ.]*, SP-1093, 191–207 (1995).
175. Tat, M.E., J.H. Van Gerpen, S. Soyulu, M. Canakci, A. Monyem, and S. Wormley, The Speed of Sound and Isentropic Bulk Modulus of Biodiesel at 21°C from Atmospheric Pressure to 35MPa, *J. Am. Oil Chem. Soc.* 77: 285–289 (2000).
176. McCormick, R.L. M.S. Graboski, T.L. Alleman, and A.M. Herring, Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine, *Environ. Sci. Technol.* 35: 1742–1747 (2001).
177. Monyem, A., J.H. Van Gerpen, and M. Canakci, The Effect of Timing and Oxidation on Emissions from Biodiesel-Fueled Engines, *Trans. ASAE* 44: 35–42 (2001).
178. Ladommatos, N., M. Parsi, and A. Knowles, The Effect of Fuel Cetane Improver on Diesel Pollutant Emissions, *Fuel* 75: 8–14 (1996).
179. Vaitilingom, G., P. Higelin, J. Andrzejewski, and A. Sapinski, Effect of Hexyl Nitrate and Intake Air Temperature on the Ignition Delay of Vegetable Oils, *Entropie* 27: 39–43 (1991).
180. Knothe, G., M.O. Bagby, and T.W. Ryan III, Cetane Numbers of Fatty Compounds: Influence of Compound Structure and of Various Potential Cetane Improvers, *SAE Technical Pap. Ser.* 971681 in *State of Alternative Fuel Technologies*, SAE Publication SP-1274, Society of Automotive Engineers, Warrendale, PA, pp. 127–132 (1997).
181. Starr, M.E., Influence on Transient Emissions at Various Injection Timings, Using Cetane Improvers, Bio-Diesel, and Low-Aromatic Fuels, *SAE Tech. Pap. Ser.* 972904, Society of Automotive Engineers, Warrendale, PA (1997).
182. Poirier, M.-A., D.E. Steere, J.A. Krogh, Cetane Improver Compositions Comprising Nitrated Fatty Acid Derivatives, U.S. Patent 5,454,842, October 3, 1995.
183. Mason, M.H., Z. Chen, C. Tat, J.A. Heppert, and G.J. Suppes, Synthesis of Low Nitrogen Cetane Improvers, *Prepr. Am. Chem. Soc., Div. Pet. Chem.* 43: 579–581 (1998).
184. Suppes, G.J., Z. Chen, Y. Rui, M. Mason, and J.A. Heppert, Synthesis and Cetane Improver Performance of Fatty Acid Glycol Nitrates, *Fuel* 78: 73–81 (1999).
185. Suppes, G.J. and M.A. Dasari, Synthesis and Evaluation of Alkyl Nitrates from Triglycerides as Cetane Improvers, *Ind. Eng. Chem.* 42: 5042–5053 (2003).

186. Mills, G.A., and A.G. Howard, A Preliminary Investigation of Polynuclear Aromatic Hydrocarbon Emissions from a Diesel Engine Operating on Vegetable Oil-Based Alternative Fuels, *J. Inst. Energy* 56: 131–137 (1983).
187. Stalder, K., V. Gerhard, J. Krah, and A. Munack, How Carcinogenic are RME Emissions? *Landtechnik* 50: 266–267 (1995).
188. Bagley, S.T., L.D. Gratz, J.H. Johnson, and J.F. McDonald, Effects of an Oxidation Catalytic Converter and a Biodiesel Fuel on the Chemical, Mutagenic, and Particle Size Characteristics of Emissions from a Diesel Engine, *Environ. Sci. Technol.* 32: 1183–1191 (1998).
189. Carraro, E., A.L. Locatelli, C. Ferrero, E. Fea, and G. Cilli, Biological Activity of Particle Exhaust Emissions from Light-Duty Diesel Engines, *J. Environ. Pathol., Toxicol. Oncol.* 16: 101–109 (1997).
190. Bünger, J., M.M. Müller, J. Krah, K. Baum, A. Weigel, E. Hallier, and T.G. Schulz, Mutagenicity of Diesel Exhaust Particles from Two Fossil and Two Plant Oil Fuels, *Mutagenesis* 15: 391–397 (2000).
191. Bünger, J., J. Krah, H.U. Franke, A. Munack, and E. Hallier, Mutagenic and Cytotoxic Effects of Exhaust Particulate Matter of Biodiesel Compared to Fossil Diesel Fuel, *J. Mutation Res.* 415: 13–23 (1998).
192. Anon., Biodiesel Alternative Fuel Wins Health Test Okay, *Oil Gas J.* 98: 53 (2000).
193. Zubik, J., S.C. Sorenson, and C.E. Goering, Diesel Engine Combustion of Sunflower Oil Fuels, *Trans. ASAE* 27: 1262–1256 (1984).
194. Purcell, D.L., B.T. McClure, J. McDonald, and H.N. Basu, Transient Testing of Soy Methyl Ester Fuels in an Indirect Injection, Compression Ignition Engine, *J. Am. Oil Chem. Soc.* 73: 381–388 (1996).
195. Scholl, K.W., and S.C. Sorenson, Combustion of Soybean Oil Methyl Ester in a Direct Injection Diesel Engine, in *Alternate Fuels: A Decade of Success and Promise* (R.M. Bata, ed.), Society of Automotive Engineers, Warrendale, PA, pp. 555–567 (1994).
196. Knothe, G., M.O. Bagby, and T.W. Ryan III, Precombustion of Fatty Acids and Esters of Biodiesel, A Possible Explanation for Differing Cetane Numbers, *J. Am. Oil Chem. Soc.* 75: 1007–1013 (1998).
197. Chandler, J.E., F.G. Horneck, and G.I. Brown, The Effect of Cold Flow Properties on Low Temperature Operability of Diesel Fuels, in *Proc., SAE International Fuels and Lubricants Meeting and Exposition, San Francisco, CA*, Society of Automotive Engineers, Warrendale, PA, Paper No. 922186 (1992).
198. Lewtas, K., R.D. Tack, D.H.M. Beiny, and J.W. Mullin, Wax Crystallization in Diesel Fuel: Habit Modification and the Growth of n-Alkane Crystals, in *Advances in Industrial Crystallization* (J. Garside, R.J. Davey, and A.G. Jones, eds.), Butterworth-Heinemann, Oxford, pp. 166–179 (1991).
199. Owen, K., and T. Coley, in *Automotive Fuels Handbook*, Society of Automotive Engineers, Warrendale, PA, pp. 353–403 (1990).
200. Brown, G.I., E.W. Lehmann, and K. Lewtas, Evolution of Diesel Cold Flow—The Next Frontier, in *SAE Tech. Pap. Ser.*, Society of Automotive Engineers, Warrendale, PA, Paper No. 890031 (1989).
201. Zielinski, J., and F. Rossi, Wax and Flow in Diesel Fuels, in *Proc., SAE Fuels and Lubricants Meeting and Exposition*, Society of Automotive Engineers, Warrendale, PA, Paper No. 841352 (1984).
202. Westbrook, S.R., in *Significance of Tests for Petroleum Products*, (ed. S.J. Rand), 7th edn., ASTM International, West Conshohocken, PA, pp. 63–81 (2003).

203. Nadkarni, R.A.K., in *Guide to ASTM Test Methods for the Analysis of Petroleum Products and Lubricants*, American Society for Testing and Materials, West Conshohocken, PA, pp. 66–274 (2000).
204. Botros, M.G., Enhancing the Cold Flow Behavior of Diesel Fuels, in *SAE Spec. Publ. SP-1302 (Gasoline and Diesel Fuel: Performance and Additives)*, Society of Automotive Engineers, Warrendale, PA, Paper No. 972899 (1997).
205. Chandler, J.E., and J.A. Zechman, Low Temperature Operability Limits of Late Model Heavy Duty Diesel Trucks and the Effect Operability Additives and Changes to the Fuel Delivery System Have on Low Temperature Performance, in *SAE Spec. Publ. SP-1563 (Gasoline and Diesel Fuel: Performance and Additives 2000)*, Society of Automotive Engineers, Warrendale, PA, Paper No. 2001-01-2883 (2001).
206. Heraud, A., and B. Poulligny, How Does a “Cloud Point” Diesel Fuel Additive Work? *J. Colloid Interface Sci.* 153: 378–391 (1992).
207. Brown, G.I., and G.P. Gaskill, Enhanced Diesel Fuel Low Temperature Operability, *Erdöle und Kohle-Erdgas Petrochemie* 43: 196–204 (1990).
208. Coley, T.R., Diesel Fuel Additives Influencing Flow and Storage Properties, in *Critical Reports on Applied Chemistry, Vol. 25, Gasoline and Diesel Fuel Additives* (ed. K. Owen), Wiley and Sons, Chichester, UK, pp. 105–131 (1989).
209. Brown, G.I., R.D. Tack, and J.E. Chandler, An Additive Solution to the Problem of Wax Settling in Diesel Fuels, in *Proc., SAE International Fuels and Lubricants Meeting and Exposition*, Society of Automotive Engineers, Warrendale, PA, Paper No. 881652 (1988).
210. McMillan, M.L., and E.G. Barry, Fuel and Vehicle Effects on Low-Temperature Operation of Diesel Vehicles—The 1981 CRC Field Test, in *Proc., SAE International Congress and Exposition*, Society of Automotive Engineers, Warrendale, PA, Paper No. 830594 (1983).
211. Rieckard, D.J., S.J. Cartwright, and J.E. Chandler, The Impact of Ambient Conditions, Fuel Characteristics and Fuel Additives on Fuel Consumption of Diesel Vehicles, in *Proc., SAE International Fuels and Lubricants Meeting and Exposition*, Society of Automotive Engineers, Warrendale, PA, Paper No. 912332 (1991).
212. Machado, A.L.C., and E.F. Lucas, Influence of Ethylene-co-Vinyl Acetate Copolymers on the Flow Properties of Wax Synthetic Systems, *J. Appl. Polym. Sci.* 85: 1337–1348 (2002).
213. Zanier, A., Application of Modulated Temperature DSC to Distillate Fuels and Lubricating Greases, *J. Thermal Anal.* 54: 381–390 (1998).
214. Heino, E.L., Determination of Cloud Point for Petroleum Middle Distillates by Differential Scanning Calorimetry, *Thermochim. Acta* 117: 125–130 (1987).
215. Claudy, P., J.-M. Létoffé, B. Neff, and B. Damin, Diesel Fuels: Determination of Onset Crystallization Temperature, Pour Point and Filter Plugging Point by Differential Scanning Calorimetry, Correlation with Standard Test Methods, *Fuel* 65: 861–864 (1986).
216. Damin, B., A. Faure, J. Denis, B. Sillion, P. Claudy, and J.M. Létoffé, New Additives for Diesel Fuels: Cloud-Point Depressants, in *SAE Spec. Publ. SP-675 (Diesel Fuels: Performance and Characteristics)*, Society of Automotive Engineers, Warrendale, PA, Paper No. 861527 (1986).
217. Wu, W.-H., T.A. Foglia, W.N. Marmer, R.O. Dunn, C.E. Goering, and T.E. Briggs, Low-Temperature Property and Engine Performance Evaluation of Ethyl and Isopropyl Esters of Tallow and Grease, *J. Am. Oil Chem. Soc.* 75: 1173–1178 (1998).

218. Lee, I., L.A. Johnson, and E.G. Hammond, Use of Branched-Chain Esters to Reduce the Crystallization Temperature of Biodiesel, *J. Am. Oil Chem. Soc.* 72: 1155–1160 (1995).
219. Lyde, D.R., in *Handbook of Chemistry and Physics*, 71st edn., CRC Press, Boca Raton, FL, pp. C359–C466, (1990).
220. Foglia, T.A., L.A. Nelson, R.O. Dunn, and W.N. Marmer, Low-Temperature Properties of Alkyl Esters of Tallow and Grease, *J. Am. Oil Chem. Soc.* 74: 951–955 (1997).
221. Kalligeros, S., F. Zannikos, S. Stournas, E. Lois, G. Anastopoulos, Ch. Teas, and F. Sakellaropoulos, An Investigation of Using Biodiesel/Marine Diesel Blends on the Performance of a Stationary Diesel Engine, *Biomass Bioenergy* 24: 141–149 (2003).
222. Lang, X., A. K. Dalai, N.N. Bakhshi, M.J. Reaney, and P.B. Hertz, Preparation and Characterization of Bio-Diesels from Various Bio-Oils, *Bioresource Technol.* 80: 53–62 (2001).
223. Peterson, C.L., J.S. Taberski, J.C. Thompson, and C.L. Chase, The Effect of Biodiesel Feedstock on Regulated Emissions in Chassis Dynamometer Tests of a Pickup Truck, *Trans. ASAE* 43: 1371–1381 (2000).
224. Dunn, R.O., and M.O. Bagby, Low-Temperature Properties of Triglyceride-Based Diesel Fuels: Transesterified Methyl Esters and Petroleum Middle Distillate/Ester Blends, *J. Am. Oil Chem. Soc.* 72: 895–904 (1995).
225. Dunn, R.O., and M.O. Bagby, Low-Temperature Filterability Properties of Alternative Diesel Fuels from Vegetable Oils, in *Proc., Third Liquid Fuel Conference: Liquid Fuel and Industrial Products from Renewable Resources* (eds. J. S. Cundiff, E.E. Gavett, C. Hansen, C. Peterson, M.A. Sanderson, H. Shapouri, and D.L. VanDyne), American Society of Agricultural Engineers, St. Joseph, MI, pp. 95–103 (1996).
226. Dunn, R.O., M.W. Shockley, and M.O. Bagby, Improving the Low-Temperature Properties of Alternative Diesel Fuels: Vegetable Oil-Derived Methyl Esters, *J. Am. Oil Chem. Soc.* 73: 1719–1728 (1996).
227. Dunn, R.O., Thermal Analysis of Alternative Diesel Fuels from Vegetable Oils, *J. Am. Oil Chem. Soc.* 76: 109–115 (1999).
228. Lee, I., L.A. Johnson, and E.G. Hammond, Reducing the Crystallization Temperature of Biodiesel by Winterizing Methyl Soyate, *J. Am. Oil Chem. Soc.* 73: 631–636 (1996).
229. Scherer, M., and J. Souchik, Synthesis of Long-Chain Polymethacrylates by Atom Transfer Radical Polymerization for Manufacture of Lubricating oil Additives, PCT Int. Appl. WO 0140334, June 7, 2001.
230. Scherer, M., J. Souchik, and J.M. Bollinger, Block Copolymers of Long-Chain Alkyl Methacrylates and Acrylates as Lubricating and Biodiesel Additives, PCT Int. Appl. WO 0140339, June 7, 2001.
231. Nylund, N.-O., and P. Aakko, Characterization of New Fuel Qualities, in *SAE Spec. Publ. SP-1545 (State of Alternative Fuel Technologies 2000)*, Society of Automotive Engineers, Warrendale, PA, Paper No. 2000-01-2009 (2000).
232. Auschra, C., J. Vetter, U. Bohmke, and M. Neusius, Methacrylate Copolymers as Low-Temperature Flow Improvers for Biodiesel Fuels and Biologically-Derived Fuel Oils, PCT Int. Appl. WO 9927037, June 3, 1999.
233. Desai, N.M., A.S. Sarma, and K.L. Mallik, Application of Performance Polymers in Petroleum Products: Studies on Viscosity Modifiers and Pour Point Depressants, *Polym. Sci.* 2: 706–712 (1991).

234. Holder, G.A., and Thorne, J., Inhibition of Crystallisation by Polymers, in ACS Polymer Chemistry Division, *Polymer Preprints* 20: 766–769 (1979).
235. Knothe, G., R.O. Dunn, M.W. Shockley, and M.O. Bagby, Synthesis and Characterization of Some Long-Chain Diesters with Branched or Bulky Moieties, *J. Am. Oil Chem. Soc.* 77: 865–871 (2000).
236. Nouredдини, H., System and Process for Producing Biodiesel with Reduced Viscosity and a Cloud Point Below 32°F, U.S. Patent No. 6,015,440, January 16, 2000.
237. Larsson, K., and P.J. Quinn, Physical Properties: Structural and Physical Characteristics, in *The Lipid Handbook* (eds. F. D. Gunstone, J.L. Harwood, and F.B. Padley), 2nd edn., Chapman and Hall, London, 1994, pp. 401–430.
238. Clark, S.J., M.D. Schrock, L.E. Wagner, and P.G. Pienaar, in *Soybean Oil Esters as a Renewable Fuel for Diesel Engines*, in Final Report, Research Project No. 5980, USDA, ARS, Peoria, IL (1983).
239. Zhang, Y., and J.H. Van Gerpen, Combustion Analysis of Esters of Soybean Oil in a Diesel Engine, in *SAE Spec. Publ. No. SP-1160 (Performance of Alternative Fuels for SI and CI Engines)*, Society of Automotive Engineers, Warrendale, PA, Paper No. 960765 (1996).
240. Illingworth, D., Fractionation of Fats, in *Physical Properties of Lipids* (A.G. Marangoni and S.S. Narine, eds.), Marcel Dekker, New York, pp. 411–447 (2002).
241. Kellens, M., and M. Hendrix, Fractionation, in *Introduction to Fats and Oils Technology* (R.D. O'Brien, W.E. Farr, and P.J. Wan, eds.), 2nd edn., AOCS Press, Champaign, IL, pp. 194–207 (2000).
242. O'Brien, RD., *Fats and Oils: Formulating and Processing for Applications*, Technomic, London, UK, pp. 109–121 (1998).
243. Anderson, D., A Primer on Oils Processing Technology, in *Bailey's Industrial Oil and Fat Products Vol. 4 (Edible Oil and Fat Products: Processing Technology)* (Y.H. Hui, ed.), 5th edn., Wiley-Interscience, New York, pp. 31–45 (1996).
244. Krishnamurthy, R., and M. Kellens, Fractionation and Winterization, in *Bailey's Industrial Oil and Fat Products Vol. 4 (Edible Oil and Fat Products: Processing Technology)* (Y.H. Hui, ed.), 5th edn., Wiley-Interscience, New York, pp. 301–338 (1996).
245. Duff, H.G., Winterizing, in *Introduction to Fats and Oils Chemistry* (P.J. Wan, ed.), American Oil Chemists' Society, Champaign, IL, pp. 105–113 (1991).
246. Brown, J.B., and D.K. Kolb, Applications of Low-Temperature Crystallization in the Separation of the Fatty Acids and Their Compounds, in *Progress in the Chemistry of Fats and other Lipids Vol. 3* (R.T. Holman, W.O. Lundberg, and T. Malkin, ed.), Pergamon Press, New York, pp. 58–80 (1955).
247. Bailey, A.E., in *Melting and Solidification of Fats*, Interscience, New York, pp. 328–346 (1950).
248. Rajah, K.K., Fractionation of Fat, in *Separation Processes in the Food and Biotechnology Industries: Principles and Applications* (A.S. Grandison and M.J. Lewis, ed.), Technomic, Lancaster, UK, pp. 207–242 (1996).
249. González Gómez, M.E., R. Howard-Hildige, J.J. Leahy, and B. Rice, Winterization of Waste Cooking Oil Methyl Ester to Improve Cold Temperature Fuel Properties, *Fuel* 81: 33–39 (2002).
250. Dunn, R.O., M.W. Shockley, and M.O. Bagby, Winterized Methyl Esters from Soybean Oil: An Alternative Diesel Fuel with Improved Low-Temperature Flow

- Properties, in *SAE Spec. Publ. No. SP-1274 (State of Alternative Fuel Technologies)*, Society of Automotive Engineers, Warrendale, PA, pp. 133–142 (1997). SAE Paper No. 971682.
251. Yu, L., Lee, I., Hammond, E.G., Johnson, L.A., and Van Gerpen, J.H., The Influence of Trace Components on the Melting Point of Methyl Soyate, *J. Am. Oil Chem. Soc.* 75: 1821–1824 (1998).
252. Giles, H.N., Methods for Assessing Stability and Cleanliness of Liquid Fuels, in *Significance of Tests for Petroleum Products* (S.J. Rand, ed.), 7th edn., ASTM International, West Conshohocken, PA, pp. 108–118 (2003).
253. Frankel, E.N., *Lipid Oxidation*, The Oily Press, Dundee, Scotland 1998.
254. Bondioli, P., A. Gasparoli, L. Della Bella, S. Tagliabue, and G. Toso, Biodiesel Stability under Commercial Storage Conditions over One Year, *Eur. J. Lipid Sci. Technol.* 105: 735–741 (2003).
255. Mittelbach, M., and S. Schober, The Influence of Antioxidants on the Oxidation Stability of Biodiesel, *J. Am. Oil Chem. Soc.* 80: 817–823 (2003).
256. Lacoste, F., and L. Lagardere, Quality Parameters Evolution During Biodiesel Oxidation Using Rancimat Test, *Eur. J. Lipid Sci. Technol.* 105: 149–155 (2003).
257. Knothe, G., and R.O. Dunn, Dependence of Oil Stability Index of Fatty Compounds on Their Structure and Concentration and Presence of Metals, *J. Am. Oil Chem. Soc.* 80: 1021–1026 (2003).
258. Dunn, R.O., Effect of Oxidation Under Accelerated Conditions on Fuel Properties of Methyl Soyate (Biodiesel), *J. Am. Oil Chem. Soc.* 79: 915–920 (2002).
259. Dunn, R.O., Analysis of Oxidative Stability of Methyl Soyate by Pressurized-Differential Scanning Calorimetry, *Trans. ASAE* 43: 1203–1208 (2000).
260. Dunn, R.O., Effect of Winterization on Fuel Properties of Methyl Soyate, in *Proc., Commercialization of Biodiesel: Producing a Quality Fuel* (C.L. Peterson, ed.), University of Idaho, Moscow, ID, pp. 164–186 (1998).
261. Bondioli, P., A. Gasparoli, L. Della Bella, and S. Tagliabue, Evaluation of Biodiesel Storage Stability Using Reference Methods, *Eur. J. Lipid Sci. Technol.* 104: 777–784 (2002).
262. Dunn, R.O., Effect of Oxidation Under Accelerated Conditions on Fuel Properties of Methyl Soyate (biodiesel). *J. Am. Oil Chem. Soc.* 79: 915–920 (2002), Erratum: *J. Am. Oil Chem. Soc.* 80: 193 (2003).
263. Mittelbach, M., and S. Gangl, Long Storage Stability of Biodiesel Made from Rapeseed and Used Frying Oil, *J. Am. Oil Chem. Soc.* 78: 573–577 (2001).
264. A. Monyem, M. Canakci, and J.H. Van Gerpen, Investigation of Biodiesel Thermal Stability Under Simulated In-Use Conditions, *Appl. Eng. Agric.* 16: 373–378 (2000).
265. Canakci, M., A. Monyem, and J. Van Gerpen, J., Accelerated Oxidation Processes in Biodiesel, *Trans. ASAE* 42: 1565–1572 (1999).
266. Simkovsky, N.M., and A. Ecker, Effect of Antioxidants on the Oxidative Stability of Rapeseed Oil Methyl Esters, *Erdoel, Erdgas, Kohle* 115: 317–318 (1999).
267. Simkovsky, N.M., and A. Ecker, Influence of Light and Tocopherol Content on the Oxidative Stability of Fatty Acid Methyl Esters, *Fett/Lipid* 100: 534–538 (1998).
268. Thompson, J.C., C.L. Peterson, D.L. Reece, D.L., S.M. Beck, Two-Year Storage Study with Methyl and Ethyl Esters of Rapeseed, *Trans. ASAE* 41: 931–939 (1998).
269. Bondioli, P., and L. Folegatti, Evaluating the Oxidation Stability of Biodiesel, *Riv. Ital. Sostanze Grasse*, 73: 349–353 (1996).

270. Bondioli, P., A. Gasparoli, A. Lanzani, E. Fedeli, S. Veronese, and M. Sala, Storage Stability of Biodiesel, *J. Am. Oil Chem. Soc.* 72: 699–702 (1995).
271. Du Plessis, L.M., J.B.M. de Villiers, and W.H. van der Walt, Stability Studies on Methyl and Ethyl Fatty Acid Esters of Sunflowerseed Oil, *J. Am. Oil Chem. Soc.* 62: 748–752 (1985).
272. Du Plessis, L.M., Plant Oils as Diesel Fuel Extenders: Stability Tests and Specifications on Different Grades of Sunflower Seed and Soyabean Oils, *CHEMSA* 8: 150–154 (1982).
273. Sharma, B.K., and A.J. Stipanovic, Development of a New Oxidation Stability Test Method for Lubricating Oils Using High-Pressure Differential Scanning Calorimetry, *Thermochim. Acta* 402: 1–18 (2003).
274. Gamelin, C. D., N. K. Dutta, N. Roy Choudhury, D. Kehoe, and J. Matison, Evaluation of Kinetic Parameters of Thermal and Oxidative Decomposition of Base Oils by Conventional, Isothermal and Modulated TGA, and Pressure DSC, *Thermochim. Acta* 392–393: 357–369 (2002).
275. Yao, J., Evaluation of Sodium Acetylacetonate as a Synergist for Arylamine Antioxidants in Synthetic Lubricants, *Tribology Int.* 30: 795–799 (1997).
276. Patterson, G.H., and A.T. Riga, Factors Affecting Oxidation Properties in Differential Scanning Calorimetric Studies, *Thermochim. Acta* 226: 201–210 (1993).
277. Kaufman, R.E., and W.E. Rhine, Development of a Remaining Useful Life of a Lubricant Evaluation Technique, Part I: Differential Scanning Calorimetric Technique, *Lubr. Eng.* 44: 154–161 (1988).
278. Noel, F., Thermal Analysis of Lubrication Oils, *Thermochim. Acta* 4: 377–392 (1972).
279. Zeman, A., A. Sprengel, D. Niedermeier, and M. Späth, Biodegradable Lubricants—Studies on Thermo-Oxidation of Metal-Working and Hydraulic Fluids by Differential Scanning Calorimetry (DSC), *Thermochim. Acta* 268: 9–15 (1995).
280. Cross, C.K., Oil Stability: A DSC Alternative for the Active Oxygen Method, *J. Am. Oil Chem. Soc.* 47: 229–230 (1970).
281. Hassel, R.L., Thermal Analysis: An Alternative Method of Measuring Oil Stability, *J. Am. Oil Chem. Soc.* 53: 179–181 (1976).
282. Tan, C.P., Y.B. Che Man, J. Selamat, and M.S.A. Yusoff, Comparative Studies of Oxidative Stability of Edible Oils by Differential Scanning Calorimetry and Oxidative Stability Index Methods, *Food Chem.* 76: 385–389 (2002).
283. Raemy, A., I. Froelicher, and J. Loeliger, Oxidation of Lipids Studied by Isothermal Heat Flux Calorimetry, *Thermochim. Acta* 114: 159–164 (1987).
284. Stavinoha, L.L., and K.S. Kline, in *Report, Oxidation Stability of Methyl Soyates—Modified ASTM D 5304 and D 6186 for Biodiesel B100*, U.S. Army, TACOM, TARDEC, National Automotive Center, Warren, MI (2001).
285. Litwinienko, G., A. Daniluk, and T. Kasprzyska-Guttman, Study on Autoxidation Kinetics of Fats by Differential Scanning Calorimetry, 1. Saturated C₁₂–C₁₈ Fatty Acids and Their Esters, *Ind. Eng. Chem. Res.* 39: 7–12 (2000a).
286. Litwinienko, G., and T. Kasprzyska-Guttman, Study on the Autoxidation Kinetics of Fat Components by Differential Scanning Calorimetry, 2. Unsaturated Fatty Acids and Their Esters, *Ind. Eng. Chem. Res.* 39: 13–17 (2000b).
287. Litwinienko, G., A. Daniluk, and T. Kasprzyska-Guttman, A Differential Scanning Calorimetry Study on the Oxidation of C₁₂–C₁₈ Saturated Fatty Acids and Their Esters, *J. Am. Oil Chem. Soc.* 76: 655–657 (1999).

288. Litwinienko, G., T. Kasprzyska-Guttman, and M. Studzinski, Effects of Selected Phenol Derivatives on the Autoxidation of Linolenic Acid Investigated by DSC Non-Isothermal Methods, *Thermochim. Acta* 307: 97–106 (1997).
289. Knothe, G., Structure Indices in FA Chemistry, How Relevant Is the Iodine Value? *J. Am. Oil Chem. Soc.* 79: 847–854 (2002).
290. Dunn, R.O., Alternative Jet Fuels from Vegetable Oils, *Trans. ASAE* 44: 1751–1757 (2001).
291. Goodrum, J.W., E.S. Law, Rheological Properties of Peanut Oil-Diesel Fuel Blends, *Trans. ASAE* 25: 897–900 (1982).
292. Chang, D.Y.Z., Van Gerpen, J.H., Lee, I., Johnson, L.A., Hammod, E.G., and Marley, S.J., Fuel Properties and Emissions of Soybean Oil Esters as Diesel Fuel, *J. Am. Oil Chem. Soc.* 73: 1549–1555 (1996).
293. Sims, R.E.H., Tallow Esters as an Alternative Diesel Fuel, *Trans. ASAE* 28: 716–721 (1985).
294. Lepori, W.A., Engler, C.R., Johnson, L.A., and Yarbrough, C.M., Animal Fats as Alternative Diesel Fuels, in *Liq. Fuels Renewable Resour., Proc. Altern. Energy Conf.* (ed J.S. Cundiff), American Society of Agricultural Engineers, St. Joseph, MI, pp. 89–98 (1992).
295. Ali, Y., and Hanna, M.A., Physical Properties of Tallow Ester and Diesel Fuel Blends. *Bioresour. Technol.* 47: 131–134 (1994).
296. Ali, Y., Hanna, M.A., and Borg, J.E., Optimization of Diesel, Methyl Tallowate and Ethanol Blend for Reducing Emissions from Diesel Engines, *Bioresour. Technol.* 52: 237–243 (1995).
297. Zhang, Y., M.A. Dubé, D.D. McLean, and M. Kates, Biodiesel Production from Waste Cooking Oil: 2. Economic Assessment and Sensitivity Analysis, *Bioresour. Technol.* 90: 229–240 (2003).
298. Mittelbach, M., Pokits, B., and Silberholz, A., Production and Fuel Properties of Fatty Acid Methyl Esters from Used Frying Oil, in *Liq. Fuels Renewable Resour., Proc. Altern. Energy Conf.* (J.S. Cundiff, ed.), American Society of Agricultural Engineers, St. Joseph, MI, p. 74–78 (1992).
299. Reed, T.B., M.S. Graboski, and S. Gaur, Development and Commercialization of Oxygenated Diesel Fuels from Waste Vegetable Oils, *Energy Biomass Wastes* 15: 907–914 (1991).
300. Karaosmanoglu, F., Isisigür, A., Hamdallahpur, F., Gülder, Ö.L., and Aksoy, H.A., Used Canola Oil as a Diesel Fuel Alternative, in *Renewable Energy: Technol. Environ., Proc. World Renewable Energy Congr.*, 2nd ed (Sayigh, A.A.M., ed.), Vol. 3, Pergamon, Oxford, p. 1455–1459 (1992).
301. Nye, M.J., Williamson, T.W., Deshpande, S., Schrader, J.H., Snively, W.H., Yurkevich, T.P., and French, C.L., Conversion of Used Frying Oil to Diesel Fuel by Transesterification: Preliminary Tests, *J. Am. Oil Chem. Soc.* 60: 1598–1601 (1983).
302. Mittelbach, M., and H. Enzelsberger, Transesterification of Heated Rapeseed Oil for Extending Diesel Fuel, *J. Am. Oil Chem. Soc.* 76: 545–550 (1999).
303. Rakopoulos, C.D., Comparative Performance and Emission Studies When Using Olive Oil as a Fuel Supplement in DI and IDI Diesel Engines, *Renewable Energy* 2: 327–331 (1992).
304. Özaktas, T., Compression Ignition Engine Fuel Properties of a Used Sunflower Oil-Diesel Fuel Blend, *Energy Sources* 22: 377–382 (2000).

305. Dorado, M.P., E. Ballesteros, J.M. Arnal, J. Gómez, and F.J. López Giménez, Testing Waste Olive Oil Methyl Ester as a Fuel in a Diesel Engine, *Energy Fuels* 17: 1560–1565 (2003).
306. Al-Widyan, M.I., and A.O. Al-Shyoukh, Experimental Evaluation of the Transesterification of Waste Palm Oil into Biodiesel, *Bioresour. Technol.* 85: 253–256 (2002).
307. Tashtoush, G., M.I. Al-Widyan, and A.O. Al-Shyoukh, Combustion Performance and Emissions of Ethyl Ester of a Waste Vegetable Oil in a Water-Cooled Furnace, *Appl. Therm. Eng.* 23, 285–293 (2003).
308. Zaher, F.A., O.A. Megahed, and O.S. El Kinawy, Utilization of Used Frying Oil as Diesel Engine Fuel, *Energy Sources* 25: 819–826 (2003).
309. Gunstone, F.D., J. L. Harwood, and F. B. Padley, eds., *The Lipid Handbook*, 2nd edn., Chapman and Hall, London, 1994.
310. Gouw, T.H., J.C.Vlugter, and C.J.A. Roelands, Physical Properties of Fatty Acid Methyl Esters. VI. Viscosity, *J. Am. Oil Chem. Soc.* 43: 433–434 (1966).
311. Allen, C.A.W., K.C. Watts, R.G. Ackman, and M.J. Pegg, Predicting the Viscosity of Biodiesel Fuels from Their Fatty Acid Ester Composition, *Fuel* 78: 1319–1326 (1999).
312. Serdari, A., K. Fragioudakis, S. Kalligeros, S. Stournas, and E. Lois, Impact of Using Biodiesels of Different Origin and Additives on the Performance of a Stationary Diesel Engine, *J. Eng. Gas Turbines Power (Trans. ASME)* 122: 624–631 (2000).
313. Geyer, S.M., M.J. Jacobus, and S.S. Lestz, Comparison of Diesel Engine Performance and Emissions from Neat and Transesterified Vegetable Oils, *Trans. ASAE* 27: 375–381 (1984).
314. F. Avella, A. Galtieri, and A. Fiumara, Characteristics and Utilization of Vegetable Derivatives as Diesel Fuels, *Riv. Combust.* 46: 181–188 (1992).
315. Krah, J., K. Baum, U. Hackbarth, H.-E. Jeberien, A. Munack, C. Schütt, O. Schröder, N. Walter, J. Bünger, M.M. Müller, and A. Weigel, Gaseous Compounds, Ozone Precursors, Particle Number and Particle Size Distributions, and Mutagenic Effects Due to Biodiesel, *Trans. ASAE* 44: 179–191 (2001).
316. Isigigür, A., F. Karaosmanoglu, H.A. Aksoy, F. Hamdullahpur, and Gülder, Ö.L., Performance and Emission Characteristics of a Diesel Engine Operating on Safflower Seed Oil Methyl Ester, *Appl. Biochem. Biotechnol.* 45–46: 93–102 (1994).
317. A. Yahya, and S.J. Marley, Physical and Chemical Characterization of Methyl Soy Oil and Methyl Tallow Esters as CI Engine Fuels, *Biomass Bioenergy* 6: 321–328 (1994).
318. M. Canakci, and J.H. Van Gerpen, The Performance and Emissions of a Diesel Engine Fueled with Biodiesel from Yellow Grease and Soybean Oil, *ASAE Paper No.* 01–6050 (2001).