

Chapter 15

Biodiesel Production, Properties, and Feedstocks

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Abstract Biodiesel, defined as the mono-alkyl esters of vegetable oils or animal fats, is an environmentally attractive alternative to conventional petroleum diesel fuel (petrodiesel). Produced by transesterification with a monohydric alcohol, usually methanol, biodiesel has many important technical advantages over petrodiesel, such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flash point and biodegradability, negligible sulfur content, and lower exhaust emissions. Important disadvantages of biodiesel include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low-temperature operability, and in some cases, higher NO_x exhaust emissions. This chapter covers the process by which biodiesel is prepared, the types of catalysts that may be used for the production of biodiesel, the influence of free fatty acids on biodiesel production, the use of different monohydric alcohols in the preparation of biodiesel, the influence of biodiesel composition on fuel properties, the influence of blending biodiesel with other fuels on fuel properties, alternative uses for biodiesel, and value-added uses of glycerol, a co-product of biodiesel production. A particular emphasis is placed on alternative feedstocks for biodiesel production. Lastly, future challenges and outlook for biodiesel are discussed.

Keywords Alternative feedstocks • Biodiesel • Fatty acid FAME • Fuel properties • Methanolysis • Transesterification

Disclaimer: Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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Introduction

Biodiesel is defined by ASTM International as a fuel composed of monoalkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats meeting the requirements of ASTM D6751 (ASTM 2008a). Vegetable oils and animal fats are principally composed of triacylglycerols (TAG) consisting of long-chain fatty acids chemically bound to a glycerol (1,2,3-propanetriol) backbone. The chemical process by which biodiesel is prepared is known as the transesterification reaction and involves a TAG reacting with a short-chain monohydric alcohol normally in the presence of a catalyst at elevated temperature to form fatty acid alkyl esters (FAAE) and glycerol (Fig.15.1). The conversion of TAG to biodiesel is a stepwise process whereby the alcohol initially reacts with TAG as the alkoxide anion to produce FAAE and diacylglycerols (DAG, reaction [1], Fig.15.1), which react further with alcohol (alkoxide) to liberate another molecule of FAAE and generate monoacylglycerols (MAG, reaction [2], Fig.15.1). Lastly, MAG undergo alcoholysis to yield glycerol and FAAE (reaction [3], Fig.15.1), with the combined FAAE collectively known as biodiesel. Three moles of biodiesel and one mole of glycerol are produced for every mole of TAG that undergoes complete conversion. The transesterification reaction is reversible, although the reverse reaction (production of MAG from FAAE and glycerol, for instance) is negligible largely because glycerol is not miscible with FAAE, especially fatty acid FAME (FAME) when using methanol as the alcohol component. The

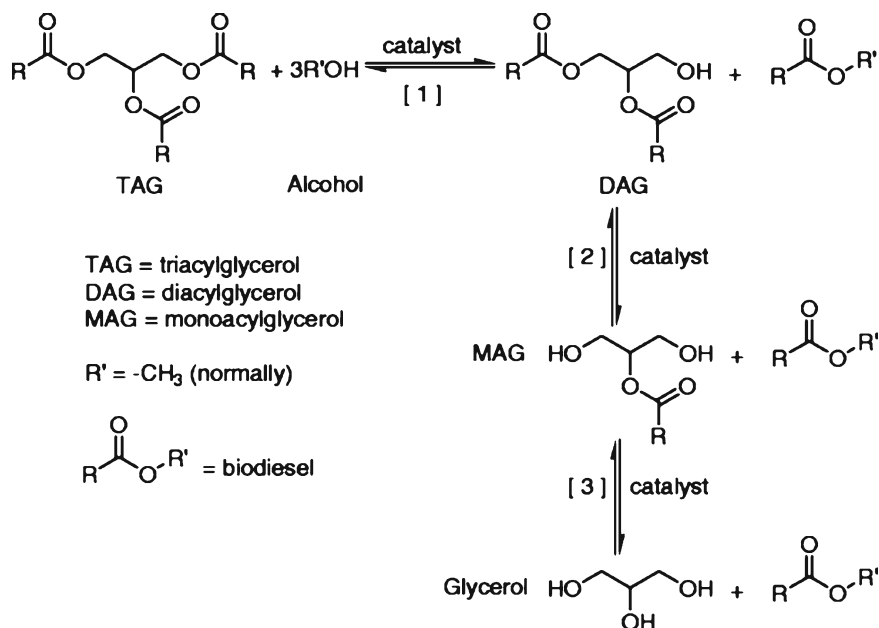


Fig. 15.1 Transesterification of triacylglycerols to yield fatty acid alkyl esters (biodiesel)

reaction system is biphasic at the beginning and the end of biodiesel production, as methanol and vegetable oil and glycerol and FAME are not miscible. Methanol is most commonly used in the commercial production of biodiesel, since it is generally less expensive than other alcohols, but ethanol prevails in regions such as Brazil where it is less expensive than methanol. Other alcohols aside from methanol and ethanol are also of interest for biodiesel production because FFAE produced from higher alcohols have different fuel properties in comparison to methyl or ethyl esters (Knothe 2005). A more detailed discussion of the influence of ester head group on the fuel properties of biodiesel will be presented in a subsequent section of this chapter.

Inexpensive homogenous alkaline base catalysts such as sodium or potassium hydroxide or methoxide are typically used in the commercial preparation of biodiesel from refined or treated oils. The classic alcoholysis conditions described by Freedman et al. (1984) include TAG reacting with an excess of six molar equivalents of methanol (with respect to TAG) and 0.5 weight percent (wt.%) alkali catalyst (with respect to TAG) at 60°C for 1 h to produce fatty acid FAME (FAME, biodiesel) and glycerol. The chemical composition of biodiesel is dependent upon the feedstock from which it is produced, as vegetable oils and animal fats of differing origin have dissimilar fatty acid compositions (Table 15.1). The fatty ester composition of biodiesel is essentially identical to that of the parent oil or fat from which it was produced.

Table 15.1 Typical fatty acid composition (wt.%)^a of a number of common feedstock oils^b and fats that may be used for biodiesel production

Fatty acid ^c	CO	PO	SBO	SFO	COO	CSO	CCO	CF	BT
C6:0							1		
C8:0							7		
C10:0							7		
C12:0							47		1
C14:0		1				1	18	1	4
C16:0	4	45	11	6	11	23	9	25	26
C18:0	2	4	4	5	2	2	3	6	20
C20:0									
C22:0				1					
C16:1						1		8	4
C18:1	61	39	23	29	28	17	6	41	28
C18:2	22	11	54	58	58	56	2	18	3
C18:3	10		8	1	1			1	
C20:1	1								
Other									14

^aFrom Gunstone and Harwood (2007); trace amounts (<1%) of other constituents may also be present

^bCO canola (low erucic acid rapeseed oil) oil, PO palm oil, SBO soybean oil, SFO sunflower oil, COO corn oil (maize), CSO cottonseed oil, CCO coconut oil, CF chicken fat, BT beef tallow

^cC6:0 methyl caproate, C8:0 methyl caprylate, C10:0 methyl caprate, C12:0 methyl laurate, C14:0 methyl myristate, C16:0 methyl palmitate, C18:0 methyl stearate, C20:0 methyl arachidate, C22:0 methyl behenate, C16:1 methyl palmitoleate, C18:1 methyl oleate, C18:2 methyl linoleate, C18:3 methyl linolenate, C20:1 methyl eicosenoate

A recent report (International Grains Council 2008) indicated that rapeseed oil was the predominant feedstock for worldwide biodiesel production in 2007 (48%, 4.6 million metric tons, MMT). The remaining oils primarily included soybean (22%, 2.1 MMT) and palm (11%, 1.0 MMT), with the rest (19%, 1.8 MMT) distributed among other unspecified vegetable oils and animal fats. The leading vegetable oils produced worldwide during the 2008 fiscal year (October 1, 2008 to September 30, 2009) were palm (43.20 MMT), soybean (37.81 MMT), rapeseed (19.38 MMT), and sunflower (11.68 MMT) oils (USDA 2008). Not surprisingly, vegetable oil production and biodiesel feedstock usage are intimately related. Feedstocks for biodiesel production vary with location according to climate and

Table 15.2 ASTM D6751 biodiesel fuel standard

Property	Test method	Limits	Units
Flash point (closed cup)	ASTM D93	93 min ^a	°C
Alcohol control			
One of the following must be met:			
1. Methanol content	EN 14110	0.2 max ^a	% volume
2. Flash point	ASTM D93	130.0 min	°C
Water and sediment	ASTM D2709	0.050 max	% volume
Kinematic viscosity, 40°C	ASTM D445	1.9–6.0	mm ² /s
Sulfated ash	ASTM D874	0.020 max	% mass
Sulfur ^b	ASTM D5453	0.0015 max (S15) 0.05 max (S500)	% mass (ppm)
Copper strip corrosion	ASTM D130	No. 3 max	
Cetane number	ASTM D613	47 min	
Cloud point	ASTM D2500	report	°C
Cold soak filterability	ASTM D7501	360 max ^c	s
Carbon residue	ASTM D4530	0.050 max	% mass
Acid value	ASTM D664	0.50 max	mg KOH/g
Free glycerin	ASTM D6584	0.020	% mass
Total glycerin	ASTM D6584	0.240	% mass
Oxidation stability	EN 14112	3.0 min	h
Phosphorous content	ASTM D4951	0.001 max	% mass
Sodium and potassium, combined	EN 14538	5 max	ppm
Calcium and magnesium, combined	EN 14538	5 max	ppm
Distillation temperature, Atmospheric equivalent temperature, 90% recovered	ASTM D1160	360 max	°C

^aFor all Tables: min refers to minimum and max refers to maximum

^bThe limits are for Grade S15 and Grade S500 biodiesel, with S15 and S500 referring to maximum allowable sulfur content (ppm)

^cB100 intended for blending into petrodiesel that is expected to give satisfactory performance at fuel temperatures at or below –12°C shall comply with a maximum cold soak filterability limit of 200 s

availability. Generally, the most abundant commodity oils or fats in a particular region are the most common feedstocks. Thus, rapeseed and sunflower oils are principally used in Europe for biodiesel production, palm oil predominates in tropical countries, and soybean oil and animal fats are most commonly used in the USA (Demirbas 2006). However, even combining these feedstocks does not suffice to fully replace the volume of conventional petroleum diesel fuel (petrodiesel). Therefore, exploration of additional feedstocks for biodiesel production has been continuously gaining significance, as discussed later.

Biodiesel standards are in place in a number of countries in an effort to ensure that only high-quality biodiesel reaches the marketplace. The two most important fuel standards, ASTM D6751 (ASTM 2008a) in the United States and EN 14214 (European Committee for Standardization, CEN) (CEN 2003a) in the European Union, are summarized in Tables 15.2 and 3, respectively. In addition, a

Table 15.3 European Committee for Standardization EN 14214 biodiesel fuel standard

Property	Test method(s)	Limits	Units
Ester content	EN 14103	96.5 min	% (mol/mol)
Density, 15°C	EN ISO 3675, EN ISO 12185	860–900	kg/m ³
Kinematic viscosity, 40°C	EN ISO 3104, ISO 3105	3.5–5.0	mm ² /s
Flash point	EN ISO 3679	120 min	°C
Sulfur content	EN ISO 20846, EN ISO 20884	10.0 max	mg/kg
Carbon residue (10% distillation residue)	EN ISO 10370	0.30 max	% (mol/mol)
Cetane number	EN ISO 5165	51 min	
Sulfated ash	ISO 3987	0.02 max	% (mol/mol)
Water content	EN ISO 12937	500 max	mg/kg
Total contamination	EN 12662	24 max	mg/kg
Copper strip corrosion (3 h, 50°C)	EN ISO 2160	1	Degree of corrosion
Oxidation stability, 110°C	EN 14112	6.0 min	h
Acid value	EN 14104	0.50 max	mg KOH/g
Iodine value	EN 14111	120 max	g I ₂ /100 g
Linolenic acid content	EN 14103	12.0 max	% (mol/mol)
Polyunsaturated (≥4 double bonds) FAME	EN 14103	1 max	% (mol/mol)
Methanol content	EN 14110	0.20 max	% (mol/mol)
MAG content	EN 14105	0.80 max	% (mol/mol)
DAG content	EN 14105	0.20 max	% (mol/mol)
TAG content	EN 14105	0.20 max	% (mol/mol)
Free glycerol	EN 14105 EN 14106	0.020 max	% (mol/mol)
Total glycerol	EN 14105	0.25 max	% (mol/mol)
Group I metals (Na, K)	EN 14108 EN 14109	5.0 max	mg/kg
Group II metals (Ca, Mg)	EN 14538	5.0 max	mg/kg
Phosphorous content	EN 14107	10.0 max	mg/kg

Table 15.4 ASTM D7467 biodiesel-petrodiesel blend (B6–B20) fuel standard

Property	Test method	Limits	Units
Biodiesel content	ASTM D7371	6–20	% volume
Flash point (closed cup)	ASTM D93	52 min	°C
One of the following must be met			
1. Cetane index	ASTM D976	40 min	
2. Aromaticity	ASTM D1319	35 max	% volume
Water and sediment	ASTM D2709	0.050 max	% volume
Kinematic viscosity, 40°C	ASTM D445	1.9–4.1	mm ² /s
Sulfur content ^a	ASTM D5453	15 max (S15)	ppm
	ASTM D2622	500 max (S500)	
Copper strip corrosion	ASTM D130	No. 3 max	
Cetane number	ASTM D613	40 min	
Ramsbottom Carbon residue	ASTM D524	0.35 max	% mass
Acid value	ASTM D664	0.30 max	mg KOH/g
Oxidation stability	EN 14112	6.0 min	h
Ash content	ASTM D482	0.01 max	% mass
Lubricity, HFRR, 60°C	ASTM D6079	520 max	µm
Cloud point or LTFT/CFPP	ASTM D2500, D4539, D6371	only guidance provided	°C
Distillation temperature, 90% recovered	ASTM D86	343 max	°C

^aThe limits are for Grade S15 and Grade S500 biodiesel, with S15 and S500 referring to maximum allowable sulfur content (ppm)

petrodiesel–biodiesel blend standard, ASTM D7467 (ASTM 2008b), was recently introduced that covers blends of biodiesel in petrodiesel from 6 to 20 vol.%, and is summarized in Table 15.4. The petrodiesel standards ASTM D975 (ASTM 2008c) and EN 590 (CEN 2004) allow for inclusion of up to 5 (B5) and 7 (B7) vol.% biodiesel, respectively, as a blend component in petrodiesel. The heating oil standard ASTM D396 (ASTM 2008d) specifies that up to B5 is permissible as well. In Europe, biodiesel (B100; 100% biodiesel) may be directly used as heating oil, which is covered by a separate standard, EN 14213 (CEN 2003b). In the cases of ASTM D7467, D975, and D396, the biodiesel component must satisfy the requirements of ASTM D6751 before inclusion in the respective fuels. Correspondingly, in the European Union, biodiesel must be satisfactory according to EN 14214 before inclusion in petrodiesel, as mandated by EN 590.

Advantages and Disadvantages of Biodiesel

Biodiesel has attracted considerable interest as an alternative fuel or extender for petrodiesel for combustion in compression–ignition (diesel) engines. Biodiesel is miscible with petrodiesel in any proportion and possesses several technical advantages over ultra-low sulfur diesel fuel (ULSD, <15 ppm S), such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flash

point and biodegradability, negligible sulfur content, and lower overall exhaust emissions. Important disadvantages of biodiesel include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low-temperature operability versus petrodiesel, and in some cases, higher NO_x exhaust emissions (DeOliveira et al. 2006; Knothe 2008). Many of these deficiencies can be mitigated through cold flow improver (Chiu et al. 2004; Soriano et al. 2005, 2006; Sern et al. 2007; Hancsok et al. 2008; Moser et al. 2008; Moser and Erhan 2008;) and antioxidant (Mittelbach and Schober 2003; Loh et al. 2006; Tang et al. 2008) additives, blending with petrodiesel (Benjumea et al. 2008; Moser et al. 2008), and/or reducing storage time (Bondioli et al. 2003). Additional methods to enhance the low-temperature performance of biodiesel include crystallization fractionation (Dunn et al. 1997; Kerschbaum et al. 2008;) and transesterification with long- or branched-chain alcohols (Lee et al. 1995; Foglia et al. 1997; Wu et al. 1998). Strategies to improve the exhaust emissions of biodiesel, petrodiesel, and blends of biodiesel in petrodiesel include various engine or after-treatment technologies such as selective catalytic reduction (SCR), exhaust gas recirculation (EGR), diesel oxidation catalysts, and NO_x or particulate traps (McGeehan 2004; Knothe et al. 2006). However, feedstock acquisition currently accounts for over 80% of biodiesel production expenses, which is a serious threat to the economic viability of the biodiesel industry (Paulson and Ginder 2007; Retka-Schill 2008). One potential solution to this problem is employment of alternative feedstocks of varying type, quality, and cost. These feedstocks may include soapstocks, acid oils, tall oils, used cooking oils, and waste restaurant greases, various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae. However, many of these alternative feedstocks may contain high levels of free fatty acids (FFA), water, or insoluble matter, which affect biodiesel production.

Influence of Free Fatty Acids on Biodiesel Production

Feedstock quality in large part dictates what type of catalyst or process is needed to produce FFAE that satisfies relevant biodiesel fuel standards such as ASTM D6751 or EN 14214. If the feedstock contains a significant percentage of FFA (>3 wt.%), typical homogenous alkaline base catalysts such as sodium or potassium hydroxide or methoxide will not be effective as a result of an unwanted side reaction (reaction [1], Fig.15.2) in which the catalyst reacts with FFA to form soap (sodium salt of fatty acid) and water (or methanol in the case of sodium methoxide), thus irreversibly quenching the catalyst and resulting in an undesirable mixture of FFA, unreacted TAG, soap, DAG, MAG, biodiesel, glycerol, water, and/or methanol (Lotero et al. 2005). In fact, base-catalyzed transesterification will not occur or will be significantly retarded if the FFA content of the feedstock is 3 wt.% or greater (Canakci and Van Gerpen 1999, 2001). For instance, nearly quantitative yields of biodiesel are achieved with homogenous alkaline base catalysts in cases where the FFA content of the feedstock is 0.5 wt.% or less (Naik et al. 2008). However, the

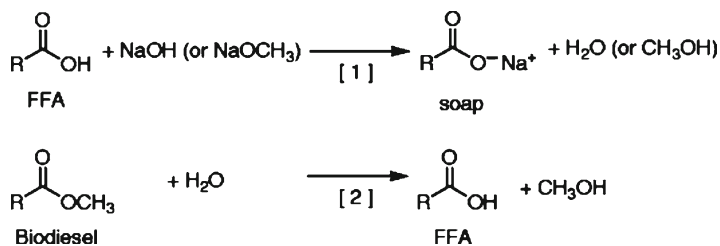


Fig. 15.2 Formation of soap from reaction of free fatty acids (FFA) with catalyst (reaction [1]) and hydrolysis of biodiesel (reaction [2]) to yield FFA and methanol

yield of biodiesel plummets to 6% with an increase in FFA content to 5.3 wt.% (Naik et al. 2008). A further complicating factor of high FFA content is the production of water upon reaction with homogenous alkaline base catalysts (reaction [1], Fig. 15.2). Water is particularly problematic because, in the presence of any remaining catalyst, it can participate in hydrolysis of biodiesel to produce additional FFA and methanol (reaction [2], Fig. 15.2).

A common approach in cases where the FFA content of a feedstock is in excess of 1.0 wt.% (Freedman et al. 1984; Mbaraka et al. 2003; Zhang et al. 2003; Wang et al. 2005) is a two-step process in which mineral acid pretreatment of the feedstock to lower its FFA content is followed by transesterification with homogenous alkaline base catalysts to produce biodiesel. In a typical mineral acid pretreatment procedure, FFA are esterified to the corresponding FAME in the presence of heat, excess methanol, and sulfuric acid catalyst (Ramadhas et al. 2005; Nebel and Mittelbach 2006; Veljkovic et al. 2006; Issariyakul et al. 2007; Kumartiwari et al. 2007; Sahoo et al. 2007; Meng et al. 2008; Naik et al. 2008; Rashid et al. 2008a). The two-step procedure readily accommodates high FFA-containing low-cost feedstocks for the preparation of biodiesel (Canakci and Van Gerpen 1999, 2001, 2003a). For example, the FFA content of crude jatropha oil (*Jatropha curcas*) was lowered to less than 1 from 14 wt.% upon treatment at 60°C for 88 min with 1.43 vol.% H₂SO₄ catalyst and 28 vol.% methanol. Subsequent alkaline-catalyzed (0.5 wt.% KOH) transesterification at 60°C for 30 min with 20 vol.% methanol yielded the corresponding FAME in essentially quantitative yield (Kumartiwari et al. 2007). In another example, the acid value (AV) of tung oil (from the “tung” tree, *Vernicia fordii*) was reduced from 9.55 to 0.72 mg KOH/g using Amberlyst-15 (20.8 wt.%), a heterogeneous acid catalyst, and methanol (7.5:1 molar ratio of methanol to tung oil) at 80°C for 2 h. Tung oil FAME were then prepared with a final purity of 90.2 wt.% employing 0.9 wt.% KOH and methanol (6:1 molar ratio of methanol to tung oil) at 80°C for 20 min (Park et al. 2008a).

Despite the added capital costs associated with production, the integrated two-step process is being increasingly applied to prepare biodiesel from low-cost feedstocks with high FFA content with good results (Lotero et al. 2005). Table 15.5 lists a number of recent examples of biodiesel prepared from feedstocks with high FFA content. Other potential strategies for the production of biodiesel from feedstocks with high FFA content include feedstock purification such as refining, bleaching,

Table 15.5 Examples of biodiesel production from feedstocks high in free fatty acids (FFA)

Feedstock	FFA (wt %)	Pretreatment method	Catalyst for transesterification	R ^a	Yield (wt %)	Ref
<i>Pongamia pinnata</i>	Up to 20	H ₂ SO ₄	KOH	Me	97	Naik et al. 2008
<i>Moringa oleifera</i>	2.9/0.953 ^b	H ₂ SO ₄	NaOCH ₃	Me	n.r. ^c	Rashid et al. 2008a
<i>Jatropha curcas</i>	14/<1	H ₂ SO ₄	KOH	Me	99+	Kumari et al. 2007
<i>Madhuca indica</i>	20	None	<i>Pseudomonas cepacia</i>	Et	96+ ^d	Kumari et al. 2007
<i>Nicotiana tabacum</i>	35/<2	H ₂ SO ₄	KOH	Me	91	Veljkovic et al. 2006
<i>Catophyllium inophyllum</i>	22/<2	H ₂ SO ₄	KOH	Me	85	Sahoo et al. 2007
<i>Zanthoxylum bungeanum</i>	45.5/1.16 ^b	None	H ₂ SO ₄	Me	98	Zhang and Jiang 2008
<i>Hevea brasiliensis</i>	17/<2	H ₂ SO ₄	NaOH	Me	n.r.	Ramadas et al. 2005
<i>Heterotrophic microalgal</i>	8.97 ^b	None	H ₂ SO ₄	Me	n.r.	Miao and Wu 2006
Acid oil	59.3	None	H ₂ SO ₄	Me	95	Haas et al. 2003
Fat from meat and bone meal	11	H ₂ SO ₄	KOH	Me	45.7	Nebel and Mittelbach 2006
Brown grease	40/<1	Diarylammonium catalysts	NaOCH ₃	Me	98+ ^d	Ngo et al. 2008
Waste cooking oil	7.25/<1 ^b	H ₂ SO ₄	NaOH	Me	90 ^d	Meng et al. 2008
Waste fryer grease	5.6	H ₂ SO ₄	KOH	Me/Et	90+	Issariyakul et al. 2007
Tung oil	9.55/0.72 ^b	Amberlyst-15	KOH	Me	90.2	Park et al. 2008a, b
Tall oil	100%	None	HCl	Me	n.r.	Demirbas 2008
Sorghum bug oil	10.5	None	H ₂ SO ₄	Me/Et	77.4/97.6	Mariod et al. 2006

^aR refers to ester head group. *Me methyl, Et ethyl.*^bAcid value (mg KOH/g) was given instead of FFA. In cases where two values are given, the first value is prior to pretreatment and the second is after.^cNot reported^dConversion to esters (wt %) is provided instead of yield

and deodorization to remove FFA and other undesirable materials, if present (Zappi et al. 2003). However, feedstock refining further increases production costs as a result of the additional equipment, time, and manpower that are required. Lastly, the employment of catalysts that are not destroyed by FFA in the production of biodiesel is another alternative to the methods listed above.

Catalysts for Biodiesel Production

Biodiesel is produced commercially using homogenous alkaline base catalysts such as sodium (or potassium) hydroxide or methoxide because the transesterification reaction is generally faster, less expensive, and more complete with these materials than with acid catalysts (Boocock et al. 1996a). The biodiesel industry currently uses sodium methoxide, since methoxide cannot form water upon reaction with alcohol such as with hydroxides (*see* Fig. 15.2; Zhou and Boocock 2006a). Other alkoxides, such as calcium ethoxide, have also effectively catalyzed biodiesel production, albeit with higher methanol and catalyst requirements (Liu et al. 2008). The homogenous alkaline base-catalyzed transesterification reaction is about 4,000 times faster than the corresponding mineral acid-catalyzed process (Reid 1911; Srivastava and Prasad 2000). Furthermore, alkaline base-catalyzed reactions are performed at generally lower temperatures, pressures, and reaction times and are less corrosive to industrial equipment than mineral acid-catalyzed methods. Therefore, fewer capital and operating costs are incurred by biodiesel production facilities in the case of the alkaline base-catalyzed transesterification method (Freedman et al. 1986; Demirbas 2008). However, the homogenous acid-catalyzed reaction holds an important advantage over the base-catalyzed method in that the performance of acid catalysts is not adversely influenced by the presence of FFA. In fact, acids can simultaneously catalyze both esterification and transesterification (Haas et al. 2003; Lotero et al. 2005; Miao and Wu 2006; Demirbas 2008; Zhang and Jiang 2008). For instance, FAME were prepared from acid oil, which consisted of 59.3 wt.% FFA, by mineral acid-catalyzed transesterification at 65°C for 26 h with H₂SO₄ (1.5:1 molar ratio of catalyst to oil) and methanol (15:1 molar ratio of methanol to oil) in 95 wt.% purity. The remaining products consisted of FFA (3.2 wt.%), TAG (1.3 wt.%), and DAG (0.2 wt.%) (Haas et al. 2003).

A wide range of catalysts may be used for biodiesel production, such as homogenous and heterogeneous acids and bases, sugars, lipases, ion exchange resins, zeolites, and other heterogeneous materials. A recent exotic example is that of KF/Eu₂O₃, which was used to prepare rapeseed oil FAME with 92.5% conversion efficiency (Sun et al. 2008). In general, acids are more appropriate for feedstocks high in FFA content. Homogeneously catalyzed reactions generally require less alcohol, shorter reaction times, and more complicated purification procedures than heterogeneously catalyzed transesterification reactions. Heterogeneous lipases are generally not tolerant of methanol, so production of ethyl or higher esters is more common with enzymatic methods. For a recent comprehensive review on catalysts used for biodiesel preparation, please *see* Narasimharao et al. (2007).

Noncatalytic transesterification of biodiesel may be accomplished in supercritical fluids such as methanol, but a very high pressure (45–65 bar), temperature (350°C), and amount of alcohol (42:1 molar ratio) are required (Saka and Kusdiana 2001; Demirbas 2003, 2005, 2006; Kusdiana and Saka 2004). Advantages of supercritical transesterification versus various catalytic methods are that only very short reaction times (4 min, for instance) are needed, and product purification is simplified because there is no need to remove a catalyst. Disadvantages of this approach include limitation to a batch-wise process, elevated energy and alcohol requirements during production, and increased capital expenses and maintenance associated with pressurized reaction vessels (Saka and Kusdiana 2001; Demirbas 2003, 2005, 2006; Kusdiana and Saka 2004).

Alcohols Used in the Production of Biodiesel

As previously mentioned, methanol is the most common alcohol used in the production of biodiesel. Other alcohols may also be used in the preparation of biodiesel, such as ethanol, propanol, iso-propanol, and butanol (Freedman et al. 1984, 1986; Schwab et al. 1987; Ali and Hanna 1994; Lee et al. 1995; Peterson et al. 1996; Foglia et al. 1997; Wu et al. 1998; Nimcevic et al. 2000; Canakci and Van Gerpen 2001; Lang et al. 2001; Encinar et al. 2002, 2007; Zhou et al. 2003; Wang et al. 2005; Mariod et al. 2006; Meneghetti et al. 2006; Yao and Hammond 2006; Dantas et al. 2007; Issariyakul et al. 2007; Kulkarni et al. 2007; Alamu et al. 2008; Domingos et al. 2008; Georgogianni et al. 2008; Lima et al. 2008; Rodrigues et al. 2008; Stavarache et al. 2008). Ethanol is of particular interest primarily because it is less expensive than methanol in some regions of the world, and biodiesel prepared from bio-ethanol is completely bio-based. Butanol may also be obtained from biological materials (Qureshi et al. 2008a, b), thus yielding completely bio-based biodiesel as well. Methanol, propanol, and iso-propanol are normally produced from hydrocarbon materials such as methane obtained from natural gas in the case of methanol.

Methanolysis. The classic reaction conditions for the methanolysis of vegetable oils or animal fats are 6:1 molar ratio of methanol to oil, 0.5 wt.% alkali catalyst (with respect to TAG), 600+ rpm, 60°C reaction temperature, and 1 h reaction time to produce FAME and glycerol (Freedman et al. 1984). A number of recent studies described optimal reaction conditions for biodiesel production from various feedstocks using response surface methodology (RSM). Parameters that are normally optimized to produce the highest yield of biodiesel include catalyst type and amount, reaction time and temperature, amount of alcohol, and/or agitation intensity. Please refer to Table 15.6 for a summary of recent examples of biodiesel process optimization employing RSM. In addition to the studies listed in Table 15.6 are the following: Park et al. (2008a), Rashid and Anwar (2008a), Yuan et al. (2008), Wang et al. (2008), Cetinkaya and Karaosmanoglu (2004), Antolin et al. 2002. A representative example of reaction conditions optimized by RSM is the work of

Table 15.6 Recent examples of optimization of reaction conditions^a for production of biodiesel from various feedstocks using response surface methodology

Feedstock oil or fat	Catalyst (wt %)	Temp (°C)	MeOH	rpm	Time (min)	Yield (wt.%)	Ref
Pork lard	1.26 KOH	65	7.5:1	n.r. ^b	20	97.8 ^c	Jeong et al. 2009
Rapeseed	1.0 KOH	65	6:1	600	120	95–96	Rashid and Anwar 2008a
Sunflower	1.0 NaOH	60	6:1	600	120	97.1	Rashid et al. 2008b
Safflower	1.0 NaOCH ₃	60	6:1	600	120	98	Rashid and Anwar 2008b
Jajoba	1.35 KOH	25	6:1	600	60	83.5	Bouaid et al. 2007
Rice bran	0.75 NaOH	55	9:1	n.r.	60	90.2	Sinha et al. 2008
Waste cooking oil	1.0 NaOH	50	9:1	n.r.	90	89.9 ^c	Meng et al. 2008
<i>Jatropha curcas</i>	0.55 KOH	60	5:1	n.r.	24	99	Kumartiwari et al. 2007
<i>Madhuca indica</i>	0.70 KOH	60	6:1	n.r.	30	98	Ghadge and Raheman 2006
<i>Pongamia pinnata</i>	1.0 KOH	65	6:1	360	180	97–98	Meher et al. 2006b
<i>Brassica carinata</i>	1.2 KOH	25	6:1	600	60	97	Vicente et al. 2005
Used frying oil	1.1 NaOH	60	7:1	600	20	88.8	Leung and Guo 2006
canola	1.0 NaOH	40	6:1	600	60	93.5	Leung and Guo 2006
Cottonseed	1.07 KOH	25	20:1 ^d	600	30	98	Joshi et al. 2008a, b
<i>Raphanus sativus</i>	0.6 NaOH	38	11.7:1 ^d	n.r.	60	99.1	Domingos et al. 2008

^aTemp temperature of the reaction, MeOH mole ratio of methanol to oil, rpm (rotations per min) agitation intensity, time how long the reaction was conducted

^bNot reported

^cConversion to esters (wt %) is provided instead of yield

^dEthanol was used to produce the corresponding ethyl esters

Kumartiwari et al. (2007) in which *Jatropha curcas* oil FAME were produced (after acid pretreatment) using 0.55 wt.% KOH, 60°C reaction temperature, 5:1 molar ratio of methanol to oil, and 24 min reaction time to provide biodiesel in 99% yield. The reaction parameters do not vary by a significant amount from the classic reaction conditions elucidated by Freedman et al. 1984.

The transesterification reaction employing methanol commences as two immiscible phases as a result of the very low solubility of TAG in methanol (Boocock et al. 1998; Stavarache et al. 2003, 2008; Zhou et al. 2003; Mao et al. 2004; Mahajan et al. 2006, 2007; Zhou and Boocock 2006a, b; Doell et al. 2008). Illustrative of this point is the fact that only 7.5 g of soybean oil is soluble in 1 L of methanol at 30°C (Boocock et al. 1996b). The polar homogenous alkali catalyst is exclusively dissolved in the polar methanol phase at the beginning of the reaction and does not come into contact with the TAG phase unless sufficient agitation is introduced. Stirring of sufficient magnitude causes TAG to transport into the methanol phase where it is rapidly converted into FAME and glycerol, as depicted in Fig. 15.1. The rate at which FAME are produced during the transesterification reaction is thus controlled by mass-transfer limitations, which results in a lag time before conversion to FAME begins (Boocock et al. 1998; Zhou and Boocock 2006b; Doell et al. 008). Once the DAG and MAG intermediates are formed in sufficient quantity during the transesterification reaction, they serve as surfactants that improve mass transfer of TAG into the methanol phase. The reaction eventually transforms into another biphasic system that consists of ester-rich (FAME) and glycerol-rich phases. The alkali catalyst is preferentially soluble in the more polar glycerol-rich phase, which may result in a retardation of the rate of reaction (Mao et al. 2004). The glycerol-rich phase facilitates purification by settling to the bottom of the reaction vessel when agitation is ceased.

As a result of the biphasic nature of the reaction mixture, there is a lag time at the beginning of the methanolysis reaction before FAME begins to form, after which the reaction speeds up, but then quickly decelerates (Freedman et al. 1984; Darnoko and Cheryan 2000). Addition of co-solvents such as tetrahydrofuran (THF) significantly accelerates the production of FAME as a result of the formation of a monophasic as opposed to a biphasic reaction mixture (Boocock et al. 1998; Mahajan et al. 2006; Doell et al. 2008). However, the molar ratio of methanol to oil must be increased to at least 25:1, which results in additional solvent recovery during purification. Other possibilities for accelerating the methanolysis reaction are microwave (Breccia et al. 1999) or ultrasonic (Stavarache et al. 2003, 2008) irradiation.

Ethanolysis. The classic conditions for ethanolysis of vegetable oils or animal fats are 6:1 molar ratio of ethanol to oil, 0.5 wt.% catalyst (with respect to TAG), 600+ rpm, 75°C reaction temperature, and 1 h reaction time to produce fatty acid ethyl esters (FAEE) and glycerol (Freedman et al. 1984). Ethyl esters have been prepared from a number of feedstocks for use or evaluation as potential biodiesel fuels (Schwab et al. 1987; Peterson et al. 1996; Foglia et al. 1997; Wu et al. 1998; Nimcevic et al. 2000; Lang et al. 2001; Lee et al. 2002; Encinar et al. 2002, 2007; Zhou et al. 2003; Mariod

et al. 2006; Meneghetti et al. 2006; Dantas et al. 2007; Issariyakul et al. 2007; Kucek et al. 2007; Kulkarni et al. 2007; Kumari et al. 2007; Moreira et al. 2007; Alamu et al. 2008; Domingos et al. 2008; Georgogianni et al. 2008; Hamad et al. 2008; Joshi et al. 2008, 2009; Lima et al. 2008; Rodrigues et al. 2008; Rosa et al. 2008; Stavarache et al. 2008). In addition, mixtures of methyl and ethyl esters have been reported whereby the transesterification reaction was conducted with both methanol and ethanol (Issariyakul et al. 2007; Kulkarni et al. 2007; Joshi et al. 2009). As in the case of methanolysis, the ethanolysis reaction has been optimized using RSM (Kucek et al. 2007; Domingos et al. 2008; Joshi et al. 2008). Please refer to Table 15.6 for two recent examples from the literature. A representative example is that of the ethanolysis of crude *Raphanus sativus* oil (Domingos et al. 2008) in which 0.60 wt.% NaOH, 11.7:1 molar ratio of ethanol to oil, 38°C reaction temperature, and a 1-h reaction time afforded the corresponding FAEE in 99.1% yield. The reaction temperature and amount of ethanol in this case varied considerably from the conditions initially reported by Freedman et al. (1984).

Ethanolysis proceeds at a slower rate than methanolysis because of the higher reactivity of the methoxide anion in comparison to ethoxide. As the length of the carbon chain of the alkoxide anion increases, a corresponding decrease in nucleophilicity occurs, resulting in a reduction in the reactivity of ethoxide in comparison to methoxide (Sridharan and Mathai 1974). An example of this phenomenon is the transesterification (at 25 and 75°C) of canola oil with a 1:1 mixture of ethanol to methanol (to provide an overall molar ratio of alcohol to oil of 6:1) that results in 50% more methyl than ethyl esters (Kulkarni et al. 2007). Another example is the transesterification of canola oil at 25 and 75°C with a 1:1 mixture of ethanol to methanol that results in methyl to ethyl ester ratios of 2.7:1 and 1.3:1, respectively (Joshi et al. 2009). These results indicate that FAME are preferentially formed at both ambient and elevated reaction temperatures, but the preference is diminished at elevated temperatures. Even though the formation of FAEE is comparatively slow, the overall rate of formation of esters is faster than with methanol alone due to the better solubility of TAG in a mixture of methanol and ethanol, which results in a reduction of mass transfer limitations (Kulkarni et al. 2007). For example, ultrasonically assisted transesterification of *Melia azedarach* (syringa) oil is complete after 40 and 20 min and with methanol and ethanol respectively (Stavarache et al. 2008).

The base-catalyzed formation of FAEE is more complicated than the production of FAME. Specifically, the formation of stable emulsions during ethanolysis is problematic during subsequent purification (Korus et al. 1993; Zhou et al. 2003; Zhou and Boocock 2006a). In the case of methanolysis, these emulsions quickly and easily separate to form a lower glycerol-rich and an upper FAME-rich phase after agitation of the reaction has ceased. In ethanolysis, these emulsions are much more stable and complicate separation and purification of biodiesel (Zhou et al. 2003; Zhou and Boocock 2006a). Ethanol is less polar than methanol, so it is slightly more miscible with TAG at ambient temperature than methanol, but mechanical agitation during the transesterification reaction is once again required to facilitate sufficient mass transfer between phases (Kulkarni et al. 2007).

Butanolysis. The classic conditions for butanolysis of vegetable oils or animal fats are 6:1 molar ratio of butanol to oil, 0.5 wt.% catalyst (with respect to TAG), 600+ rpm, 114°C reaction temperature, and 1 h reaction time to produce fatty acid butyl esters and glycerol (Freedman et al. 1984). Butyl esters have been prepared from a variety of feedstocks for use or evaluation as potential biodiesel fuels (Freedman et al. 1986; Schwab et al. 1987; Ali and Hanna 1994; Foglia et al. 1997; Nimcevic et al. 2000; Lang et al. 2001; Zhou and Boocock 2006a, b; Rodrigues et al. 2008). To date, the butanolysis reaction has not yet been optimized by RSM.

Butanol is completely miscible with vegetable oils and animal fats due to its lower polarity versus methanol and ethanol (Boocock et al. 1996a). Consequently, transesterification reactions employing butanol are monophasic throughout (Zhou and Boocock 2006a, b). The monophasic nature of butanolysis influences the rate and extent of the reaction. There are no mass transfer limitations in the case of butanolysis, since all reactants and catalysts are contained in a single phase. As a result, the initial rate of butanolysis is considerably faster than that of methanolysis. For example, the yield of esters after 1 min is 88 wt.% in the case of butanolysis (114°C reaction temperature) but only 78 wt.% for methanolysis (60°C; Schwab et al. 1987). Another study found that butanolysis (30°C) was 50% complete after only 15 s of reaction, and 60% and 63.5% complete after 90 and 150 s, respectively. However, methanolysis (40°C) was only 55% complete after 10 min (Freedman et al. 1986). In a more recent example, 15.4 wt.% of TAG remained after 3 min of butanolysis as opposed to 84.4 wt.% in the case of methanolysis (Zhou and Boocock 2006a). At up to 40% conversion to alkyl esters, methanolysis is 12–16 times slower than butanolysis if lag time in the case of methanolysis is ignored and even slower if it is not ignored (Boocock et al. 1996a; Freedman et al. 1986). The difference in reactivity would be even more striking had the reactions in the above example been performed at similar temperatures (methanolysis was conducted at 40°C as opposed to 30°C for butanolysis).

Because the reactions depicted in Fig. 15.1 for the conversion of TAG into alkyl esters are reversible, the monophasic nature of butanolysis affects the extent of reaction. In the case of methanolysis, glycerol separation from FAME severely curtails the unwanted reverse reactions. In the case of butanolysis, the reverse reactions are more likely to occur because all materials are in contact throughout the reaction. The monophasic nature of butanolysis also complicates purification of the resultant butyl esters, as gravity separation of glycerol at the conclusion of the reaction is not possible. The weaker nucleophilicity of butoxide versus methoxide is another factor that affects the extent of reaction. Although butanolysis proceeds at a faster initial rate than methanolysis, the final conversion to products after 1 h reaction (114°C and 60°C reaction temperatures, respectively) is 96 wt.% versus 98 wt.% for methanolysis (Schwab et al. 1987). In addition, after 1 h (at 23°C), 14.4 wt.% of bound glycerol (TAG + DAG + MAG) remained, whereas only 11.7 and 7.2 wt.% remained in the cases of methanolysis and ethanolysis, respectively (Zhou and Boocock 2006b). In summary, the butanolysis reaction is monophasic throughout, which results in a faster initial rate of reaction but may yield lower overall conversion to butyl esters in comparison to methyl or ethyl esters.

Influence of Biodiesel Composition on Fuel Properties

The fatty ester composition, along with the presence of contaminants and minor components, dictates the fuel properties of biodiesel fuel. Because each feedstock has a unique chemical composition, biodiesel produced from different feedstocks will in turn have different fuel properties. Important properties of biodiesel that are directly influenced by fatty ester composition and the presence of contaminants and minor components include low-temperature operability, oxidative and storage stability, kinematic viscosity, exhaust emissions, cetane number, and energy content. In the context of biodiesel, minor components (Fig.15.3) are defined as naturally occurring species

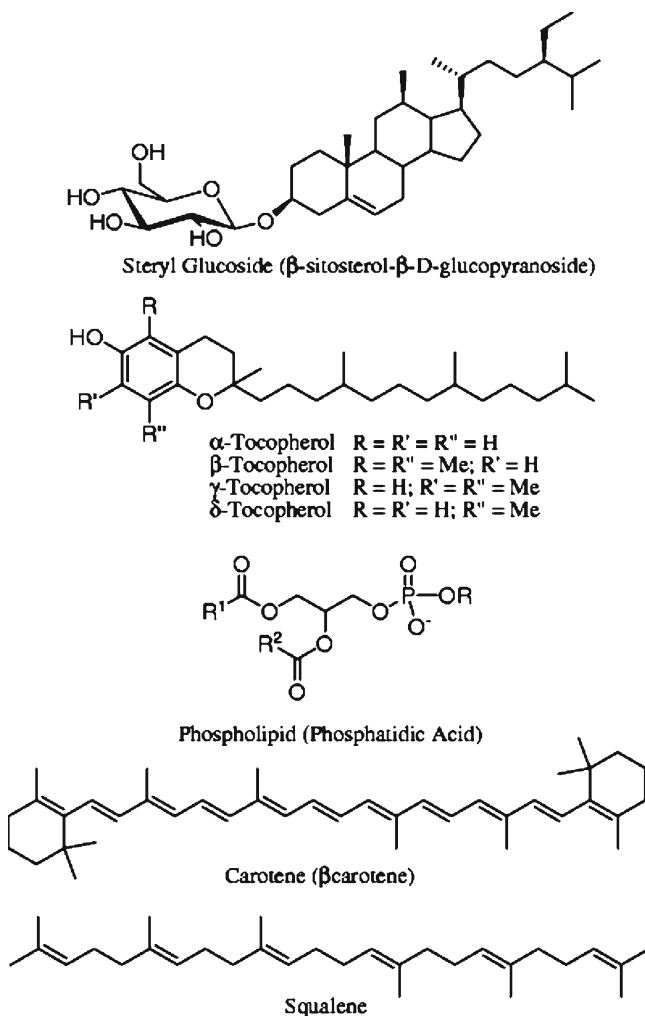


Fig. 15.3 Representative examples steryl glucosides, tocopherols, phospholipids and hydrocarbons that may be found in biodiesel

found in vegetable oils and animal fats and may include tocopherols, phospholipids, steryl glucosides (also called sterol glucosides, steryl glycosides, sterol glycosides, or phytosterols), chlorophyll, fat soluble vitamins, and hydrocarbons (such as alkanes, squalene, carotenes, and polycyclic aromatic hydrocarbons; Gunstone 2004). Contaminants are defined as incomplete or unwanted reaction products, such as FFA, soaps, TAG, DAG, MAG, alcohol, catalyst, glycerol, metals, and water.

Low-temperature operability. Low-temperature operability of biodiesel is normally determined by three common parameters: cloud point (CP; ASTM D2500 or D5773), pour point (PP; ASTM D97 or D5949), and cold filter plugging point (CFPP; ASTM D6371). For a list of low-temperature specifications contained within ASTM D6751 and EN 14214, please refer to Tables 15.2 and 15.3. A fourth parameter, the low-temperature flow test (LTFT; ASTM D4539), is less user friendly and less commonly used. The cloud point is defined as the temperature at which crystal growth is large enough (diameter $\geq 0.5 \mu\text{m}$) to be visible to the naked eye. At temperatures below the CP, larger crystals fuse together and form agglomerations that eventually become extensive enough to prevent pouring of the fluid. The lowest temperature at which the fluid will pour is defined as the PP. The CFPP is defined as the lowest temperature at which a given volume of biodiesel completely flows under vacuum through a wire mesh filter screen within 60 s. The CFPP is generally considered to be a more reliable indicator of low-temperature operability than CP or PP, since the fuel will contain solids of sufficient size to render the engine inoperable due to fuel filter plugging once the CFPP is reached (Dunn and Bagby 1995; Dunn et al. 1996; Park et al. 2008b). It should be noted that it is inappropriate to measure CP, PP, and CFPP of chemically pure compounds (pure methyl oleate, for instance). Instead, determination of melting point (mp) as a means to measure low-temperature operability is appropriate for chemically pure compounds. The CP, PP, CFPP, and LTFT attempt to quantify low-temperature behavior of complex mixtures (such as biodiesel) that are composed of constituents that generally exhibit a relatively wide range of mp (or freezing points, fp). For instance, in the case of CP, it is very likely that initial crystal growth that occurs upon cooling of biodiesel to sub-ambient conditions is primarily a result of higher melting constituents undergoing crystallization.

The low-temperature behavior of chemical compounds is dictated by molecular structure. Structural features such as chain length, degree of unsaturation, orientation of double bonds, and type of ester head group strongly influence mp of individual chemical constituents of biodiesel. As can be seen from Table 15.7, as the chain length of saturated FAME is increased from 12 (C12:0, methyl laurate, mp 5°C) to 18 (C18:0, methyl stearate, mp 39°C) carbons, a corresponding increase in mp is observed. With respect to unsaturation, compounds of similar chain length but increasing levels of unsaturation display lower mp, as evidenced by the mp of C18:0 (mp 39°C), C18:1 (methyl oleate, mp -20°C), C18:2 (methyl linoleate, mp -35°C), and C18:3 (methyl linolenate, mp -52°C). The orientation of the double bond(s) is another important factor influencing mp. Nearly all naturally occurring unsaturated fatty acids contain *cis*-oriented double bonds. However, *trans*-isomers may be chemically introduced through catalytic partial hydrogenation.

Table 15.7 Melting point (mp), standard heat of combustion ($\Delta_c H^\circ$), kinematic viscosity (ν , 40°C), oil stability index (OSI, 110°C), cetane number (CN), and lubricity (Lub, 60°C) of fatty acid alkyl esters (FAAE) commonly found in biodiesel

FAAE ^a	mp ^b (°C)	$\Delta_c H^\circ$ (MJ/mol; MJ/kg) ^c	ν^d (mm ² /s)	OSI ^e (h)	CN ^f	Lub ^g (μm)
C12:0 ME	5	8.14/37.97	2.43	>40	67	416
C12:0 EE	-2		2.63	>40		
C14:0 ME	19	10.67/39.45	3.30	>40		353
C14:0 EE	12		3.52	>40		
C16:0 ME	31	10.67/39.45	4.38	>40	86	357
C16:0 EE	19		4.57		93	
C16:1 ME	-34	10.55/39.30	3.67	2.1	51	246
C16:1 EE	-37					
C18:0 ME	39	11.96/40.07	5.85	>40	101	322
C18:0 EE	32		5.92	>40	97	
C18:0 BE	28		7.59		92	
C18:1 ME	-20	11.89/40.09	4.51	2.5	59	290
C18:1 EE	-20		4.78	3.5	68	
C18:1 BE	-26		5.69		62	303
C18:2 ME	-35	11.69/39.70	3.65	1.0	38	236
C18:2 EE			4.25	1.1	40	
C18:3 ME	-52	11.51/39.34	3.14	0.2	23	183
C18:3 EE			3.42	0.2	27	

^aRefer to Table 15.1 for explanation of notation. *ME* methyl ester, *EE* ethyl ester, *BE* butyl ester

^bValues are from Anonymous (2007) or Knothe (2008)

^cValues from Moseret et al. (2009)

^dValues from Knothe and Steidley (2005a)

^eValues from Knothe (2008) or Moser (2008b)

^fValues from Knothe et al. (2003) or Knothe (2008)

^gValues from Knothe and Steidley (2005b)

Constituents that contain *trans*- double bonds exhibit higher mp than the corresponding *cis*- isomers. For example, the mp of methyl elaidate (methyl 9*E*-octadecenoate) is 13°C (Anonymous 2007), which is considerably higher than the *cis* isomer (methyl oleate, mp -20°C). With respect to ester head group, the mp of FAAE is generally lower with larger alkyl head groups up to about eight carbons. For instance, methyl, ethyl, and butyl stearates have mp of 39°C, 32°C, and 28°C, respectively. Refer to Table 15.8 for a summary of the effects of various structural features on the low-temperature operability of FAAE.

Applying the above trends to biodiesel, one can see a pronounced effect in the case of ester head group: the CP of soybean oil methyl, ethyl, isopropyl, and 2-butyl esters is -2, -2, -9 and -12°C, respectively (Lee et al. 1995). The CP of beef tallow methyl, ethyl, propyl, and butyl esters is 17°C, 15°C, 12°C, and 9°C, respectively (Foglia et al. 1997). The examples of soybean oil (14% saturated FAAE) and tallow (25% saturated FAAE) esters are illustrative of the influence of double bond content on low-temperature operability: soybean oil alkyl esters contain a lower amount of saturated FAAE than do tallow esters, which results in superior low-temperature properties. Another example of the influence of saturated FAME on low-temperature

Table 15.8 Effect of fatty acid alkyl ester structural features on melting point (mp), oxidative stability (OSI), kinematic viscosity (ν), standard heat of combustion ($\Delta_c H^\circ$), cetane number (CN), and lubricity (Lub)

Structural feature	mp	OSI	ν	$\Delta_c H^\circ$	CN	Lub
Chain length	↑ ^a	↑	↑	↑	↑	↓
Number of double bonds	↓	↓	↓	↓	↓	↓
<i>cis</i> double bond(s) ^b	↓	↓	↓	— ^c	? ^d	? ^d
Larger ester head groups	↓	— ^c	↑	↑	— ^c	— ^c

^a↑ higher numeric value, ↓ lower numeric value. For mp, ν , and lubricity, ↓ indicates that the property is improved. For OSI, $\Delta_c H^\circ$, and CN, ↓ indicates that the property is negatively impacted

^bIn comparison to the corresponding *trans* isomer

^cNegligible or no impact

^dEffect has not been reported

operability is that of soybean and palm oil FAME (SME and PME), which have PP values of 0°C and 18°C, respectively, and CFPP of −4°C and 12°C, respectively (Moser 2008a). The influence of double bond orientation is evidenced by comparison of the CP and PP values of SME (0°C and −2°C) with *trans*-containing partially hydrogenated SME (3°C and 0°C; Moser et al. 2007).

Oxidative stability. Oxidative stability of biodiesel is determined through measurement of the oil stability index (OSI) by the Rancimat method (EN 14112). The Rancimat method indirectly measures oxidation by monitoring the gradual change in conductivity of a solution of water caused by volatile oxidative degradation products that have been transported via a stream of air (10 L/h) from the vessel (at 110°C) containing the biodiesel sample. The OSI is mathematically determined as the inflection point of a computer-generated plot of conductivity ($\mu\text{S}/\text{cm}$) of distilled water versus time (h). The units for OSI are normally expressed in hours. Biodiesel fuels with longer OSI times are more stable to oxidation than samples with shorter values. For a list of oxidative stability specifications contained within ASTM D6751 and EN 14214, please refer to Tables 15.2 and 15.3. The American Oil Chemists' Society (AOCS) official method Cd 12b-92 is nearly identical to EN 14112 and provides essentially interchangeable data.

Oxidation initiates in the case of lipids at methylene carbons allylic to sites of unsaturation (Frankel 2005). Autoxidation of lipids, including biodiesel, produces free radicals through hydrogen abstraction in the presence of various initiators such as light, heat, peroxides, hydroperoxides, and transition metals (Fig. 15.4). These free radicals further react exothermically with molecular oxygen to produce peroxides, which in turn react with unoxidized lipids to produce additional free radicals (Frankel 2005). Generally, the rate-limiting step in the autoxidation of lipids is initial hydrogen abstraction. Accelerated methods to determine oxidative stability of lipids, such as EN 14112 or AOCS Cd 12b-92, use elevated temperatures to greatly accelerate initial hydrogen abstraction. The EN 14112 method increases the amount of oxygen available to react with lipid-free radicals by pumping air at a constant rate through the sample. Products that ultimately form through oxidation of lipids may include aldehydes, shorter-chain fatty acids, other oxygenated species

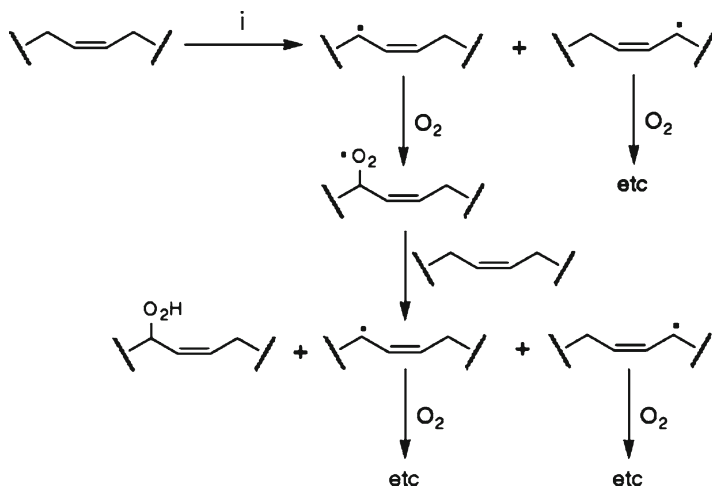


Fig. 15.4 Simplified pathway of initial lipid autoxidation (*i* initiator)

(such as ketones), and polymers (Frankel 2005). The rate of autoxidation is dependant on the number and location of methylene-interrupted double bonds contained within FAAE. Materials that contain more methylene carbons allylic to sites of unsaturation (such as polyunsaturated esters) are particularly vulnerable to autoxidation, as evidenced by the relative rates of oxidation of the unsaturates: 1, 41, and 98 for ethyl esters of oleic, linoleic, and linolenic acids (Holman and Elmer 1947). Not only will easily oxidized biodiesel fail oxidative stability requirements contained within ASTM D6751 and EN 14214 (*see* Tables 15.2 and 15.3), but oxidative degradation negatively impacts AV and kinematic viscosity (Plessis et al. 1985; Mittelbach and Gangl 2001; Bondioli et al. 2003), both of which are specified in ASTM D6751 and EN 14214.

Structural features such as degree of unsaturation, double bond orientation, chain length, and type of ester head group influence the OSI of FAAE. Esters that are otherwise similar but contain a greater number of methylene-interrupted double bonds undergo oxidative degradation at progressively faster rates (Holman and Elmer 1947; Knothe and Dunn 2003; Frankel 2005; Knothe 2008; Moser 2009a), which is confirmed through examination of the OSI values (Table 15.7) of FAME of stearic (>40 h), oleic (2.5 h), linoleic (1.0 h), and linolenic (0.2 h) acids. Applying these results to biodiesel, superior oxidative stability is expected from biodiesel fuels prepared from feedstocks relatively high in saturated fatty acid content or relatively low in polyunsaturated fatty acid content. For example, PME (50 wt.% saturated FAME, 11% polyunsaturated FAME, Table 15.1) are considerably more stable to oxidation than SME (15% saturates, 62% polyunsaturates) according to EN 14112 (Moser 2008a; Park et al. 2008b).

Double bond orientation (*cis* versus *trans* isomers) also impacts oxidative stability, as seen by the contrasting OSI values of FAME of oleic (2.5 h) and elaidic (7.7 h) acids (Moser 2009a). This is not surprising, as it is known that *trans* isomers

are generally thermodynamically more stable than the corresponding *cis* isomers. Alkyl substituents are separated by a greater distance in *trans* than they are in *cis* isomers, thus keeping the influence of steric hinderance to a minimum. Applying these observations to biodiesel, fuels that contain at least some *trans* constituents exhibit enhanced stability to oxidation according to EN 14112 than biodiesel fuels that contain a similar number of entirely *cis* double bonds. According to a recent study (Moser et al. 2007), partially hydrogenated SME (7.7% *trans* FAME, 16.4% saturated FAME, 44.7% polyunsaturated FAME) yielded an OSI value of 6.2 h (110°C, AOCS Cd 12b-92) versus 2.3 h for SME (0% *trans*, 16.9% saturated, 59.8% polyunsaturated).

Due to the nature of the AOCS and EN 14112 methods, a bias is introduced whereby compounds of higher molecular weight (MW; i.e., longer chain length) will appear to be more stable to oxidation than compounds of similar double bond content but lower MW. The parameters of the method are the cause of this bias: a specified mass (3.0 g in the case of EN 14112) of material is required as opposed to a specified molar amount. Compounds of longer chain length will have fewer molecules in the experimental sample, which will reduce the number of double bonds available for oxidation versus molecules of similar double bond content but with lower MW. Illustrative of this point are the FAME of palmitoleic (MW 268.44), oleic (MW 296.49), and gondoic (C20:1; MW 324.54) acids, which have similar double bond content but increasing OSI values of 2.1, 2.5, and 2.9 h, respectively (Table 15.7 and Moser 2009a). Concomitant with these results is the variation in ester head group among otherwise similar compounds. Ethyl oleate (MW 310.52) appears to have greater oxidative stability than methyl oleate, as evidenced by OSI values of 3.5 and 2.5 h, respectively. The effect of ester head group on OSI is less pronounced for polyunsaturated compounds such as methyl and ethyl linoleates and methyl and ethyl linolenates. The increased double bond content of these materials results in an accelerated rate of oxidation that essentially masks the aforementioned MW effect on OSI (Moser 2009a). Applying these results to biodiesel, one may expect improved oxidative stability according to EN 14112 with the use of FFAE (or larger ester head groups) as opposed to FAME with feedstocks not particularly high in polyunsaturated FAME content. Analogously, biodiesel produced from feedstocks with generally longer chain lengths but similar double bond content may also be more stable to oxidation according to EN 14112. To date, these suppositions remain unexplored in the scientific literature. Refer to Table 15.8 for a summary of the influence of various structural features on oxidative stability of FFAE.

Oxidative stability and low-temperature operability are normally inversely related: structural factors that improve oxidative stability adversely influence low-temperature operability and vice versa. Ester head group is the only exception to this relationship, as larger ester head groups tend to improve both low-temperature performance and oxidative stability.

Kinematic viscosity. Kinematic viscosity is the primary reason why biodiesel is used as an alternative fuel instead of neat vegetable oils or animal fats. The high kinematic viscosities of vegetable oils and animal fats ultimately lead to operational problems such as engine deposits when used directly as fuels (Knothe and

Steidley 2005a). The kinematic viscosity of biodiesel is approximately an order of magnitude less than typical vegetable oils or animal fats and is slightly higher than petrodiesel. For instance, the kinematic viscosities (40°C) of soybean oil, SME, and ULSD are 31.49, 4.13, and 2.32 mm²/s, respectively (Moser et al. 2008, 2009). Kinematic viscosity is determined following ASTM D445 at 40°C. For a list of kinematic viscosity specifications contained within ASTM D6751 and EN 14214, please refer to Tables 15.2 and 15.3. Several structural features influence the kinematic viscosities of FFAE, such as chain length, degree of unsaturation, double bond orientation, and type of ester head group. As seen from Table 15.7, factors such as longer chain length and larger ester head group result in increases in kinematic viscosity. For example, FAME of lauric, myristic, palmitic, and stearic acids have kinematic viscosities of 2.43, 3.30, 4.38, and 5.85 mm²/s, respectively. Furthermore, methyl, ethyl, and butyl esters of stearic acid exhibit kinematic viscosities of 5.85, 5.92, and 7.59 mm²/s, respectively. Increasing the degree of unsaturation results in a decrease in kinematic viscosity, as evidenced by the methyl esters of stearic (5.85 mm²/s), oleic (4.51 mm²/s), linoleic (3.65 mm²/s), and linolenic (3.14 mm²/s) acids. Double bond orientation also impacts kinematic viscosity, as seen by comparison of methyl elaidate (5.86 mm²/s) and methyl linoelaidate (5.33 mm²/s) to the corresponding *cis* isomers (methyl oleate and linoleate; Knothe and Steidley 2005a). Refer to Table 15.8 for a summary of the effects of various structural features on kinematic viscosity of FFAE.

The influence of ester head group is indicated by comparison of the kinematic viscosities ethyl and isopropyl esters of tallowate (5.2 and 6.4 mm²/s, respectively) (Wu et al. 1998). The methyl and ethyl esters of canola oil have kinematic viscosities of 3.9 and 4.4 mm²/s, respectively (Kulkarni et al. 2007). The influence of saturated FAME on viscosity is illustrated by comparison of SME (4.12 mm²/s) to PME (4.58 mm²/s; Moser 2008a). The impact of double bond orientation is demonstrated by comparison of SME to partially hydrogenated SME (5.0 mm²/s; Moser et al. 2007).

Exhaust emissions. Exhaust emissions regulated by title 40, section 86 of the U.S. Code of Federal Regulations (CFR) include oxides of nitrogen (NO_x), PM (particulate matter), THC (total hydrocarbons), and carbon monoxide (CO). Procedures outlined in title 40, section 86, subpart N of the CFR describe how regulated exhaust emissions are measured. Neither ASTM D6751 nor EN 14214 contains specifications relating to exhaust emissions. Combustion of biodiesel (B100) in diesel engines results in an average increase in NO_x exhaust emissions of 12% and decreases in PM, THC, and CO emissions of 48%, 77%, and 48%, respectively, relative to petrodiesel (Graboski and McCormick 1998; Choi and Reitz 1999; EPA 2002; Song et al. 2002; Hess et al. 2005, 2007). For B20 blends of SME in petrodiesel, NO_x emissions are increased by 0–4% versus neat petrodiesel, but PM, THC, and CO emissions are reduced by 10%, 20%, and 11%, respectively (Hess et al. 2007; EPA 2002). Another study demonstrated that combustion of B5 and B20 blends of ULSD in a modern diesel engine equipped with EGR showed no significant difference in NO_x emissions from that of neat ULSD (Williams et al. 2006).

The increase in NO_x emissions with combustion of biodiesel and in some cases biodiesel–petrodiesel blends is of concern in environmentally sensitive areas such as national parks and urban centers. Reduction of smog-forming NO_x exhaust emissions to levels equal to or lower than those observed for petrodiesel is essential for universal acceptance of biodiesel.

The Zeldovich (thermal) and Fenimore (prompt) mechanisms are two pathways by which NO_x may be produced during combustion of biodiesel or petrodiesel (Miller and Bowman 1989; McCormick et al. 2003; Hess et al. 2005; Fernando et al. 2006). Thermal NO_x is formed at high temperatures in the combustion chamber of diesel engines when atmospheric molecular oxygen (O_2) combines with atmospheric molecular nitrogen (N_2). To reduce the rate of NO_x formation by this mechanism, the flame temperature inside of the combustion chamber must be reduced (Fernando et al. 2006). Prompt NO_x is produced by a complex pathway whereby hydrocarbon radicals react with N_2 to form species that subsequently react with O_2 to form NO_x . However, prompt NO_x has only been detected in the laboratory, and none has been observed during combustion of petrodiesel in diesel engines (Newhall and Shahed 1971). Consequently, the Zeldovich mechanism is responsible for NO_x exhaust emissions during combustion of petrodiesel (Newhall and Shahed 1971; Heywood 1998) and biodiesel (Fernando et al. 2006; Ban-Weiss et al. 2007) in diesel engines. A third mechanism largely irrelevant to biodiesel is the fuel NO_x pathway whereby nitrogen that is chemically bound to the fuel combines with excess O_2 during combustion (Fernando et al. 2006). Biodiesel does not normally contain nitrogen, so NO_x formation by the fuel NO_x mechanism is negligible.

Several engine or after-treatment technologies, such as EGR, SCR, diesel oxidation catalysts, and NO_x or particulate traps, may reduce NO_x exhaust emissions of biodiesel and blends with petrodiesel (McGeehan 2004). A factor influencing NO_x emissions is the chemical nature of FFAE that constitute biodiesel. Specifically, decreasing the chain length and/or increasing the number of double bonds (i.e., higher iodine value (IV)) of FFAE results in an increase in NO_x emissions (McCormick et al. 2001; Szybist et al. 2005; Knothe et al. 2006). The chemical composition of biodiesel varies according to the feedstock from which it is prepared. As a result, biodiesel obtained from feedstocks of significantly different compositions will exhibit different NO_x exhaust emissions behavior, as evidenced by a comparison of beef tallow FAME (IV 54; +0.0% increase in NO_x over petrodiesel), lard FAME (IV 63; +3.0%), chicken fat FAME (IV 77; +2.4%), and SME (IV 129; +6.2%; Wyatt et al. 2005). Enrichment of SME with up to 76% methyl oleate resulted in the elimination of the increase in NO_x exhaust emissions normally observed with B20 blends (Szybist et al. 2005). Additional studies have confirmed the influence of differing FAME compositions among various biodiesel fuels on NO_x exhaust emissions of B100 and blends with petrodiesel (Haas et al. 2001; Canakci and Van Gerpen 2003b; Kocak et al. 2007).

Cetane number. Cetane number (CN) is determined in accordance with ASTM D613 and is one of the primary indicators of diesel fuel quality. It is related to the

ignition delay time a fuel experiences once injected into the combustion chamber. Generally, shorter ignition delay times result in higher CN and vice versa. Hexadecane, also known as cetane (trivial name), which gives the cetane scale its name, is the high-quality reference standard with a short ignition delay time and an arbitrarily assigned CN of 100. The compound 2,2,4,4,6,8,8-heptamethylnonane is the low-quality reference standard with a long ignition delay time and an arbitrarily assigned CN of 15 (Knothe et al. 1997). The end points of the CN scale indicate that branching negatively impacts CN. Also influencing CN is chain length, which yields higher CN for longer chain compounds, as seen in Table 15.7 in the case of the FAME of lauric (CN 67), palmitic (CN 86), and stearic (CN 101) acids. Increasing levels of unsaturation negatively impact CN, as evidenced by the FAME of stearic (101), oleic (59), linoleic (38), and linolenic (23) acids. The effect of ester head group on CN is not well-defined. Generally, it would be expected that CN would increase with increasing ester head group size, but this is not necessarily the case. For instance, the CN of methyl, ethyl, propyl, and butyl esters of oleic acid are 59, 68, 59, and 62 (Knothe et al. 2003). The concomitant influences of chain length and unsaturation on CN of biodiesel is evident by comparison of PME (62, DeOliveira et al. 2006) and SME (54, Knothe et al. 2006). Refer to Table 15.8 for a summary of the effects of various structural features on CN of FFAE. For a list of CN specifications contained within ASTM D6751 and EN 14214, please refer to Tables 15.2 and 15.3.

It is important to point out that the cetane index (ASTM D976 or D4737) is not applicable to biodiesel. The cetane index is used in the case of middle distillate fuels (i.e., ULSD) as an estimation of CN and is calculated from density, API gravity, and boiling range. However, biodiesel has dramatically different distillation qualities (e.g., much higher boiling range) than diesel fuels, thus rendering the equation used to calculate the cetane index inapplicable to biodiesel. Nevertheless, the scientific literature contains numerous erroneous examples of calculated cetane index values for biodiesel, which should be viewed with skepticism.

Heat of combustion. Heat of combustion of liquid hydrocarbons is determined according to ASTM D240, but it is not specified in ASTM D6741 nor EN 14214. Heat of combustion is the thermal energy that is liberated upon combustion, so it is commonly referred to as energy content. The heats of combustion of diesel fuel, B20 SME, and SME are 46.7, 43.8, and 38.1 MJ/kg, respectively (DeOliveira et al. 2006). As can be seen, as the biodiesel component in the fuel is increased from 0% to 100%, a concomitant decrease in energy content is observed.

Factors that influence the energy content of biodiesel include the oxygen content and carbon to hydrogen ratio. Generally, as the oxygen content of FFAE is increased, a corresponding reduction in energy content is observed. As seen in Table 15.7, methyl stearate possesses greater energy content (11.96 MJ/mol or 40.07 MJ/kg) than methyl laurate (8.14 MJ/mol or 37.97 MJ/kg). Therefore, the energy content of FFAE is directly proportional to chain length (Knothe 2008; Moser 2009b), since longer-chain FFAE contain more carbons but a similar number of oxygen atoms.

Another important factor is the carbon to hydrogen ratio. Generally, FFAE of similar chain length but lower carbon to hydrogen ratios (i.e., more hydrogen) exhibit greater energy content. For instance, FAME with 18 carbons in the fatty acid backbone include FAME of stearic (largest hydrogen content), oleic, linoleic, and linolenic (smallest hydrogen content) acids. As seen in Table 15.7, methyl stearate possesses the highest energy content and methyl linolenate the lowest. Therefore, lower energy content is obtained from progressively greater levels of unsaturation with otherwise similar chain length. Biodiesel fuels with larger ester head groups (such as ethyl, propyl, or butyl) are expected to have higher energy content as a result of their greater carbon to oxygen ratios. Refer to Table 15.8 for a summary of the effects of various structural features on energy content of FFAE. The heats of combustion of PME (37.86 MJ/kg) and SME (38.09 MJ/kg) are somewhat similar, but PME has a greater amount of saturated (increases energy content) and shorter-chain (reduces energy content) FAME than does SME (DeOliveira et al. 2006).

Lubricity. Lubricity is determined at 60°C in accordance to ASTM D6079 using a high-frequency reciprocating rig instrument. During the course of the experiment, a ball and disk are submerged in a liquid sample and rubbed at 60°C against each other for 75 min at a rate of 50 Hz to generate a wear scar. At the conclusion of the experiment, the maximum length of the wear scar is determined, and this value represents the lubricity of the sample. Shorter wear scar values indicate has superior lubricity versus samples with wear scars. Lubricity is not prescribed in ASTM D6751 or EN 14214. However, the petrodiesel standards, ASTM D975 and EN 590, contain maximum allowable wear scar limits of 520 and 460 μm , respectively. Biodiesel possesses inherently good lubricity, especially when compared to petrodiesel (Drown et al. 2001; Hughes et al. 2002; Goodrum and Geller 2005; Hu et al. 2005; Knothe and Steidley 2005b; Bhatnagar et al. 2006; Moser et al. 2008). For instance, the lubricity of ULSD (without lubricity-enhancing additives) is 551 μm , whereas SME displays a substantially lower value of 162 μm (Moser et al. 2008b). In another example, the lubricities of additive-free ULSD and SME were 651 and 129 μm , respectively (Knothe and Steidley 2005b). As seen from the above two examples, additive-free ULSD fails to satisfy either of the petrodiesel fuel standards (ASTM D975 and EN 590) with respect to lubricity. The poor lubricity of petrodiesel requires lubricity-enhancing additives or blending with another fuel of sufficient lubricity to achieve satisfactory lubricity. The reason for the poor lubricity of ULSD is not exclusively the removal of sulfur-containing compounds during hydrodesulfurization, but rather that polar compounds with other heteroatoms such as oxygen and nitrogen are also removed (Barbour et al. 2000; Dimitrakis 2003; Knothe and Steidley 2005b). As such, biodiesel serves as an excellent lubricity-enhancing additive for ULSD. For example, B2 and B20 blends of SME in ULSD improve lubricity from 551 to 212 and 171 μm , respectively (Moser et al. 2008).

Various structural features such as the presence of heteroatoms, chain length, and unsaturation influence lubricity of biodiesel. Biodiesel fuels possess at least two oxygen atoms that in large part explains their enhanced lubricities over typical

hydrocarbon-containing petrodiesel fuels (Knothe and Steidley 2005b). Another structural feature that is known to influence lubricity is chain length. As seen in Table 15.7, compounds of increasing chain length generally display increasingly superior lubricity values (shorter wear scars), although the correlation is not perfect. For instance, the lubricities of the FAME of lauric, myristic, palmitic, and stearic acids are 416, 353, 357, and 246 μm , respectively. Increasing levels of unsaturation also impart superior lubricity to biodiesel, as evidenced by the FAME of stearic (322 μm), oleic (290 μm), linoleic (236 μm), and linolenic (183 μm) acids. Refer to Table 15.8 for a summary of the effects of various structural features on the lubricities of FFAE. Among biodiesel fuels prepared from a variety of feedstocks, some variability exists between fuels, but they are all essentially in the range of 120–200 μm , which is superior to neat ULSD (without additives; Drown et al. 2001; Bhatnagar et al. 2006; Moser et al. 2008).

Contaminants. Contaminants in biodiesel may include methanol, water, catalyst, glycerol, FFA, soaps, metals, MAG, DAG, and TAG. Methanol contamination in biodiesel is indirectly measured through flash point determination following ASTM D93. Both ASTM D6751 and EN 14214 contain flash point specifications, which can be found in Tables 15.2 and 15.3. If biodiesel is contaminated with methanol, it will fail to meet the minimum flash point specified in relevant fuel standards. Methanol contamination normally results from insufficient purification of biodiesel following the transesterification reaction.

Water is a major source of fuel contamination. While fuel leaving a production facility may be virtually free of water, once it enters the existing distribution and storage network, it will come into contact with water as a result of environmental humidity (Knothe et al. 2005). Water in biodiesel causes three serious problems: corrosion of engine fuel system components, promotion of microbial growth, and hydrolysis of FAME. Consequently, both ASTM D6751 and EN 14214 contain strict limits on water content in biodiesel (see Tables 15.2 and 3). Water may be present in biodiesel as either dissolved or free water. Dissolved water, which is measured by the Karl Fisher titration method in EN 14214 according to EN ISO 12937 (Table 15.3), is water that is soluble in biodiesel. Free water, which is measured by a centrifugation method (ASTM D2709) in ASTM D6751 (Table 15.2), arises after biodiesel becomes saturated with water, resulting in a separate water phase.

Residual homogeneous alkali catalyst may be present in biodiesel through insufficient purification following the transesterification reaction. The catalyst can be detected through combined sodium and potassium determination (EN 14538). Calcium and magnesium, determined according to EN 14538, may also be introduced into biodiesel during purification through washing with hard water or through the use of drying agents (such as magnesium sulfate) that contain these metals. Both ASTM D6751 and EN 14214 contain limits for combined sodium and potassium and combined calcium and magnesium contents. The primary problem associated with metal contamination is elevated ash production during combustion (Knothe et al. 2005). See Tables 15.2 and 3 for the limits for combined sodium and potassium and combined calcium and magnesium specifications found in ASTM D6751 and EN 14214.

Glycerol may be present in insufficiently purified biodiesel, which is determined using ASTM D6584 or EN 14105. Both ASTM D6751 and EN 14214 contain limits for the maximum allowable levels of glycerol permitted in biodiesel (*see* Tables 15.2 and 15.3). Glycerol is suspected of contributing to engine deposit formation during combustion (Knothe et al. 2005).

Bound glycerol (MAG + DAG + TAG) is limited in ASTM D6751 by the total glycerol (total glycerol = free + bound glycerol) specification (Table 15.2) and in EN 14214 (Table 15.3) by individual MAG, DAG, and TAG limits, along with a total glycerol requirement. In the case of ASTM D6751, total glycerol is quantified by GC according to ASTM D6584. Bound glycerol in biodiesel results from incomplete conversion of TAG into FFAE during the transesterification reaction and may cause carbon deposits on fuel injector tips and piston rings of diesel engines during combustion (Knothe et al. 2005). The presence of bound glycerol in biodiesel may also influence low-temperature operability, kinematic viscosity, and lubricity. As in the case of FFA, bound glycerol has a beneficial effect on lubricity, which is apparent from the wear scar data (ASTM D6079) of MAG (139 μm), DAG (186 μm), TAG (143 μm), and methyl oleate (290 μm ; Knothe and Steidley 2005b). However, the presence of saturated bound glycerol (saturated fatty acids bound to glycerol) has a deleterious effect on low-temperature operability of biodiesel due to its very low solubility in FAME. As a result, high temperatures are required to keep them from crystallizing. For example, 0.5 wt.% 1-monostearin and dipalmitin in SME result in increases in CP from -6°C to 22°C and 11°C , respectively (Yu et al. 1998). However, a similar amount of monoolein does not adversely affect CP of biodiesel. In summary, saturated MAG are most problematic with respect to low-temperature operability of biodiesel, followed by saturated DAG and TAG. Lastly, bound glycerol adversely affects kinematic viscosity of biodiesel, as evidenced by the contrasting kinematic viscosities of triolein (32.94 mm^2/s ; Knothe and Steidley 2005a) and methyl oleate (4.51 mm^2/s).

Free fatty acids may be present in biodiesel that was prepared from a feedstock with high FFA content or may be formed during hydrolysis (*see* Fig. 15.2) of biodiesel in the presence of water and catalyst. The presence of FFA is determined by AV according to ASTM D664. Strict upper limits on AV are specified in ASTM D6751 and EN 14214 (*see* Tables 15.2 and 15.3). The presence of FFA in biodiesel may impact other important fuel properties such as low-temperature performance, oxidative stability, kinematic viscosity, and lubricity. In addition to the issues with soap formation, FFA are known to act as pro-oxidants (Miyashita and Takagi 1986; Frankel 2005), so the presence of FFA in biodiesel may also negatively impact oxidative stability. FFA also have significantly higher kinematic viscosities and mp than the corresponding FAME, as evidenced by comparison of oleic acid (19.91 mm^2/s ; 12°C) and methyl oleate (4.51 mm^2/s ; -20°C) (Knothe and Steidley 2005a; Anonymous 2007). In the case of lubricity, FFA are beneficial, as seen by the wear scar data obtained by (ASTM D6079, 60°C) for oleic acid (0 μm ; Knothe and Steidley 2005b) and methyl oleate (290 μm).

Minor components. Minor components in biodiesel may include tocopherols, phospholipids, steryl glucosides, chlorophyll, fat soluble vitamins, and hydrocarbons.

The quantities of these components depend on the feedstock from which the biodiesel is prepared, how the biodiesel is purified, and the degree of pre-processing (refining, bleaching, deodorization, degumming, etc) that is performed on the feedstock prior to transesterification. Many minor components, such as tocopherols (Mittelbach and Schober 2003; Dunn 2005a, b; Liang et al. 2006; Frohlich and Schober 2007; Bostyn et al. 2008; Moser 2008b; Tang et al. 2008), may serve as beneficial antioxidants (Frankel 2005). Chlorophylls, on the other hand, act as sensitizers for photo-oxidation (Gunstone 2004).

The presence of steryl glucosides (*see* Fig.15.3) in biodiesel is problematic because they result in significant low-temperature operability issues at temperatures above CP (Bondioli et al. 2008; Hoed et al. 2008; Moreau et al. 2008). Steryl glucoside precipitates, which form after production of biodiesel, cause engine failure due to fuel filter plugging (Lee et al. 2007; Pfalzgraf et al. 2007). Many steryl glucosides have mp in excess of 240°C and are insoluble in biodiesel (Lee et al. 2007). If present in sufficient concentration, over time, they precipitate to form solids above the CP of the fuel. This problem is especially prevalent in soybean and palm oil-based biodiesel fuels, as the parent oils contain relatively high natural levels of steryl glucosides (Hoed et al. 2008). Steryl glucoside levels are not limited in either ASTM D6751 or EN 14214, but a recent update to ASTM D6751 includes a new test method (ASTM D7501) that is designed to detect the presence of precipitates that form above the CP of the fuel, termed the “cold soak filtration test”. Either GC (Bondioli et al. 2008; Hoed et al. 2008) or high-performance liquid chromatography (Moreau et al. 2008) may be used to detect and quantify the presence of steryl glucosides. Archer Daniels Midland Company recently filed a patent application for a method to remove steryl glucosides whereby the biodiesel sample is cooled, followed by filtration through diatomaceous earth (Lee et al. 2006). Another patent application also describes a process to remove steryl glucosides and other precipitates by cold treatment and filtration (Danzer et al. 2007).

Alternative Feedstocks for Biodiesel Production

A rapid increase in biodiesel production capacity and governmental mandates for alternative fuel usage around the world in the last several years has necessitated the development of alternative biodiesel feedstocks, as it does not appear possible to meet the increased production capacity and mandated demand with traditional sources of biodiesel (soybeans, rapeseed/canola, palm, and various greases and used cooking oils, for instance). The U.S. National Biodiesel Board estimates that biodiesel production capacity for 2009 in the U.S. was 2.69 billion gallons per year in comparison to a mere 23 million gallons per year in 2003. Production capacity in the 27 countries that comprise the European Union in 2009 was estimated by the European Biodiesel Board to be 12.94 billion gallons per yr versus 1.4 billion gallons per yr in 2006. The continued drive for energy sustainability and independence among energy-consuming countries, governmental mandates for alternative fuel

usage and increased global production capacity contribute to the need for alternative sources of biodiesel fuel. For example, the U.S. Energy Independence and Security Act of 2007 includes a renewable fuels standard (RFS2) that mandates that 12.95 billion gallons of renewable fuels are to be blended into energy supplies by the end of 2010, of which 11.35 billion gallons is to be ethanol for use in gasoline. The other 1.6 billion gallons of renewable fuels must be “advanced biofuels,” of which 650 million gallons is to be biomass-based diesel fuel (which includes biodiesel). By 2012, one billion gallons of biomass-based diesel is required under the RFS2 and the total renewable fuel requirement by 2022 will be 36 billion gallons. Lastly, the high prices of commodity vegetable oils and animal fats have made exploration of economical alternative non-food feedstocks an important research topic.

Desirable characteristics of alternative oilseed feedstocks for biodiesel production include adaptability to local growing conditions (rainfall, soil type, latitude, etc.), regional availability, high oil content, favorable fatty acid composition, compatibility with existing farm infrastructure, low agricultural inputs (water, fertilizer, pesticides), definable growth season, uniform seed maturation rates, potential markets for agricultural by-products, and the ability to grow in agriculturally undesirable lands and/or in the off-season from conventional commodity crops. Biodiesel fuels prepared from feedstocks that meet at least a majority of the above criteria will hold the most promise as alternatives to petrodiesel. In general, there are four major biodiesel feedstock categories: algae, oilseeds, animal fats, and various low-value materials such as used cooking oils, greases, and soapstocks. For recent comprehensive reviews on biodiesel produced from algae, please see Meng et al. 2009, Li et al. 2008, and Chisti 2007. Table 15.9 contains reaction conditions for the preparation of biodiesel from alternative feedstocks that are not already listed in Table 15.5. Tables 15.10 and 11 contain the fatty acid profiles of the alternative feedstock oils. Cases where feedstock(s) are missing from Tables 15.9 (or 5) and/or 10 and 11 are the result of a lack of information reported in the scientific literature.

Oilseeds. Traditional oilseed feedstocks for biodiesel production predominately include soybean, rapeseed/canola, palm, corn, sunflower, cottonseed, peanut, and coconut oils. Current agronomic efforts are focused on increasing feedstock supply by increasing yields. Both molecular breeding and biotechnology have the potential to increase the rate of yield growth for many crops, including corn and soybeans. For additional information, see Eathington et al. (2007). Alternative feedstocks normally arise out of necessity from regions of the world where the above materials are not locally available or as part of a concerted effort to reduce dependence on imported petroleum. For instance, non-edible *Jatropha curcas* (Jatropha) oil has recently attracted considerable interest as a feedstock for biodiesel production in India and other climatically similar regions of the world (Mohibbeazam et al. 2005; Kumartiwari et al. 2007; Kalbande et al. 2008). The Jatropha tree is a perennial poisonous oilseed shrub (up to 5 m) belonging to the Euphorbiaceae family whose seeds contain up to 30 wt.% oil that can be found in tropical and subtropical regions such as Central America, Africa, the Indian subcontinent, and other countries in Asia (Mohibbeazam et al. 2005). Because Jatropha oil contains a relatively high percentage of saturated fatty acids (34 wt.%, see Table 15.10), the corresponding

Table 15.9 Production of biodiesel from various alternative feedstocks

Feedstock	Oil (wt.%)	FFA (wt.%)	Catalyst (wt.%)	Temp (°C)	MeOH	Time (min)	Yield (wt.%)	Ref ^a
<i>Melia azedarach</i>	10	2.8	1.0 NaOH	36	9:1 ^b	40	63.8	1
<i>Balanites aegyptiaca</i>	47	N/A	1.7 KOH	rt	6:1	60	90	2
<i>Terminalia catappa</i>	49	Trace	0.2 mol % NaOCH ₃	65	6:1	60	93	3
<i>Asclepias syriaca</i>	20–25	N/A	1.0 NaOCH ₃	60	6:1	60	99+	4
<i>Cynara cardunculus</i>	25	N/A	1.0 NaOH	75	12:1 ^c	120	94	5
<i>Camelina sativa</i>	31	1.0	1.5 KOH	rt	6:1	60	98	6
<i>Carthamus tinctorius</i>	35–45	0.2	1.0 NaOCH ₃	60	6:1	90	98	7
<i>Sesamum indicum</i>	44–58	N/A	0.5 NaOH	60	6:1	120	74	8
<i>Sclerocarya birrea</i>	N/A	2.1	18.4 H ₂ SO ₄	60	22:1	180	77	9
<i>Cucurbita pepo</i>	45	0.27	NaOH	65	6:1	60	97.5	10
Melon bug	45	3.0	18.4 H ₂ SO ₄	60	22:1	180	79	9
Soybean soapstock	50	>90	500+ H ₂ SO ₄	35	30:1	120	99+	11
Municipal sludge	Up to 30	Up to 65	5.0 H ₂ SO ₄	75	12:1	N/A	14.5	12

^a J Stavarache et al. 2008, 2 Chapagain et al. 2009, 3 dos Santos et al. 2008, 4 Holser and Harry-O'Kuru 2006, 5 Encinar et al. 2002, 6 Frohlich and Rice 2005, 7 Rashid and Anwar 2008b, 8 Saydut et al. 2008, 9 Schinas et al. 2009, 10 Mariod et al. 2006, 11 Haas 2005, 12 Mondala et al. 2009

^bMole ratio of methanol to oil

^cEthanol instead of methanol

Table 15.10 Fatty acid profile (wt.%) of biodiesel fuels prepared from various alternative oilseed feedstocks

Feedstock	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	22:0	22:1	other	Ref ^a
<i>Jatropha curcas</i>	1.4	11.3		17.0	12.8	47.3		4.7				5.5	1
<i>Pongamia pinnata</i>		10.6		6.8	49.4	19.0		4.1	2.4	5.3		2.4 ^b	2
<i>Madhuca indica</i>	1.0	17.8		14.0	46.3	17.9		3.0					3
<i>Melia azedarach</i>		10.1		3.5	21.8	64.1	0.4	0.2	0.3				4
<i>Moringa oleifera</i>		6.5		6.0	72.2	1.0		4.0	2.0	7.1			5
<i>Nicotiana tabacum</i>	0.1	11.0		3.3	14.5	69.5	0.7					0.9	6
<i>Balanites aegyptiaca</i>		13.7		11.0	43.7	31.5							7
<i>Terminalia catappa</i>		35.0		5.0	32.0	28.0							8
<i>Hevea brasiliensis</i>		10.2		8.7	24.6	39.6	16.3						9
<i>Asclepias sylvata</i>		5.9	6.8	2.3	34.8	48.7	1.2	0.2					10
<i>Zanthoxylum bungeanum</i>		10.6	5.2	1.4	32.1	25.6	24.1						11
Rice bran		18.8		2.4	43.1	33.2	0.6	0.7			1.0		12
<i>Raphanus sativus</i>		5.7		2.2	34.5	17.8	12.5	1.0	10.0	16.4			13
<i>Brassica carinata</i> ^c		5.3		0.2	43.2	36.0	15.2			43.6			14
		5.4											
<i>Catophyllum inophyllum</i>		12.0		13.0	34.1	38.3	0.3						15
<i>Cynara cardunculus</i>		14.0		3.0	25.0	56.0						2.0	16
<i>Camelina sativa</i>		5.4		2.6	14.3	14.3	38.4	0.3	16.8	1.4	2.9		17
<i>Carthamus tinctorius</i>		6.9		2.0	14.2	76.0							18
<i>Sesamum indicum</i>		11.0		7.0	43.0	35.0						4.0	19
<i>Vernicia fordii</i>		3.0		2.2	8.6	11.5			0.8	8.4		58.3 ^d	20
<i>Sclerocarya birrea</i>		14.2	0.2	8.8	67.3	5.9						0.1	21
<i>Cucurbita pepo</i>	0.1	12.5	0.2	5.4	37.1	43.7	0.2	0.4	0.1	0.1		0.2	22

^aJ Kumartiari et al. 2007, 2 Bringi 1987, 3 Singh and Singh 1991, 4 Stavarahe et al. 2008, 5 Rashid et al. 2008a, 6 Usta 2005, 7 Chapagain et al. 2009, 8 dos Santos et al. 2008, 9 Ramadhas et al. 2005, 10 Holser and Harry-O'Kuru 2006, 11 Zhang and Jiang 2008, 12 Sinha et al. 2008, 13 Domingos et al. 2008, 14 Dorado et al. 2004, 15 Sahoo et al. 2007, 16 Encinar et al. 2002, 17 Frohlich and Rice 2005, 18 Rashid and Anwar 2008b, 19 Elleuch et al. 2007, 20 Park et al. 2008a, 21 Mariot et al. 2006, 22 Schinas et al. 2009

^b2.4 wt.% 24:0

^cBoth high erucic acid (top) and low erucic acid (bottom) varieties are shown

^d63.8 wt.% eleostearic acid (18:3); 0.5 wt.% heneicosanoic acid (21:0); 1.3 wt.% unknown

Table 15.11 Fatty acid profile (wt.%) of biodiesel fuels prepared from animal fats and other low-value alternative feedstocks

Feedstock	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	22:0	24:0	other	Ref ^a
Salmon	6.8	14.9	6.1	3.2	15.6	2.1	11.5					39.8	1
Melon bug		30.9	10.7	3.5	46.6	3.9						2.4	2
Sorghum bug		12.2	1.0	7.3	40.9	34.5						0.1	2
Pork lard		26.4		12.1	44.7	12.7	1.0					3.1	3
Beef tallow	3.1	23.8	4.7	12.7	47.2	2.6	0.8					5.1 ^b	4
Chicken fat	0.7	20.9	5.4	5.6	40.9	20.5						6.0 ^c	4
Waste frying oil	1.0	30.7	0.6	5.7	40.5	19.1	0.2	0.6	0.4	0.3	0.4	0.3	5
Waste cooking oil	16.3	10.6		3.3	8.2	2.0						59.7 ^d	6
Waste cooking oil		16.0		5.2	34.3	40.8							7
Used frying oil	0.9	20.4	4.6	4.8	52.9	13.5	0.8	0.1	0.8			0.1	8
Used cooking oil	0.2	11.9	0.2	3.8	31.3	50.8		0.3		0.5	0.2		9
Waste frying oil		8.4	0.2	3.7	34.6	50.5	0.6	0.4	0.4	0.8	0.3		10
Soybean soapstock		17.2		4.4	15.7	55.6	7.1						11
Yellow grease	2.4	23.2	3.8	13.0	44.3	7.0	0.7						12
Brown grease	1.7	22.8	3.1	12.5	42.4	12.1	0.8						12

^aJ Chitou et al. 2008, 2 Mariod et al. 2006, 3 Jeong et al. 2009, 4 Wyatt et al. 2005, 5 Predojevic 2008, 6 Phan and Phan 2008, 7 Meng et al. 2008, 8 Leung and Guo 2006, 9 Cetinkaya and Karasmanoglu 2004, 10 Dias et al. 2008, 11 Haas 2005, 12 Canakci and Van Gerpen 2001

^b1.3 wt.% 14:1; 0.5 wt.% 15:0; 1.1 wt.% 17:0; 2.2 wt.% unknown

^c0.1 wt.% 14:1; 3.8 wt.% unknown

^d8.8 wt.% 8:0; 6.2 wt.% 10:0; 44.7 wt.% 12:0

FAME exhibit relatively poor low-temperature operability, as evidenced by a PP value of 2°C (Kumartiwari et al. 2007). The exhaust emission characteristics of FAME from *Jatropha* oil are summarized by Banapurmath et al. (2008). See Table 15.5 for an example of parameters used in the production of biodiesel from *Jatropha* oil.

Another non-edible feedstock of Indian origin is *Pongamia pinnata* (Karanja or Honge), which is a medium-sized (18 m) deciduous tree that grows fast in humid and subtropical environments and matures after 4 to 7 yr to provide fruit that contains one to two kidney-shaped kernels (Mohibbeazam et al. 2005). The oil content of Karanja kernels ranges between 30 and 40 wt.% (Karmee and Chadha 2005; Mohibbeazam et al. 2005). The primary fatty acid found in Karanja oil is oleic acid (45–70 wt.%; Table 15.10), followed by linoleic, palmitic, and stearic acids (Bringi 1987; Karmee and Chadha 2005; Naik et al. 2008). The low-temperature operability of the corresponding FAME is superior to that of *Jatropha* oil FAME as a result of the relatively high percentage of oleic acid in Karanja oil, as evidenced by CP and PP values of –2°C and –6°C, respectively (Srivastava and Verma 2008). The exhaust emissions characteristics of Karanja oil FAME are summarized by Raheman and Phadataré (2004) and Banapurmath et al. (2008). See Table 15.5 for an example of parameters used in the production of biodiesel from Karanja oil. *P. pinnata* may also be referred to as *P. glabra* in the scientific literature (Raheman and Phadataré 2004; Sarma et al. 2005) where it is sometimes referred to as koroch.

Madhuca indica, commonly known as Mahua, is a tropical tree found largely in the central and northern plains and forests of India. It belongs to the Sapotaceae family and grows quickly to approximately 20 m in height, possesses evergreen or semi-evergreen foliage, and is adapted to arid environments (Ghadge and Raheman 2006; Kumari et al. 2007). Non-edible fruit is obtained from the tree in 4 to 7 yr and contains one to two kidney-shaped kernels (Mohibbeazam et al. 2005). The oil content of dried Mahua seeds is around 50 wt.% (Bhatt et al. 2004). Mahua oil is characterized by an FFA content of around 20 wt.% (Ghadge and Raheman 2005, 2006) and a relatively high percentage of saturated fatty acids (Table 15.10) such as palmitic (17.8 wt.%) and stearic (14.0 wt.%) acids (Singh and Singh 1991). The remaining fatty acids are primarily distributed among unsaturated components such as oleic (46.3 wt.%) and linoleic (17.9 wt.%) acids (Singh and Singh 1991). The relatively high percentage of saturated fatty acids (35.8 wt.%, see Table 15.10) found in Mahua oil results in relatively poor low-temperature properties of the corresponding FAME, as evidenced by a PP value of 6°C (Ghadge and Raheman 2005, 2006). See Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from Mahua oil.

Melia azedarach, commonly referred to as syringa or Persian lilac, is a deciduous tree that grows between 7 and 12 m in height in the mahogany family of Meliaceae that is native to India, southern China, and Australia (Stavarache et al. 2008). The oil content of dried syringa berries, which are poisonous, is around 10 wt.% (Stavarache et al. 2008). Syringa oil is characterized by a high percentage of unsaturated fatty acids (Table 15.10) such as oleic (21.8 wt.%) and linoleic

(64.1 wt.%) acids. Other constituents that are present in greater than 1 wt.% are saturated species such as palmitic (10.1 wt.%) and stearic (3.5 wt.%) acids (Stavarache et al. 2008). Physical properties of syringa oil FAME include an IV of 127, a kinematic viscosity (40°C) of 4.37 mm²/s, and a specific gravity of 0.894 g/mL (Stavarache et al. 2008). See Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from syringa oil.

Moringa oleifera, commonly known as Moringa, is an oilseed tree that grows in height from 5 to 10 m and is the most widely known and distributed of the Moringaceae family (Rashid et al. 2008a). The Moringa tree, indigenous to sub-Himalayan regions of northwest India, Africa, Arabia, southeast Asia, the Pacific and Caribbean islands, and South America, is now also distributed in the Philippines, Cambodia, and Central and North America. It thrives best in a tropical insular climate and is plentiful near the sandy beds of rivers and streams. The fast-growing, drought-tolerant Moringa tree can tolerate poor soil, a wide rainfall range (25–300+ cm per year), and soil pH from 5.0 to 9.0 (Palada and Changl 2003; Rashid et al. 2008a). When fully mature, dried seeds contain between 33% and 41% wt.% oil, which is high in oleic acid (>70%, see Table 15.10) and is commercially known as “ben oil” or “behen oil” due to the presence of 7.1 wt.% behenic acid (Rashid et al. 2008a). As a result of the relatively high behenic acid content of moringa oil, the FAME display relatively poor low-temperature properties, as evidenced by CP and PP values of 18°C and 17°C, respectively (Rashid et al. 2008a). In addition, moringa oil FAME exhibit a high CN of 67, one of the highest for a biodiesel fuel. See Table 15.5 for an example of reaction parameters used for the preparation of biodiesel from moringa oil.

Nicotiana tabacum, commonly referred to as tobacco, is a common oilseed plant with pink flowers and green capsules containing numerous small seeds that is grown in a large number of countries around the world (Usta 2005). The leaf of the plant is a commercial product and is used in the production of cigarettes and other tobacco-containing products. The oil content of the seeds, which are by-products of tobacco leaf production, ranges from 36 to 41 wt.% (Usta 2005). Tobacco seed oil normally contains more than 17 wt.% FFA (Veljkovic et al. 2006) and is high in linoleic acid (69.5 wt.%; Table 15.10), with oleic (14.5 wt.%) and palmitic (11.0 wt.%) acids also present in significant quantities. As a result of the relatively high linoleic acid content of tobacco seed oil, the corresponding FAME display a relatively low kinematic viscosity (3.5 mm²/s; Usta 2005) in comparison to most other biodiesel fuels. In addition, the FAME have a CN of 51 and an IV of 112 (Usta 2005). See Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from tobacco seed oil.

Balanites aegyptiaca, commonly known as desert date, is a small tree that grows up to 10 m that belongs to the Zygophyllaceae family. Common uses of the desert date include timber and food, although the fruit is shunned as a food source due to its undesirable taste unless other food is scarce (Chapagain et al. 2009). The tree is highly adapted to growing in arid regions in Africa and Asia and produces as many as 10,000 fruits per annum in optimal growing conditions (Chapagain et al. 2009). Each fruit weighs between 5 and 8 g and contains a kernel that constitutes 8 to 12 wt.% of the

overall fruit mass (Chapagain et al. 2009). The kernel seeds, which are high in unsaturated fatty acids such as oleic (43.7 wt.%; Table 15.10) and linoleic (31.5 wt.%) acids, contain around 50 wt.% oil (Chapagain et al. 2009). Other common constituents found in desert date oil include saturated species such as palmitic (13.7 wt.%) and stearic (11.0 wt.%) acids. The physical properties of the resultant FAME include a CN of 53.5, IV of around 100, CP of 3–7°C, and CFPP of 1–3°C (Chapagain et al. 2009). See Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from desert date oil.

Terminalia catappa, commonly known in Brazil as castanhola, is a large tropical tree belonging to the Combretaceae family growing up to 35 m in height (dos Santos et al. 2008). The tree primarily grows in freely drained, well-aerated, sandy soils and is tolerant of strong winds, salt spray, and moderate levels of salinity in the root zone. The fruit is produced from about 3 yr of age and contains a very hard kernel with an edible almond (Thomson and Evans 2006; dos Santos et al. 2008). The seeds, which are high in palmitic (35.0 wt.%; Table 15.10), oleic (32.0 wt.%), and linoleic (28.0 wt.%) acids, contain around 49 wt.% oil (dos Santos et al. 2008). The physical properties of the resultant FAME include an IV of 83 and a kinematic viscosity (40°C) of 4.3 mm²/s (dos Santos et al. 2008). See Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from *T. catappa* oil.

Hevea brasiliensis, commonly referred to as the rubber tree, belongs to the family Euphorbiaceae and is of major economic importance because it is the primary source of natural rubber and a sap-like extract (known as latex) can be collected and used in various applications (Ramadhas et al. 2005). Growing up to 34 m in height, the tree requires heavy rainfall and produces seeds weighing from 2 to 4 g that do not currently have any major industrial applications. The oil content of the seeds, which may contain up to 17 wt.% FFA, ranges from 40 to 50 wt.% and is high in unsaturated constituents (Table 15.10) such as linoleic (39.6 wt.%), oleic (24.6 wt.%), and linolenic (16.3 wt.%) acids (Ramadhas et al. 2005). Other fatty acids found in rubber seed oil include saturated species such as palmitic (10.2 wt.%) and stearic (8.7 wt.%) acids. The physical properties of the resultant rubber seed oil FAME include CP and PP values of 4°C and –8°C, respectively, and a kinematic viscosity (40°C) of 5.81 mm²/s (Ramadhas et al. 2005). See Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from rubber seed oil.

Vernicia fordii, commonly known as tung, is a small- to medium-sized (up to 20 m in height) deciduous tree belonging to the Euphorbeaceae family that is native to China, Burma, and Vietnam. The fruit is a hard, woody pear-shaped drupe that is 4 to 6 cm long and 3 to 5 cm in diameter that contains four to five large seeds. Tung oil principally contains the unusual conjugated fatty acid eleostearic acid (9,11,13-octadecatrienoic acid; 63.8 wt.%; Table 15.10), with linoleic (11.5 wt.%), oleic (8.6 wt.%) and behenic (8.4 wt.%) acids also present in significant quantities (Park et al. 2008a). The physical properties of tung oil FAME include a CFPP of –11°C, OSI (110°C) value of 0.5 h, and kinematic viscosity (40°C) of 9.8 mm²/s (Park et al. 2008a). Refer to Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from tung oil.

Asclepias syriaca, commonly referred to as common milkweed, belongs to the family Asclepiadaceae and is native to the northeast and north–central United States where it grows on roadsides and in undisturbed habitat (Holser and Harry-O’Kuru 2006). Generally considered a nuisance by farmers, it is a herbaceous perennial oilseed plant that grows up to 2 m in height and produces a marketable fiber along with a white latex. The small flowers (1–2 cm in diameter) are grouped in several spherical umbels and contain numerous seeds that are attached to long, white flossy hairs. The dried seed contains 20 to 25 wt.% oil, which is composed mostly of unsaturated fatty acids (Table 15.10) such as linoleic (48.7 wt.%), oleic (34.8 wt.%), and palmitoleic (6.8 wt.%) acids (Holser and Harry-O’Kuru 2006). The majority of the remaining fatty acids are distributed among palmitic (5.9 wt.%) and stearic (2.3 wt.%) acids. The physical properties of the resultant milkweed seed oil FAME include CP and PP values of -1°C and -6°C , respectively, an OSI (100°C according to AOCS Cd 12b-92) value of 1.5 h, and a kinematic viscosity (40°C) of $4.6\text{ mm}^2/\text{s}$ (Holser and Harry-O’Kuru 2006). See Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from common milkweed seed oil.

Zanthoxylum bungeanum is a small (3–7 m), fast growing, deciduous tree found throughout China that is a member of the Rutaceae family (Yang et al. 2008). The fruit of *Z. bungeanum* consists of a dark seed and a red shell, which is used as a culinary spice in China and is particularly popular in Sichuan cuisine (Sichuan pepper). The seed is a by-product of spice production and contains between 24 and 31 wt.% inedible oil that is high in FFA content (25 wt.%) (Yang et al. 2008; Zhang and Jiang 2008). As seen from Table 15.10, *Z. bungeanum* seed oil contains a large percentage of unsaturated fatty acids such as oleic (32.1 wt.%), linoleic (25.6 wt.%), and linolenic (24.1 wt.%) acids, with palmitic acid (10.6 wt.%) also present in significant quantity (Zhang and Jiang 2008). The physical properties of the resultant FAME include CP and CFPP values of 2°C and a kinematic viscosity (40°C) of $4.0\text{ mm}^2/\text{s}$ (Yang et al. 2008). Refer to Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from *Z. bungeanum* seed oil.

Rice bran is a by-product of rice milling in the production of refined white rice from brown rice and is common in countries such as China and India. Rice bran contains about 15 to 23 wt.% inedible oil that is high in oleic (43.1 wt.%; Table 15.10), linoleic (33.2 wt.%), and palmitic (18.8 wt.%) acids, and has a relatively low FFA content (2.8 wt.%; Sinha et al. 2008). The physical properties of rice bran oil FAME include CP and PP values of 9°C and -2°C , respectively, a CN of 63.8, and a kinematic viscosity (40°C) of $5.29\text{ mm}^2/\text{s}$ (Sinha et al. 2008). Refer to Table 15.6 for an example of reaction parameters used in the preparation of biodiesel from rice bran oil.

Raphanus sativus, commonly known as radish, is a perennial oilseed plant of the Brassicaceae family that is widely grown and consumed throughout the world. The radish has considerable low-temperature tolerance, grows rapidly, and requires few agricultural inputs (Domingos et al. 2008). The seeds contain between 40 to 54 wt.% of inedible oil that primarily consists of oleic (34.5 wt.%; Table 15.10), linoleic

(17.8 wt.%), erucic (16.4 wt.%), linolenic (12.5 wt.%), and arachidic (10.0 wt.%) acids (Domingos et al. 2008). The physical properties of ethyl esters prepared from radish seed oil include an OSI (110°C) value of 4.65 h, kinematic viscosity (40°C) of 4.65 mm²/s, IV of 105, and a CFPP value of -2°C (Domingos et al. 2008). Refer to Table 15.6 for an example of reaction parameters used in the preparation of biodiesel from radish seed oil.

Brassica carinata, commonly known as Ethiopian or Abyssinian mustard, is an oilseed plant of the Brassicaceae family that is well-adapted to marginal lands and can tolerate arid regions such as Ethiopia (Dorado et al. 2004). *B. carinata* is of interest as a potential biodiesel crop because it displays better agronomic performance in areas with unfavorable growing conditions than *B. napus* (rapeseed; Cardone et al. 2002). Natural *B. carinata* contains up to 43.6 wt.% erucic acid. However, varieties of *B. carinata* with no erucic acid have been developed (Dorado et al. 2004). Refer to Table 15.10 for the fatty acid composition of *B. carinata* varieties that do and do not contain erucic acid. Physical properties of the corresponding FAME (with no erucic acid) include CP, PP, and CFPP values of -9°C, -6°C, and -9°C, respectively, an IV of 138, and a kinematic viscosity (40°C) of 4.83 mm²/s (Dorado et al. 2004). The exhaust emissions of FAME from *B. carinata* oil are summarized by Cardone et al. 2002. Refer to Table 15.6 for an example of reaction parameters used in the preparation of biodiesel from *B. carinata* seed oil.

Camelina sativa, commonly known as false flax or gold-of-pleasure, is a spring annual broadleaf oilseed plant of the Brassicaceae family that grows well in temperate climates. Camelina, unlike soybean, is cold weather tolerant and is well-adapted to the northern regions of North America, Europe, and Asia (Frohlich and Rice 2005). The oil content of seeds from camelina can range from 28 to 40 wt.% and is characterized by low FFA content (1.0 wt.%) and high levels of unsaturated fatty acids (Table 15.10; Frohlich and Rice 2005). Linolenic (38.4 wt.%), gondoic (16.8 wt.%), linoleic (14.3 wt.%), and oleic (14.3 wt.%) acids comprise the majority of the fatty acids found in camelina oil (Frohlich and Rice 2005). The IV of camelina oil FAME is a rather high 155 as a result of the high unsaturated fatty acid content of the parent oil (Frohlich and Rice 2005). Other physical properties of camelina oil FAME include CP, CFPP, and PP values of 3°C, -3°C, and -4°C, respectively (Frohlich and Rice 2005). Refer to Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from *C. sativa* seed oil.

Calophyllum inophyllum, commonly known as Polanga, is an inedible oilseed ornamental evergreen tree belonging to the Clusiaceae family that is found in tropical regions of India, Malaysia, Indonesia, and the Philippines. Typically growing up to 25 m in height, the Polanga tree produces a slightly toxic fruit that contains a single, large seed (Sahoo et al. 2007). The oil obtained from polanga seeds is high in FFA content (up to 22 wt.%) and unsaturated species (Table 15.10) such as linoleic (38.3 wt.%) and oleic (34.1 wt.%) acids (Sahoo et al. 2007). The remaining fatty acids include stearic (13.0 wt.%) and palmitic (12.0 wt.%) acids with a trace amount of linoleic acid (0.3 wt.%) also present (Sahoo et al. 2007).

Physical properties of polanga oil FAME include CP and PP values of 13°C and 4°C, respectively, a flash point of 140°C, and a kinematic viscosity (40°C) of 4.92 mm²/s (Sahoo et al. 2007). The exhaust emissions of FAME from polanga oil are summarized by Sahoo et al. (2007). Refer to Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from polanga seed oil.

Cynara cardunculus, commonly known as cardoon, is a Mediterranean herbaceous perennial thistle with a characteristic rosette of large spiny leaves and branched flowering stems. It belongs to the Asteraceae family and is cultivated for its branched leaf petioles, which are regarded as a great delicacy in many parts of the Mediterranean (Raccuia and Melilli 2007). *C. cardunculus* seed oil normally contains around 25 wt.% FFA (Encinar et al. 2002) and is high in linoleic acid (56.0 wt.%; Table 15.10), with oleic (25.0 wt.%), palmitic (14.0 wt.%), and stearic (3.0 wt.%) acids also present in significant quantities (Encinar et al. 2002). As a result of the relatively high linoleic acid content of *C. cardunculus* seed oil, the corresponding FAME display a relatively low kinematic viscosity (40°C) of 3.56 mm²/s, CP, and PP values of -1°C and -3°C, respectively, and a flash point of 175°C (Encinar et al. 2002). Ethyl esters from *C. cardunculus* seed oil display slightly improved CP, PP, and flash point values of -3°C, -6°C, and 188°C, respectively (Encinar et al. 2002). Refer to Table 15.9 for an example of reaction parameters used in the preparation of FAME from *C. cardunculus* seed oil.

Carthamus tinctorius, commonly known as safflower, is a highly branched, herbaceous, thistle-like annual oilseed plant belonging to the Asteraceae family that has long been cultivated in numerous regions of the world mainly for its edible oil and colorful petals, which are valued as food coloring and flavoring agents, as well as for sources of red and yellow dyes for clothing (Rashid and Anwar 2008b). India, the United States, and Mexico are the principle producers of safflower; however, it has been cultivated in many other countries, such as Australia, Argentina, Ethiopia, Russia, Kazakhstan, and Uzbekistan. Safflower has a strong taproot that enables it to thrive in dry climates, but the plant is very susceptible to frost injury (Rashid and Anwar 2008b). Safflower has many long, sharp spines on its leaves and grows from 30 to 150 cm tall with globular flower heads that contain brilliant yellow, orange, or red flowers. Each branch usually has from one to five flower heads containing from 15 to 20 seeds per head. The seeds are also used as a component in seed mixtures for the recreational feeding of birds. Safflower seeds normally contain around 35 to 45 wt.% oil. Safflower oil, which has a very low FFA content (0.2 wt.%), primarily consists of linoleic acid (76.0 wt.%; Table 15.10), followed by oleic (14.2 wt.%), palmitic (6.9 wt.%), and stearic (2.1 wt.%) acids (Rashid and Anwar 2008b). The physical properties of safflower oil FAME include an IV of 142, CP, PP, and CFPP values of -2°C, -8°C, and -6°C, respectively, flash point of 176°C, kinematic viscosity of 4.29 mm²/s, and a CN of 52 (Rashid and Anwar 2008b). Refer to Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from safflower seed oil.

Sesamum indicum, commonly known as sesame, is an annual herbaceous flowering plant of the Pedaliaceae family that has recently been adapted to

semi-arid climates and is an important oilseed crop cultivated in many regions of the world (Elleuch et al. 2007). Sesame is widely used in food, nutraceutical, and pharmaceutical applications as a result of its high oil, protein, and antioxidant content. Sesame seeds normally contain around 44 to 58 wt.% oil (Elleuch et al. 2007). Sesame seed oil primarily consists of oleic (43 wt.%; Table 15.10) and linoleic (35 wt.%) acids, with palmitic (11 wt.%) and stearic (7 wt.%) acids comprising most of the remaining constituents (Elleuch et al. 2007). The physical properties of sesame oil FAME include an IV of 98 (corrected), CN of 50, kinematic viscosity (40°C) of 4.2 mm²/s, flash point of 170°C, and CP and PP values of -6°C and -14°C, respectively (Saydut et al. 2008). The exhaust emissions of FAME from sesame seed oil are summarized by Banapurmath et al. (2008). Refer to Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from sesame seed oil.

Sclerocarya birrea, commonly known as marula, is a medium-sized (up to 18 m in height) deciduous Savannah tree belonging to the Anacardiaceae family that is found in southern and western Africa (Mariod et al. 2006). The primary fatty acids found in marula oil, which contains 2.1 wt.% FFA, are oleic (67.3 wt.%; Table 15.10), palmitic (14.2 wt.%), stearic (8.8 wt.%), and linoleic (5.9 wt.%) acids. The physical properties of the resultant FAME include a CFPP value of 5°C, an IV of 76 and a CN of 62 (Mariod et al. 2006). Refer to Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from marula seed oil.

Cucurbita pepo, commonly known as pumpkin, is a member of the Cucurbitaceae family and is grown in many regions of the world for various agricultural and ornamental applications. Pumpkin seeds are a common snack food in several cultures, and pumpkin seed oil may be used as a salad oil (Schinas et al. 2009). The primary fatty acids contained in pumpkin seed oil, which is obtained in 45 wt.% yield from seeds and has a low FFA content of 0.3 wt.%, are linolenic (43.7 wt.%; Table 15.10), oleic (37.1 wt.%), and palmitic (12.5 wt.%) acids (Schinas et al. 2009). The physical properties of pumpkin seed oil FAME include a kinematic viscosity (40°C) of 4.41 mm²/s, IV of 115, CFPP value of -9°C, and a density (15°C) of 883.7 kg/m³ (Schinas et al. 2009). Refer to Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from pumpkin seed oil.

Simmondsia chinensis, commonly known as jojoba, is a perennial shrub belonging to the Simmondsiaceae family that is native to the Mojave and Sonoran deserts of Mexico, California, and Arizona. Jojoba is unique in that the lipid content of the seeds, which is between 45 and 55 wt.%, is in the form of long-chain esters of fatty acids and alcohols (wax esters; Canoira et al. 2006; Bouaid et al. 2007) as opposed to TAG. The fatty acid component of jojoba wax esters primarily consists of eiconoic, erucic, and oleic acids with *cis*-11-eicosen-1-ol and *cis*-13-docosen-1-ol principally composing the alcohol component (Canoira et al. 2006). As a consequence of the unique composition of jojoba wax, methanolysis affords a product that consists of a mixture of FAME and long chain alcohols, as the separation of these materials is problematic. The physical properties of this mixture do not compare favorably with biodiesel prepared from other feedstocks, as the CFPP value is 4°C and the kinematic viscosity (40°C) is 11.82 mm²/s (Canoira et al. 2006).

Reduction of the alcohol component through laborious purification results in an improvement in CFPP to -14°C ; however, the kinematic viscosity (40°C ; $9.0\text{ mm}^2/\text{s}$) remains considerably above accepted American (ASTM D6751) and European Union (EN 14214) limits (Canoira et al. 2006). The reaction conditions for the production of biodiesel from jojoba wax esters have been optimized by RSM (Bouaid et al. 2007).

Animal fats. Animal fats may include materials from a variety of domesticated animals, such as cows, chickens, pigs, and other animals such as fish and insects. Animal fats are normally characterized by a greater percentage of saturated fatty acids in comparison to oils obtained from the plant kingdom. Animal fats are generally considered as waste products, so they are normally less expensive than commodity vegetable oils, which makes them attractive as feedstocks for biodiesel production.

Waste salmon oil is a by-product of the fishing industry and is obtained from fish by-product material by extraction or centrifugation from either fresh salmon by-product or from hydrolysate made from salmon by-product (Wright 2004; Chiou et al. 2008; El-Mashad et al. 2008). The major fish by-products include fish heads, viscera, and frames (Chiou et al. 2008). The hydrolysate, which contains around 10 wt.% oil, is typically produced by maceration of viscera or skinny by-products followed by enzymatic digestion of protein and removal of bones (El-Mashad et al. 2008). Acid is normally added to stabilize the final product by lowering the pH to around 3.7, which in combination with other handling procedures results in an inedible oil (El-Mashad et al. 2008). Biodiesel may be prepared from oil obtained from either fresh salmon by-product (termed non-acidified oil) or from hydrolysate (acidified oil). The FFA contents of non-acidified and acidified oils are 1.7 and 6.0 wt.%, respectively (El-Mashad et al. 2008). The fatty acid compositions of these oils is nearly identical and is characterized by a wide range of fatty acids not normally found in other materials, such as eicosapentaenoic (C20:5; 11.1 wt.%; Table 15.11), docosahexaenoic (C22:6; 13.7 wt.%), arachidonic (C20:4; 3.3 wt.%), and glupanodonic (C22:5; 3.0 wt.%) acids, along with more typical constituents such as palmitic (14.9 wt.%), linolenic (11.5 wt.%), myristic (6.8 wt.%), and palmitoleic (6.1 wt.%) acids. In addition, oleic acid, along with the 10-*cis* isomer, constitutes 15.6 wt.% of salmon oil (Chiou et al. 2008). As a result of the high FFA content of salmon oil, a two-step reaction procedure is required in which the oil initially undergoes mineral acid-catalyzed (H_2SO_4) pretreatment, followed by conventional homogenous alkaline base-catalyzed transesterification (KOH) to afford salmon oil FAME (Chiou et al. 2008; El-Mashad et al. 2008). The reaction conditions for the production of biodiesel from salmon oil have been optimized by RSM (El-Mashad et al. 2008). The physical properties of non-acidified salmon oil FAME include CP, PP, and CFPP values of -2°C , -3°C , and -8°C , respectively, and an OSI (110°C) value of 6.1 h (Chiou et al. 2008). The physical properties of acidified salmon oil FAME include PP and CFPP values of -3°C and -6°C , respectively, and an OSI (110°C) value of 12.1 h (Chiou et al. 2008).

Aspongubus viduatus, commonly known as melon bug, is an insect belonging to the Hemiptera order that is widely distributed in Sudan and other regions of Africa and is considered the primary pest of watermelon (Mariod et al. 2006). The melon

bug normally contains around 45 wt.% oil. The primary fatty acids found in melon bug oil, which contains 3.0 wt.% FFA, include oleic (46.6 wt.%; Table 15.11), palmitic (30.9 wt.%), and palmitoleic (10.7 wt.%) acids (Mariod et al. 2006). As a result of the high saturated fatty acid content of melon bug oil, the corresponding FAME display a high CFPP value of 10°C and a low IV of 56. Other parameters of note include a CN of 55 and an OSI (110°C) value of 4.9 h (Mariod et al. 2006). Refer to Table 15.9 for an example of reaction parameters used in the preparation of biodiesel from melon bug oil.

Agonoscelis pubescens, commonly known as sorghum bug, is an insect belonging to the Hemiptera order that is widely distributed in Sudan and other regions of Africa and is a pest (Mariod et al. 2006). The sorghum bug normally contains around 60 wt.% oil. The primary fatty acids found in sorghum bug oil, which contains 10.5 wt.% FFA, include oleic (40.9 wt.%; Table 15.11), linoleic (34.5 wt.%), and palmitic (12.1 wt.%) acids (Mariod et al. 2006). The physical properties of the resultant FAME include a CFPP value of 4°C, an IV of 84, a CN of 55, and an OSI (110°C) value of 1.0 h (Mariod et al. 2006). Refer to Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from sorghum bug oil.

Animal fats such as beef tallow and chicken fat are by-products of the food processing industry and represent low value feedstocks for biodiesel production. The primary fatty acids found in beef tallow (Table 15.11) include oleic (47.2 wt.%), palmitic (23.8 wt.%), and stearic (12.7 wt.%) acids. The primary fatty acids contained in chicken fat (Table 15.11) include oleic (40.9 wt.%), palmitic (20.9 wt.%), and linoleic (20.5 wt.%) acids (Wyatt et al. 2005). As a result of the very low polyunsaturated fatty acid content of beef tallow, the corresponding FAME display excellent oxidative stability, as evidenced by an OSI (110°C) value of 69 h. In addition, other physical properties of beef tallow FAME include a kinematic viscosity (40°C) of 5.0 mm²/s, a flash point of 150°C, and CP, PP, and CFPP values of 11°C, 13°C, and 8°C, respectively (Wyatt et al. 2005). As a result of the high polyunsaturated fatty acid content of chicken fat, the corresponding FAME display poor oxidative stability, as evidenced by an OSI (110°C) value of 3.5 h. In addition, other physical properties of beef tallow FAME include a kinematic viscosity (40°C) of 4.3 mm²/s, a flash point of 150°C, and CP, PP, and CFPP values of 4°C, 6°C, and 1°C, respectively (Wyatt et al. 2005). Combustion of B20 blends of beef tallow and chicken fat FAME results in an increase in NO_x exhaust emissions of only 0.0% and 2.4% versus 6.2% for a B20 blend of SME (Wyatt et al. 2005). In addition, the exhaust emissions of beef tallow FAME are summarized by McCormick et al. (2001).

Pork lard is a by-product of the food processing industry and represents a low value feedstock for biodiesel production. The primary fatty acids found in pork lard (Table 15.11) include oleic (44.7 wt.%), palmitic (26.4 wt.%), linoleic (12.7 wt.%), and stearic (12.1 wt.%) acids (Jeong et al. 2009). As a result of the relatively high saturated fatty acid content of pork lard, the corresponding FAME exhibit a relatively high CFPP value of 8°C and a relatively low IV of 72, along with a kinematic viscosity (40°C) of 4.2 mm²/s (Jeong et al. 2009). Another study determined that pork lard FAME have a kinematic viscosity (40°C) of 4.8 mm²/s,

a flash point of 160°C, OSI (110°C) value of 18.4 h, and CP, PP, and CFPP values of 11°C, 13°C, and 8°C, respectively (Wyatt et al. 2005). Furthermore, combustion of B20 blends of pork lard FAME results in an increase in NO_x exhaust emissions of only 3.0% versus 6.2% for a B20 blend of SME (Wyatt et al. 2005). In addition, the exhaust emissions of pork lard FAME are summarized by McCormick et al. (2001). Refer to Table 15.6 for an example of reaction parameters used in the preparation of biodiesel from refined and bleached pork lard that have been optimized by RSM. Exploration of the influence of pork lard and beef tallow FAME blended with rapeseed and linseed oil FAME in various ratios on CN and exhaust emissions is summarized by Lebedevas and Vaicekauskas (2006).

Other waste oils. Waste oils may include a variety of low-value materials such as used cooking or frying oils, vegetable oil soapstocks, acid oils, tall oil, and other waste materials. Waste oils are normally characterized by relatively high FFA and water contents and potentially the presence of various solid materials that must be removed by filtration prior to conversion to biodiesel. In the case of used cooking or frying oils, hydrogenation to increase the useful cooking lifetime of the oil may result in the introduction of relatively high melting *trans* constituents, which influence the physical properties of the resultant biodiesel fuel.

Used or waste frying or cooking oil is primarily obtained from the restaurant industry and may cost anywhere from free to 60% less expensive than commodity vegetable oils, depending on the source and availability (Predojevic 2008). The fatty acid profiles of several used or waste frying or cooking oils is presented in Table 15.11. Conditions for the preparation of biodiesel from used or waste frying or cooking oils is presented in Table 15.5 and 15.6. The physical properties of FAME prepared from used or waste cooking or frying oils include kinematic viscosities (40°C) of 4.23 (Meng et al. 2008), 4.79 (Cetinkaya and Karaosmanoglu 2004), and 4.89 mm²/s (Phan and Phan 2008), flash points of 171 (Meng et al. 2008), 176 (Cetinkaya and Karaosmanoglu 2004), and 120°C (Phan and Phan 2008), a CN of 55 (Meng et al. 2008), an IV of 125 (Cetinkaya and Karaosmanoglu 2004), CFPP values of 1°C (Meng et al. 2008) and -6°C (Cetinkaya and Karaosmanoglu 2004), CP values of 9°C (Cetinkaya and Karaosmanoglu 2004) and 3°C, and PP values of -3°C (Cetinkaya and Karaosmanoglu 2004) and 0°C (Phan and Phan 2008). The differences in the physical property data among the various studies may be a result of differing feedstock origin or differences in product purity. The exhaust emissions of used cooking oil FAME are summarized by Meng et al. (2008), Ozsezen et al. (2008), and Kocak et al. (2007).

Soapstock, a by-product of the refining of vegetable oils, consists of a heavy alkaline aqueous emulsion of lipids that contains around 50% water, with the remaining material made up of FFA (and soaps), phosphoacylglycerols, TAG, pigments, and other minor nonpolar components (Haas 2005). The total fatty acid content, including both FFA and lipid-linked acids, is normally around 25 to 30 wt.% (Haas et al. 2001). Soybean soapstock is generated at a rate of about 6 vol.% of crude oil refined, which equates to an annual US production of approximately one billion pounds with a market value of about one fifth of the price of crude soybean oil (Haas 2005). The fatty acid

composition of soybean soapstock (Table 15.11) is similar to that of crude soybean oil. The production of FAME from soybean soapstock is complicated by the presence of a substantial amount of water, which must be removed prior to conversion to biodiesel. Freeze-drying is an effective method for removal of water after hydrolysis and acidulation of TAG (Haas 2005). Soybean soapstock at this stage is entirely composed of FFA, so it is referred to as acid oil (Haas et al. 2003). Acid-catalyzed (H_2SO_4) esterification of acid oil may be used for conversion to FAME (Haas et al. 2003; Haas 2005). The physical properties of biodiesel prepared from soybean soapstock are similar to those of biodiesel prepared from soybean oil (Haas et al. 2003; Haas 2005). For instance, FAME prepared from soybean soapstock exhibit a kinematic viscosity (40°C) of 4.3 mm²/s, flash point of 169°C, CN of 51, IV of 129, and a CP value of 6°C (Haas et al. 2001). The exhaust emissions of soybean soapstock FAME are summarized by Haas et al. (2001). Refer to Table 15.9 and 15.5 for examples of reaction parameters used in the preparation of biodiesel from soybean soapstock and acid oil, respectively.

Rendered animal fats and restaurant waste oils are known as yellow greases if the FFA level is less than 15 wt.% and brown greases if the FFA content is in excess of 15 wt.% (Canakci and Van Gerpen 2001). The fatty acid compositions (Table 15. 11) of yellow and brown greases are similar, with oleic acid present in the greatest abundance, followed by palmitic, stearic, and linoleic acids. As a result of the high FFA content of greases, conventional homogenous alkaline base-catalyzed transesterification is not practical. Therefore, acid pretreatment must precede base-catalyzed transesterification to afford FAME (Canakci and Van Gerpen 2001). Alternatively, various diarylammonium catalysts may be used instead of homogenous alkaline base catalysts in the transesterification of acid-pretreated greases to provide FAME (Ngo et al. 2008). The exhaust emissions of yellow and brown grease FAME are summarized by Canakci and Van Gerpen (2003b) and McCormick et al. (2001). Refer to Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from brown grease.

Tall oil is obtained from coniferous wood recovered in the Kraft pulping process as a by-product of cellulose production (Keskin et al. 2008). Chemically, tall oil is a mixture of several components, including resin acids and other terpenoids (40–60 wt.%), fatty acids and TAG (30–50 wt.%), unsaponifiables (4–10 wt.%), water (0.5–3 wt.%), and ash (0.1–1.0 wt.%; Demirbas 2008). The chemical composition of tall oil varies with the age, pine species, geographical location, and the pulping process used (Keskin et al. 2008). As a result of the high FFA content of tall oil, conventional homogenous alkaline base-catalyzed transesterification is not practical. The physical properties of a B60 blend of tall oil FAME in petrodiesel include a kinematic viscosity (40°C) of 5.3 mm²/s, CN of 50, flash point of 88°C, and CP and CFPP values of –2°C and –6°C, respectively (Keskin et al. 2008). The exhaust emissions of tall oil FAME blended with petrodiesel are summarized by Keskin et al. (2008). Refer to Table 15.5 for an example of reaction parameters used in the preparation of biodiesel from tall oil.

Dried distiller's grains (DDG) are a by-product of dry-grind ethanol production and contain around 8–10 wt.% corn oil. Ordinarily, these grains are used as an

animal feed supplement, but extraction of the corn oil may represent a sizeable feedstock for biodiesel production in addition to providing a more nutritive and valuable animal feed supplement (Balan et al. 2009; Nouredini et al. 2009). However, corn oil extracted from distiller's grains may contain 7.0 wt.% FFA or more, resulting in the need for acid-catalyzed pretreatment or other alternative methods to prepare FAME in high yield. For instance, a recent study used sulfuric acid-catalyzed pretreatment to lower the FFA content of corn oil extracted from grains to 0.25 from 7.0 wt.%, followed by classic homogenous alkaline base-catalyzed (NaOH) methanolysis to yield corn oil FAME in 98 wt.% yield (Nouredini et al. 2009).

Effects of Blending Biodiesel with Other Fuels

Biodiesel–petrodiesel blends. Biodiesel is completely miscible with ULSD and can be used as a blend component in any proportion. However, ASTM D975 and D7467 only allow up to 5 and 20 vol.% biodiesel, respectively. Biodiesel and petrodiesel are not chemically similar: biodiesel is composed of long-chain FFAE, whereas petrodiesel is a mixture of aliphatic and aromatic hydrocarbons that contain approximately 10 to 15 carbons. Because biodiesel and petrodiesel have differing chemical compositions, they have differing fuel properties. Once mixed, the blend will exhibit properties different from neat biodiesel and petrodiesel fuels. Specifically, the most important fuel properties influenced by blending are lubricity, exhaust emissions, CN, flash point, oxidative stability, low-temperature operability, kinematic viscosity, and energy content.

Lubricity of petrodiesel is positively impacted through blending with biodiesel (Geller and Goodrum 2004; Goodrum and Gellar 2005; Hu et al. 2005; Knothe and Steidley 2005b; Moser et al. 2008). Specifically, B2 and B20 blends of SME in ULSD (contains no lubricity-enhancing additives) significantly improve lubricity (60°C according to ASTM D6079) from 551 to 212 and 171 μm , respectively (Moser et al. 2008). Exhaust emissions of ULSD, with the exception of NO_x , are reduced through blending with biodiesel, as previously discussed (Chang et al. 1996; Altiparmak et al. 2007; Korres et al. 2008; Lapuerta et al. 2008). The CN of petrodiesel is increased upon blending with biodiesel (Chang et al. 1996; Altiparmak et al. 2007). For example, the CN of petrodiesel, tall oil FAME, and the corresponding B50, B60, and B70 blends are 47, 54, 52, 52, and 53, respectively (Altiparmak et al. 2007). The flash point of petrodiesel is increased upon blending with biodiesel (Alptekin and Canakci 2009). The flash points of FAME are much higher than those of petrodiesel and range from around 110 to 200°C versus 50 to 60°C for petrodiesel. When blended with petrodiesel, biodiesel does not impact flash point up to B20, but beyond B20 the flash point increases significantly (Alptekin and Canakci 2009). The oxidative stability of petrodiesel is negatively impacted upon blending with biodiesel (Mushrush et al. 2003, 2004). This is because the hydrocarbon constituents of petrodiesel are more stable to

oxidation than FAME (especially in the case of unsaturated FAME). The amount of gravimetric solids formed (indicators of oxidative degradation) according to ASTM D5304 in the cases of petrodiesel and the corresponding B10 and 20 blends (SME) were 0.6, 4.2, and 9.0 mg/100 mL, respectively (Mushrush et al. 2004). The low-temperature operability of petrodiesel is negatively impacted once blended with biodiesel (Altiparmak et al. 2007; Benjumea et al. 2008; Moser et al. 2008; Alptekin and Canakci 2009). For instance, the CFPP of petrodiesel, tall oil FAME, and the corresponding B50, 60, and 70 blends were -8°C , -3°C , -7°C , -6°C , and -6°C , respectively (Altiparmak et al. 2007). In another example, the PP of ULSD and B2, 5, 20, and 100 blends (PME) were -21°C , -21°C , -18°C , -12°C , and 18°C , respectively (Moser et al. 2008b). The kinematic viscosity of petrodiesel increases upon blending with biodiesel (Altiparmak et al. 2007; Benjumea et al. 2008; Moser et al. 2008; Alptekin and Canakci 2009, 2008). For example, the kinematic viscosities (40°C) of ULSD and B1, 2, 5, and 20 (SME) blends are 2.32, 2.40, 2.48, 2.57, and 2.71 mm^2/s , respectively (Moser et al. 2008). In another example, the kinematic viscosities (40°C) of petrodiesel and B50, 60, 70, and 100 (tall oil FAME) blends are 2.60, 4.50, 4.82, 5.12, and 7.10 mm^2/s , respectively (Altiparmak et al. 2007). Lastly, the heat of combustion (energy content) of petrodiesel is reduced upon blending with biodiesel (DeOliveira et al. 2006; Altiparmak et al. 2007; Benjumea et al. 2008). Specifically, the energy contents of petrodiesel and B50, 60, 70, and 100 (tall oil FAME) blends are 43.76, 41.90, 41.51, 41.15, and 40.02 MJ/kg, respectively (Altiparmak et al. 2007). In another example, the energy contents of petrodiesel and B2, 5, 10, 20, and 100 (SME) blends are 46.65, 46.01, 45.46, 44.48, 43.75, and 39.09 MJ/kg, respectively (DeOliveira et al. 2006).

Biodiesel–alcohol blends. Low-level blends of ethanol in diesel fuel (E-diesel) significantly reduce harmful exhaust emissions such as PM, THC, and CO as a result of increased fuel oxygenation. For instance, an E20 (20% ethanol in diesel fuel) blend results in reductions of 55%, 36%, and 51% for CO, THC, and PM exhaust emissions, respectively (Ajav et al. 2000). However, drawbacks of E-diesel include reduced energy content (Can et al. 2004; Li et al. 2005), CN (Li et al. 2005), flash point (Li et al. 2005), lubricity (Fernando and Hanna 2004), and immiscibility of ethanol in diesel over a wide range of temperatures (Satge de Caro et al. 2001; Fernando and Hanna 2004; Li et al. 2005). To correct the immiscibility problem, surfactants at levels of up to 5% are required to stabilize E-diesel mixtures (Satge de Caro et al. 2001; Fernando and Hanna 2004). A recent study explored the utility of ethanol–biodiesel–diesel blends (EB–diesel) as a means to mitigate the miscibility issues of E-diesel (Fernando and Hanna 2004). The disadvantages of E-diesel are substantially reduced or eliminated in the case of EB–diesel blends prepared from 5% ethanol and 20% biodiesel (SME) in petrodiesel (Fernando and Hanna 2004). A later study (Rahimi et al. 2009) revealed that 3% ethanol, 2% biodiesel (sunflower oil FAME), and 95% low sulfur diesel (LSD, <500 ppm S) reduced the PP in comparison to neat LSD. In general, EB-diesel blends result in reduced CO and THC exhaust emissions versus neat LSD (Rahimi et al. 2009). Also discussed were the effects of blending ethanol with biodiesel (E-biodiesel) in a ratio of 6 to 4 on

PP, kinematic viscosity, and flash point. Specifically, the PP of biodiesel was reduced from -3°C to -9°C , the kinematic viscosity (40°C) was reduced from 4.22 to 1.65 mm^2/s , and the flash point was reduced from 187°C to 14°C after blending with ethanol (Rahimi et al. 2009). Analogously, a blend of ethanol and biodiesel prepared from *Madhuca indica* oil yielded lower flash point, reduced kinematic viscosity, lower PP, reduced CO emissions, slightly higher THC emissions, and lower NO_x emissions versus unblended *Madhuca indica* oil FAME (Bhale et al. 2009). Other effects of blending ethanol with biodiesel that have not yet been reported but can be reasonably speculated may be reduced lubricity, energy content, and CN in comparison to neat biodiesel.

Multi-feedstock biodiesel blends. Mixed feedstock biodiesel production may be employed to provide biodiesel with improved physical properties in comparison to the individual fuels on their own. Mixed feedstock production may also arise as a result of economic considerations. For instance, it may be economically advantageous to extend the lifetime of a comparatively more expensive feedstock through blending with a less expensive feedstock. Recent examples of the influence of blending various feedstocks on biodiesel fuel properties include blends of canola, palm, soybean, and sunflower oil FAME (Moser 2008a), blends of palm, rapeseed and soybean oil FAME (Park et al. 2008b), blends of jatropha and palm oil FAME (Sarin et al. 2007), and blends of cottonseed, soybean, and castor oil FAME (Meneghetti et al. 2007). In the case of jatropha–palm blends, the objective was to obtain a biodiesel blend with superior low-temperature performance to PME and superior oxidative stability to jatropha oil FAME. Specifically, the CFPP of PME was improved from 12°C to 3°C upon blending (20:80 by volume) with jatropha oil FAME (neat: 0°C Sarin et al. 2007). The oxidative stability of jatropha oil FAME was improved from 3 to 4 h after blending (same proportion as above) with PME (Sarin et al. 2007). The objective of another study was to evaluate the kinematic viscosities, specific gravities, and IV of biodiesel fuels obtained from binary mixtures (20 and 80 vol.%) of castor, soybean, cotton, and canola oil FAME in an effort to find combinations that were satisfactory according to the EN 14214 biodiesel standard (Albuquerque et al. 2009).

Other Uses of Biodiesel

Fatty acid alkyl esters have attracted considerable interest as alternative bio-based diesel fuels for combustion in CI engines. However, a number of additional applications have been developed or discovered for these versatile oleochemical materials. For instance, biodiesel may be used as a replacement for petroleum as a heating oil (Mushrush et al. 2001). As such, the European standard EN 14213 (CEN 2003b) was established to cover the use of biodiesel for this purpose. In the United States, blends of up to 5% biodiesel in heating oils (B5 Bioheat) have recently been approved for inclusion in the ASTM heating oil standard, D396 (ASTM 2008d). Another combustion-related application of biodiesel is as an aviation fuel, although

the relatively poor low-temperature properties of biodiesel restrict its use to low-altitude aircraft (Dunn 2001). Additionally, the use of biodiesel in diesel-fueled marine engines to reduce environmental impact is another important application of this biodegradable and non-toxic fuel (Nine et al. 2000). Because there are less harmful exhaust emissions from biodiesel than those from petrodiesel, the use of biodiesel to power underground mining equipment is another fuel-related application. Biodiesel may also be used as a fuel for generators and turbines for the generation of electricity (Hashimoto et al. 2008; Kalbande et al. 2008; Kram 2008a; Lin et al. 2008) or as a substitute for hydrogen in fuel cells (Kram 2008b). Finally, other niche uses such as in national parks and other environmentally sensitive locations are important fuel-related applications of biodiesel.

An important non-fuel application is as an industrial environmentally friendly solvent, since FFAE are biodegradable, have high flash points, and have very low volatilities (Wildes 2002). The high solvent strength of biodiesel makes it attractive as a substitute for a number of conventional and harmful organic solvents (Hu et al. 2004) in applications such as industrial cleaning and degreasing, resin cleaning, and removal (Wildes 2001, 2002), plasticizers in the production of plastics (Wehlmann 1999), liquid–liquid extractions (Spear et al. 2007), polymerization solvent (Salehpour and Dube 2008), and as a medium in site bioremediation of crude petroleum spills (Miller and Mudge 1997; Mudge and Pereira 1999; Glória Pereira and Mudge 2004; Fernandezalvarez et al. 2006). The strong solvent properties of biodiesel are particularly noticeable in cases where diesel engines have been operated with petrodiesel for many years or miles, which results in build-up of insoluble deposits in fuel tanks and lines. Upon switching to biodiesel, especially B100, the deposits will get released, which results in vehicle inoperability due to fuel filter clogging. Although biodiesel often gets blamed for clogging fuel filters with deposits in cases such as these, it is in fact the fault of the petrodiesel from which the deposits originated, since biodiesel is merely acting as a cleansing solvent.

Fatty acid alkyl esters can also serve as valuable starting materials or intermediates in the synthesis of fatty alcohols (Peters 1996), lubricants (Willing 1999; Moser et al. 2007; Sharma et al. 2007; Dailey et al. 2008; Padua 2008), cold flow improver additives (Moser and Erhan 2006, 2007; Moser et al. 2007; Dailey et al. 2008), cetane improving additives (Poirier et al. 1995), and multifunctional lubricity and combustion additives (Suppes et al. 2001; Suppes and Dasari 2003). Lastly, biodiesel in conjunction with certain surfactants can act as a contact herbicide to kill broadleaf weeds in turfgrass (Vaughn and Holser 2007).

Glycerol

Glycerol (or glycerin; 1,2,3-propanetriol) is produced in addition to FFAE during transesterification of vegetable oils and animal fats (Fig. 15.1). Prior to the increase in biodiesel production that occurred over the past decade as a result of the continued interest in renewable fuels, the market demand for glycerol was relatively balanced

with supply. However, the emergence of the biodiesel industry has spawned numerous efforts to find new applications, products, and markets using this versatile chemical. A recently published review (Behr et al. 2008) thoroughly covers recent developments on the chemistry and utility of glycerol. In general, glycerol may be used as a chemical feedstock in the production of polyurethanes, polyesters, polyethers, and other materials. Glycerol may also be found in lubricants, wrapping and packaging materials, foods, drugs, cosmetics, and tobacco products. Applications and products that displace existing petroleum-derived materials or feedstocks are of particular interest. A recent significant advance is the development of a synthetic route to propylene glycol (1,2-propanediol) from glycerol, which represents a viable alternative to the classic petrochemical route from propylene (Dasari et al. 2005; Suppes 2006; Feng et al. 2008). Propylene glycol represents a replacement for the common toxic antifreeze component ethylene glycol.

Future Outlook for Biodiesel

Despite its many advantages as a renewable alternative fuel, biodiesel presents a number of technical problems that must be resolved before it will be more attractive as an alternative to petrodiesel. These problems include improving the relatively poor low-temperature properties of biodiesel as well as monitoring and maintaining biodiesel quality against degradation during long-term storage.

Maintaining fuel quality during long-term storage is a concern for biodiesel producers, marketers, and consumers. The most cost-effective means for improving oxidative stability of biodiesel is treatment with antioxidant additives. Care must be exercised in cleaning storage tanks before filling them with biodiesel and in monitoring storage conditions inside of the tanks such as temperature, moisture content, exposure to direct sunlight, and the atmosphere (nitrogen “blanket” is preferable) over which the fuel is stored. Biodiesel stored over long periods should be monitored regularly for signs of degradation. The National Biodiesel Board recommends that biodiesel not be stored for longer than 6 mo.

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

The primary market for biodiesel in the near to long-term future is likely to be as a blend component in petrodiesel (ULSD). As such, it is critical that a thorough understanding be developed as to how biodiesel prepared from various feedstocks influences important fuel properties of the resultant petrodiesel/biodiesel blends, such as exhaust emissions, low-temperature operability, oxidative stability, water content, kinematic viscosity, AV, lubricity, and corrosiveness.

Soybean oil, which is currently the predominant feedstock for biodiesel production in the United States, is comparatively expensive, does not have an optimal fatty acid composition, has numerous competing food-related applications, and is not obtained in high yield from the seeds from which it is obtained. Development of alternative feedstocks for biodiesel production is another important area of current and future research. Additionally, genetic modification of existing oilseed sources to yield higher oil content and optimal fatty acid compositions is another potential strategy to yield improved quantity and fuel properties of biodiesel. However, genetically modified crops require extensive testing, regulatory evaluation, and approval prior to widespread commercial production.

Biodiesel in the coming years may face competition from non-ester renewable diesel fuels such as those produced from catalytic hydroprocessing of vegetable oils or animal fats. Although many of the benefits of biodiesel may be lost in the production of hydrocarbons from vegetable oils or animal fats, some of the negative aspects of biodiesel are lost as well. From a commercial standpoint, the traditional petroleum industry is more comfortable with these non-ester renewable diesel fuels than with biodiesel, which may present a substantial challenge to the widespread deployment of biodiesel as an alternative fuel in the future. However, the many environmental benefits and applications of biodiesel will continue to ensure that a substantial market exists for this attractive alternative to conventional petroleum diesel fuel.

Further Reading

For additional recent reviews on biodiesel production and processing, *see* Sharma et al. (2008), Vasudevan and Briggs (2008), Marchetti et al. (2007), Meher et al. (2006a), and Gerpen 2005. For further reading on catalysts for the production of biodiesel, *see* Ranganathan et al. (2008; enzymatic catalysts), Narasimharao et al. (2007; general catalyst review), and Demirbas (2005; supercritical methanol). For more information on alternative feedstocks for biodiesel production, *see* Meng et al. (2009; microorganisms), Canakci, Sanli (2008; various), Li et al. (2008; microbial oils), Scholz and da Silva (2008; castor oil), Chisti (2007; microalgae), and Mohibbeazam et al. (2005; Indian oils). For additional reading on the influence of structure on the physical properties of biodiesel, *see* Knothe (2008), Knothe (2007), and Knothe (2005). Further reviews on additives (Ribeiro et al. 2007), glycerol (Behr et al. 2008), standards (Knothe 2006), methods (Monteiro et al. 2008), renewable diesel (Demirbas and Dincer 2008; Huber and Corma 2007),

and progress and trends in biofuels (Demirbas 2007) are also available. Several recent books also discuss biodiesel in whole or in part, which include Hou and Shaw (2008), Nag (2008), Erhan (2005), Knothe et al. (2005), Mittelbach and Renschmidt (2004).

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