Food versus Fuel Characteristics of Vegetable Oils and Animal Fats

A. C. Hansen, B. B. He, N. J. Engeseth

ABSTRACT. *Vegetable oils and animal fats are major components of food products and are used extensively for cooking. Recently, attention has been focused on their uses for making fuels for engines and heating. Vegetable oils and animal fats comprise mixtures of fatty acids in proportions that depend on the source materials. These fatty acids vary with respect to carbon chain length and degree of saturation. Fatty acid composition has been shown to have impacts on the properties of oils and fats and thus on both food and fuel quality. Some of these source materials also contain natural antioxidants that are beneficial for both food and fuel applications. The objectives of this article are to highlight the different requirements in the properties of vegetable oils and animal fats for health and for fuel, and to provide an assessment of the suitability of different materials as sources for food and/or fuel.*

Keywords. Animal fat, Biodiesel, Fuel characteristics, Food characteristics, Vegetable oil.

Vegetable oils and animal fats are used extensively in food products and food processing. Recently, attention has been focused on their use as fuel for engines and heating. In their commercial application as fuel for engines, these oils and fats are typically converted into biodiesel via a transesterification process (Dunn and Bagby, 1995). Recently, processes have been developed that are able to convert vegetable oil feedstock into an isoparaffin-rich diesel substitute referred to as "green diesel" (Kalnes et al., 2007). This article focuses on the characteristics of the vegetable oils and animal fats as they pertain to biodiesel produced through transesterification.

Vegetable oils and animal fats comprise mixtures of fatty acids in proportions that depend on the source materials (He et al., 2009). These fatty acids vary with respect to carbon chain length and degree of saturation. Fatty acid composition has been shown to have a major impact on the properties of the oil or fat and thus on both food and fuel quality (Beardsell et al., 2002; Knothe, 2005). Knowledge of this impact should facilitate the process of selecting oil sources for the purpose of producing either food or fuel with optimal characteristics.

In addition, this information will assist in identifying oil traits that should be targeted when genetically designing oil crops to achieve desired properties for either food or fuel. While inevitably the blend of fatty acids in a vegetable oil or animal fat will likely yield a less-than-perfect set of properties, there is still sufficient scope to identify oils that will provide either better food quality with a positive impact on health, or high-quality fuel that will yield efficient combustion while maximizing oxidative stability and ensuring acceptable cold flow characteristics.

The objectives of this review are to highlight the different requirements in the properties of vegetable oils and animal fats and to provide a means of comparing source materials in terms of their suitability for food and fuel uses.

COMPOSITIONS OF VEGETABLE OILS AND ANIMAL FATS

There is an enormous range of oils and fats that can be extracted from various source materials. Table 1 lists some common oils and fats with their respective fatty acid compositions. Oleic acid, for example, is shown to have a $C_{18:1}$ carbon chain structure, which implies that there are 18 carbon atoms in the straight chain and one double bond. Linolenic acid has the same number of carbon atoms but three double bonds. The number of bonds reflects the degree of unsaturation of the fatty acid. No double bonds indicate that the fatty acid is saturated. Table 1 highlights the considerable variation among different sources of lipids or oils and fats that can be used for food or conversion into fuel. However, not all seed oils are edible. For example jatropha oil, from *Jatropha curcas*, is a non-edible oil source that contains toxins and is being investigated in a number of different countries, notably India, as a viable feedstock for biodiesel production.

The authors are **Alan C. Hansen, ASABE Member,** Professor, Department of Agricultural and Biological Engineering, University of Illinois, Urbana, Illinois; **B. Brian He, ASABE Member,** Associate Professor, Department of Agricultural and Biological Engineering, University of Idaho, Moscow, Idaho; and **Nicki J. Engeseth,** Associate Professor, Department of Food Science and Human Nutrition, University of Illinois, Urbana, Illinois. **Corresponding author:** Alan C. Hansen, Department of Agricultural and Biological Engineering, University of Illinois, 1304 W. Pennsylvania Avenue, Urbana, IL 61801; phone: 217-333-2969; e-mail: achansen@illinois.edu.

Table 1. Percent fatty acid composition by weight of selected seed oils and fats (He et al., 2009). Percentages may not add up to 100% because of exclusion of small percentages of other fatty acids not listed.

No.	Sample	Lauric ($C_{12:0}$)	Myristic ($C_{14:0}$)	Palmitic ($C_{16:0}$)	Stearic ($C_{18:0}$)	Oleic ($C_{18:1}$)	Linoleic ($C_{18:2}$)	Linolenic ($C_{18:3}$)	Eicosanoic ($C_{20:1}$)	Erucic ($C_{22:1}$)
1	Avocado	--	--	20.5	1.0	58.5	13.6	1.0	--	--
2	Camelina	--	--	6.1	2.9	18.2	24.8	24.3	12.8	2.6
3	Candlenut	--	--	5.7	2.7	26.0	39.7	24.5	--	--
4	Canola	--	--	4.0	1.9	61.9	19.3	9.3	1.2	--
5	Coconut	54.9	20.9	10.5	3.3	--	--	2.1	--	--
6	Corn	--	-	13.5	1.9	27.9	52.8	1.3	0.4	--
7	Crambe	--	--	1.7	0.7	15.9	7.9	5.1	2.2	57.2
8	Croton nut	--	--	4.8	3.7	7.7	77.8	3.2	1.3	--
9	Jatropha	--	--	7.2	38.6	43.4	6.0	3.2	--	--
10	Mustard[a]	--	--	2.8	1.1	27.8	10.4	9.2	9.6	32.8
11	Mustard[b]	--	--	2.8	1.4	17.5	20.5	12.8	12.0	24.9
12	Olive[c]	--	--	12.0	2.0	75.6	9.7	0.7	--	--
13	Palm	--	--	41.1	5.3	40.3	10.8	--	--	--
14	Rapeseed	--	--	2.7	1.0	14.2	11.7	7.3	7.3	48.4
15	Safflower	--	--	6.4	2.5	26.1	75.0	--	--	--
16	Soybean	--	--	10.2	4.2	21.7	53.1	7.0	0.0	--
17	Fish oil[d]	--	--	10.9	2.7	13.8	--	11.6	5.9	22.8[e]
18	Tallow[f]	--	3.0	26.0	14.0	47.0	3.0	1.0	--	--

[a] Cultivar of Ida Gold.
[b] Cultivar of Pacific Gold.
[c] From Beardsell et al. (2002), table 1.
[d] Low overall percentage caused by exclusion of short-chain fatty acids and unsaturated 16-carbon acids.
[e] Total of unsaturated fatty acids of 22 or more carbons.
[f] NAS (1976).

FATTY ACIDS AND THEIR IMPACT ON HEALTH

Much focus has been centered on fat intake and human health. High fat intake is often associated with elevated risk of cardiovascular disease and obesity. Typical dietary fats and oils naturally include both saturated and unsaturated fatty acids. Not only is total intake of fats and oils important, but also extremely important is fatty acid composition. In general, diets have tended to shift away from animal fats over time to higher intake of plant fats, causing shifts of fatty acid consumption (Simopoulos, 1999; NIH, 2001). From a health standpoint, research has shown that saturated fats (saturated fatty acids) and trans-fats both promote heart disease through raising cholesterol (Mozaffarian et al., 2006). Trans-fats are often caused by the partial hydrogenation of oils, primarily to increase their melting point and alter their physical properties as well as to enhance oxidative stability and enhance stability during operations such as deep-fat frying (Ascherio et al., 1999). In an attempt to reduce trans-fats in their products, food manufacturers have resorted to using oils that are high in saturated fatty acids such as palm oil (Dunford, 2008). The use of these oils eliminates the need for hydrogenation and hence the trans-fat content is significantly reduced. Nevertheless, while less harmful than trans-fats, palm oil, which contains a large proportion of saturated fats, is still far more conducive to heart disease than other "heart-protective" oils such as olive, soy, and canola, which contain less saturated fat content (Mozaffarian et al., 2006).

Palm oil is the one of the most widely used edible oils in the world, and its world production exceeds that of soybean oil (USDA, 2009). Palm oil is highly attractive not only because of its taste and cooking properties but also because of its lower cost (it is about one-third lower than the cost of soybean oil). Oil palm plants yield 10 times more oil per acre than soybeans.

One of the major factors involved in cardiovascular disease is the low-density lipoprotein (LDL) cholesterol in the bloodstream. In contrast, elevation of high-density lipoprotein (HDL) cholesterol is linked to a reduced risk of coronary heart disease (Beardsell et al., 2002). Saturated fats are regarded as being harmful to human health, generally due to their ability to raise the LDL (or "bad") cholesterol. The reason for trans-fats having a more dramatic impact on human health has been associated with their ability to also raise LDL cholesterol similarly to saturated fats; however, trans-fats also result in lowering of beneficial HDL cholesterol (Mensink and Katan, 1990).

Stearic acid behaves differently from many saturated fatty acids in that it does not generally raise serum cholesterol levels (Grundy, 1994). Stearic acid ($C_{18:0}$) is thought to be immediately converted into monounsaturated oleic acid ($C_{18:1}$) in the body and therefore should not raise the LDL cholesterol. Another possible reason is that stearic acid does not impact LDL-receptor activity, as Beardsell et al. (2002) suggested that the impact of saturated fats on LDL cholesterol appears to be inversely related to the number of carbon atoms, with lauric acid ($C_{12:0}$) > myristic acid ($C_{14:0}$) > palmitic acid ($C_{16:0}$) > stearic acid ($C_{18:0}$), although more research is required to verify this trend. In general, lauric, myristic, and palmitic acid tend to be associated with increased LDL and total cholesterol, while stearic acid appears to be either neutral or may lower these parameters.

The fats and oils that are considered beneficial for human health include both the monounsaturated fats that contain one double bond in the acid molecule and the polyunsaturated fats that contain more than one double bond. In general, monounsaturated and polyunsaturated fatty acids tend to have a positive impact on total cholesterol and result in lower LDL cholesterol in comparison to saturated fatty acids (Mattson and Grundy, 1985). However, monounsaturates are noted
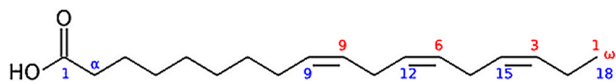
Figure 1. Molecule of α-linolenic acid with three double bonds showing the ω-3 positions in the C_{18} chain.
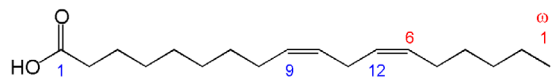

Figure 2. Molecule of linoleic acid with two double bonds showing the ω-6 position in the C_{18} chain.

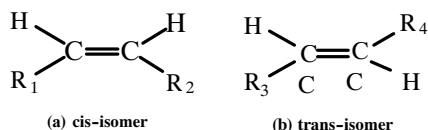(a) cis–isomer   (b) trans–isomer

Figure 3. Illustration of *trans-* and *cis-*isomers in oils and fats (C = carbon, H = hydrogen, and R_i = alkyl segments of variable lengths of carbon chains).

(a)

(b)

Figure 4. Structures of (a) *cis-* and *trans-*fatty acids (Mozaffarian et al., 2006) and (b) acids of varying chain length and saturation (Wikipedia, 2006).

to be more "heart healthy," as polyunsaturates generally cause a simultaneous reduction in HDL, while HDL is maintained with monounsaturate consumption. In the case of polyunsaturated fats, the position of the double bonds is also of significance for human health. Consumers are increasingly aware of the need for omega-3 fatty acids in their diet. Omega-3 polyunsaturated fatty acids have a double bond situated at the third carbon-carbon bond as numbered from the terminal methyl end of the chain on the right, as shown in figure 1. Omega-6 polyunsaturated fatty acids have a double bond at the sixth carbon-carbon bond counted from the terminal methyl end of the chain. An example is linoleic acid ($C_{18:2}$) with two double bonds, as shown in figure 2.

Evidence suggests that a proper balance of omega-3 and omega-6 is essential to human health (Simopoulos, 1999; Abbott et al., 2010). Competition for enzymes associated with desaturation and elongation of linoleic acid and α-linolenic acid will result in decreased elongation of α-linolenic to eicosapentaenoic acid (EPA), a more biologically active form of omega-3 fatty acid, in the presence of linoleic acid (Emken et al., 1994), thus making possible the deleterious impact of the eicosonoids associated with omega-6 fatty acids (i.e., linoleic), which oppose the positive impacting eicosonoids of the omega-3 fatty acids (Simopoulos, 1999), including improvement of blood pressure and reduction of clotting and inflammation. Although marine oils contain the much more efficient EPA and DHA (docosahexaenoic acid) omega-3 fatty acids, they are not often associated with the same vitamin E intake (serving as protection against oxidative stress) as are the plant sources of omega-3 fatty acids.

Saturated and unsaturated fats differ in their energy content and melting points. Since an unsaturated fat contains fewer hydrogen atoms than a saturated fat with the same number of carbon atoms, unsaturated fats will yield slightly less energy during metabolism than saturated fats. Saturated fats can stack themselves in a closely packed arrangement, so they can crystallize easily and are typically solid at room temperature. But the rigid double bond in an unsaturated oil or fat fundamentally changes its chemistry. There are two ways 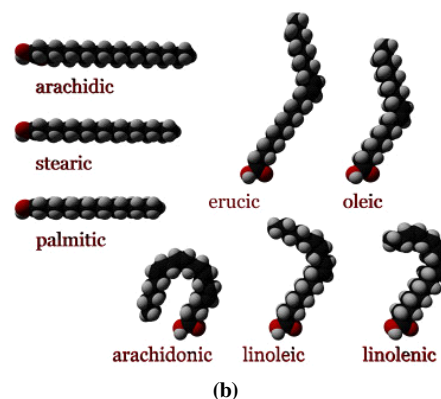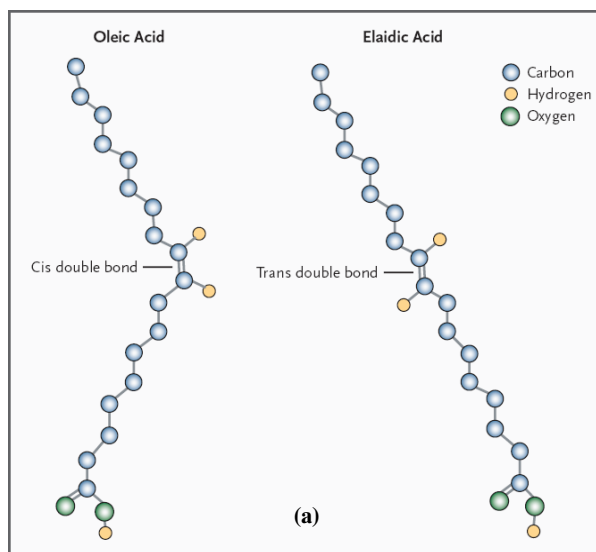the double bond may be arranged: the isomer with both parts of the carbon chain on the same side of the double bond (the *cis-*isomer, fig. 3a), or the isomer with two parts of the carbon chain on the opposite sides of the double bond (the *trans-*isomer, fig. 3b). Most *trans-*isomer fats (commonly called *trans-*fats) are commercially produced rather than naturally occurring. The *cis-*isomer introduces a kink into the molecule, as shown in figure 4, that prevents the fats from stacking efficiently, as with saturated chains. This decreases the intermolecular forces between the fat molecules, making it more difficult for unsaturated *cis-*fats to crystallize; they are typically liquid at room temperature. *Trans-*fats may still stack like saturated fats because of a straighter carbon chain (fig. 4) and are not as susceptible to metabolization as other fats. *Trans-*fats significantly increase the risk of coronary heart disease (Mozaffarian et al., 2006).

Both oleic acid and elaidic acid, shown in figure 4a, are 18-carbon fatty acids with one double bond. However, oleic acid has a *cis-*double bond (hydrogen atoms are on the same side of the bond), which causes a bend or kink in the fatty acid chain, whereas elaidic acid has a *trans-*double bond (hydrogen atoms are on opposite sides of the bond), which straightens the fatty acid chain. The *trans-*bond imparts a structure more similar to that of saturated fats, altering the physiological properties and effects of the fatty acid.

The thermal stability of oils depends on the fatty acid profile and antioxidant content (Beardsell et al., 2002). Antioxidants are also implicated in a wide range of health-promoting benefits. Edible oils from plants contain a wide range of antioxidants, such as polyphenols, carotenoids, and tocopherols (vitamin E). Antioxidants may prevent oxidation of lipids in the bloodstream and thus protect LDL cholesterol from oxidation (Beardsell et al., 2002).

While acknowledging the difficulty of defining a composition for the ideal "healthy" oil, Beardsell et al. (2002) nevertheless provide some useful principles by which to constrain the composition of the ideal oil. First of all, the fatty acid content should be dominated by 80% to 90% monounsaturates, such as oleic acid, with the remainder being mostly the polyunsaturated linoleic acid. Both linoleic and linolenic acids are regarded as essential to human nutrition; studies in the U.S. recommend that healthy oils should contain 4 to 10 times as much linoleic acid as linolenic acid. In addition, linolenic acid should be kept to a minimum unless it is accompanied by antioxidants. In terms of saturated fatty acids, myristic, lauric, and palmitic acids should be kept to a minimum. As shown in table 1, canola oil has a fatty acid profile approaching the specification above, although a lower linolenic acid content would bring it closer to the ideal healthy oil. Apart from a fairly high palmitic oil content, olive oil also matches the desired oil characteristics fairly closely.

For food manufacturers, the ideal oil described by Beardsell et al. (2002) cannot be used to meet all food applications. Lui (1999) defined an edible oil triangle with three points: oxidative stability, functionality, and nutrition. Hence, an ideal oil would have high oxidative stability at all temperatures; enough solid fat to provide functionality to food products such as spreads, confectionery, and chocolate; and a minimum of saturated fats (Talbot, 2006). Oxidative stability and functionality tend to be stacked on the side of more saturated fats, while nutrition requires a focus on more unsaturated fats. Emphasis on the middle-of-road stearic and oleic acids may help to provide an acceptable compromise, depending on the food application.

FATTY ACIDS AND THEIR IMPACT ON BIODIESEL FUEL PROPERTIES

Biodiesel, a collective name for the mixture of methyl and/or ethyl esters of long-chain fatty acids, is made by transesterifying vegetable oils and/or animal fats with primary alcohols, typically methanol or ethanol. Biodiesel is biodegradable and one of the most viable renewable fuels. Utilization of biodiesel in diesel engines reduces key regulated emissions substantially and has very little negative effect on engine operability and durability, provided that the fuel complies with the quality standards. The specifications for biodiesel as an alternative fuel for diesel engines have been defined by ASTM standard D6751 (ASTM, 2007a). A variety of vegetable oils and animal fats can be used for biodiesel production. Currently, rapeseed oil is the dominant feedstock in Europe, while soybean oil is the major feedstock in the U.S. Other vegetable oils, such as mustard, safflower, sunflower, palm oil, jatropha, and algae oil, have been studied and used for biodiesel production. Animal fats and greases (waste food processing oils) are also appropriate feedstocks (He et al., 2009).

Due to the variability of vegetable oils and animal fats, the FA compositions of the feedstocks for biodiesel production vary widely. This, in turn, affects the fuel properties, mainly in ignition quality, oxidative properties, and cold flow properties.

IGNITION QUALITY

Ignition quality is an important characteristic of diesel fuels. It measures how well a fuel is suited for a diesel engine. Unlike gasoline-powered "spark ignition" engines, diesel engines use compression alone to ignite the fuel and are therefore referred as "compression ignition" (CI) engines. Cetane number is commonly used to quantify a fuel's ignition quality. The higher the cetane number, the more readily the fuel ignites in the engine, thus the more preferable.

Cetane number is measured using a specifically designed engine (known as a cetane engine) that follows the specified procedures of ASTM standards D613 (ASTM, 2005) and D6890 (ASTM, 2007b). The fuel being measured is compared to fuels of known cetane numbers and ignited at different compression ratios. Most diesel fuels have cetane numbers in the range of 40 to 50 and meet the specifications of ASTM standard D975 (ASTM, 2007c).

Generally, biodiesel has a higher cetane numbers than fossil diesel. Depending on the source of feedstock, the cetane number of biodiesel could be as high as 100. Van Gerpen (1996) summarized the cetane numbers of biodiesel from 12 studies and found that the cetane numbers were 40 to 60 for biodiesel from soybean oil and 48 to 64.8 for biodiesel from rapeseed oil.

ASTM standard D6751 specifies that a biodiesel fuel has to have a minimum cetane number of 47, while European standards require a cetane number of 51. Higher cetane numbers imply that engines running on biodiesel have advantages of easy cold starting and low idle noise. However, not all biodiesel fuels have the same cetane number. The number varies according to the feedstocks used.

Biodiesel is a mixture of different types of alkyl esters. Therefore, the cetane number of a biodiesel depends largely on the fatty acid profile of the feedstock used. In other words, the cetane number of a biodiesel is the weighted combination of the individual cetane numbers of alkyl esters in the fuel. Table 2 summarizes the cetane numbers of alkyl esters of fatty acids. When the composition of esters in a biodiesel is known, the cetane number (CN) of the mixture can be estimated by using empirical charts (e.g., Harrington, 1986) or

Table 2. Cetane numbers of selected fatty acid alkyl esters.

Fatty Acid	Alkyl Ester	Cetane No.	Reference
Palmitic ($C_{16:0}$)	Methyl	74.5	Klopfenstein, 1985
	Ethyl	85.9	Knothe et al., 2003
	Iso-propyl	85.0	Knothe et al., 2003
Stearic ($C_{18:0}$)	Methyl	86.9	Klopfenstein, 1985
	Ethyl	97.7	Knothe et al., 2003
	Iso-propyl	96.5	Knothe et al., 2003
Oleic ($C_{18:1}$)	Methyl	59.3	Knothe et al., 2003
	Ethyl	67.8	Knothe et al., 2003
	Iso-propyl	86.6	Knothe et al., 2003
Linoleic ($C_{18:2}$)	Methyl	38.2	Knothe et al., 2003
	Ethyl	39.6	Knothe et al., 2003
Linolenic ($C_{18:3}$)	Methyl	20.6	Klopfenstein, 1985
Erucic ($C_{22:1}$)	Methyl	76.0	Knothe et al., 1996

prediction equations such as the one below (Cheenkachorn, 2004):

$$CN = 33.6 + 0.539(C_{18:0}) + 0.303(C_{18:1}) + 0.0878(C_{18:2}) + 0.233(C_{22:1})$$

Based on the cetane numbers of different alkyl esters, it is summarized that the cetane number increases with the increase in (1) the chain length, (2) the number of side branches, and (3) the degree of saturation. Therefore, from an ignition quality point of view, vegetable oils and animal fats of long-chain, saturated fatty acid components are preferred for biodiesel production.

OXIDATIVE STABILITY

Stability is one of the technical issues that biodiesel producers have to deal with. Feedstock for biodiesel production, especially vegetable oils of high unsaturation, is vulnerable to being oxidized when exposed to open air. Oxidation leads to the formation of insoluble gum or sediments, and an increase in acidity (carboxylic acid formation). The consequences are injector fouling, combustion deposit, filter plugging, more rapid biodegradation, and corrosion of engine and fuel systems. During the oxidation process, intermediate products may form larger molecules through C-O-C (in oxygen-rich environment) or C-C (in oxygen-lean environment) bonds (Waynick, 2003). Multiple families of chemicals form as the result of oxidation, including aliphatic alcohols (causing reduced flash point), aldehydes (causing rancidity and bad odors), and short-chain fatty acids (causing acidity and corrosiveness). The presence of free fatty acids and some minerals, such as Cu, Fe, and Ni, will increase susceptibility to oxidation.

Three measures are typically used to present the stability of lipids in oleochemistry: iodine value, acid value, and peroxide value. Iodine value (IV), or iodine number, is an indirect measure of unsaturated double bonds. It reflects the potential of being oxidized but is not a very good indicator of fuel stability. The maximum iodine number in biodiesel is specified as less than 120 in European standard EN 14214 (CEN, 2003b). Iodine number is not specified in ASTM standard D6751 (ASTM, 2007a). The range of iodine numbers is approximately 94 to 120 for rapeseed oil and 117 to 143 for soybean oil (Knothe et al., 1996).

Acid value (AV), or acid number, is a measure of the amount of carboxylic acid groups in the sample and is expressed as the mass of potassium hydroxide in milligrams per gram of sample to be neutralized (mg KOH g^{-1}). The maximum acid value specified in biodiesel standards is 0.5 mg g^{-1} in both ASTM 6751 and EN 14214.

Peroxide value (PV), or peroxide number, is a measure of the concentration of peroxides and hydroperoxides formed in lipid oxidation. Samples are measured by titration of free iodine, generated from oxidation of potassium iodide, with sodium thiosulfate and expressed in milliequivalents of peroxide per unit mass of sample (meq g^{-1}). High peroxide value is an indication of high vulnerability of being oxidized. The PV of samples of vegetable oil and/or biodiesel depends heavily on the testing conditions and the devices used. Therefore, the PV range varies widely in different reports (Chao and Schwarzerb, 1998; BLT, 2003).

The current ASTM standard D6751 has adopted an oxidative stability test in biodiesel specifications, which is based on European standard EN 14112 (CEN, 2003a). This is an accelerated oxidation, or Rancimat, method run at 110°C. ASTM standard D6751 requires that the minimum oxidative stability has to be 3 h, while the European standard is 6 h minimum by the same test method (CEN, 2003b).

There are multiple factors that affect biodiesel fuel stability, especially those caused by improper processing, such as high moisture content, free and bound glycerol, free fatty acids, and catalyst residue. The major factor that relates to feedstock and affects the oxidative stability of biodiesel is the level of unsaturation, or the number of double bonds, of some fatty acids in vegetable oils and/or biodiesel. The rate of oxidation of biodiesel depends on the number of double bonds contained in the fatty acids. The more double bonds a fatty acid contains, the more vulnerable it is to be oxidized. Studies have shown that the mechanism behind the oxidation is complex, and many theories have been proposed (Waynick, 2003). Generally, the more double bonds in a vegetable oil or fat, the more prone it is to oxidation. The relative rates of the double bonds to be oxidized were proposed long ago (Gunstone and Hilditch, 1945) and are shown below:

oleic (C$_{18:1}$):linoleic (C$_{18:2}$):linolenic (C$_{18:3}$) = 1:12:25

It is generally agreed that oxidative stability depends heavily on the unsaturation levels of vegetable oils and/or biodiesel. The more double bonds the oil or biodiesel contains, the less stable it is. Removing polyunsaturated fatty acids, such as linoleic (C$_{18:2}$) and linolenic (C$_{18:3}$), can dramatically improve the oxidative stability of vegetable oils and thus biodiesel. This conclusion is in agreement with the requirement for better ignition quality (or higher cetane number), where high levels of saturation in vegetable oils and biodiesel are preferred.

COLD FLOW PROPERTIES

In industry, cold flow properties of biodiesel are mainly described by three related properties: cloud point, pour point, and cold filter plugging point. Each is expressed by a unit of temperature (°F or °C). In the U.S., the biodiesel specification (ASTM standard D6751) does not require reporting the pour point and cold filter clogging point. It requires reporting the cloud point; however, no specific value is given in the specification.

When environmental temperature decreases to a low temperature, the long-chain, larger molecules of organic substances, such as C$_{18}$-C$_{30}$ paraffin in fossil diesel and C$_{16}$-C$_{22}$ fatty esters in biodiesel, begin to form fine wax crystals. As crystals accumulate and the size of the crystals increases, they become visible to the naked eye. The fuel appears "cloudy." The temperature at which the "cloud" starts to appear is defined as the cloud point (CP).

If the environmental temperature continues to drop, an increasing number of wax crystals form. Eventually, the temperature reaches such a low point that the fuel mixture looks like a gel and cannot be poured anymore. This temperature is defined as the pour point (PP). PP is a rough criterion for fuel that is not readily pumpable if the temperature is lower than PP.

In some cases, even when the environmental temperature is below CP but above PP, wax crystals form but the fuel is still flowable or pumpable through fuel filters. However, the wax builds up and eventually plugs the fuel filters after an ex–

		CP (°C)		PP (°C)		CFPP (°C)	
No.	Oil or Fat	Methyl	Ethyl	Methyl	Ethyl	Methyl	Ethyl
1	Canola	1	-1	-9	-6	--	--
2	Coconut	--	5	--	-3	--	--
4	Linseed	0	-2	-9	-6	--	--
5	Mustard	--	1	--	-15	--	--
6	Olive	-2	--	-3	--	-6	--
7	Palm	13	8	16	6	--	--
8	Rapeseed	-2	-2	-9	-15	-8	--
9	Safflower	--	-6	-6	-6	--	--
10	Soybean	0	1	-2	-4	-2	--
11	Sunflower	2	-1	-3	-5	-2	--
12	Tallow	17	15	15	12	9	8
13	Used HO soy	--	7	--	6	--	--
14	Waste grease	--	9	--	-3	--	0
15	Waste olive	-2	--	-6	--	-9	--

Table 3. Cold flow properties of selected biodiesel derived from oils and fats (Dunn, 2005).

Table 4. Melting point temperatures of selected fatty acid alkyl esters (Knothe, 2005).

Fatty Acid	Alkyl Ester	Melting Point (°C)
Palmitic ($C_{16:0}$)	Methyl	30.5
	Ethyl	19.3
	Iso-propyl	13/14
Stearic ($C_{18:0}$)	Methyl	39
	Ethyl	31/33.4
Oleic ($C_{18:1}$)	Methyl	-20
Linoleic ($C_{18:2}$)	Methyl	-35
Linolenic ($C_{18:3}$)	Methyl	-57/-52

tended period of operation. Cold filter plugging point (CFPP) is defined as the highest temperature at which a fuel fails to pass through a standardized filter at a specified volumetric flow rate. CFPP gives an estimate for the lowest temperature at which a fuel will flow in fuel systems without any clogging problems. Therefore, it is a more practical factor then CP and PP in fuel utilization for both fossil diesel and biodiesel. CFPP was shown to have a linear relationship with CP in diesel-biodiesel blends (Dunn and Bagby, 1995); however, other researchers proposed CFPP as a non-linear function of CP and PP (Chiu et al., 2004).

Cold flow properties of biodiesel depend on many processing factors, such as alcohol used, free and bounded glycerol present, catalyst residue, and other impurities in biodiesel; however, the major factor determining cold flow properties is the fatty acid profile of the vegetable oil or animal fat used in making the biodiesel. Biodiesel from different feedstocks will have different values of CP, PP, and CFPP. Table 3 illustrates some CP, PP, and CFPP values of biodiesel from various vegetable oils and animal fats.

Again, biodiesel is a mixture of different alkyl esters. The substances that crystallize first when the temperature drops are typically the substances with the highest melting point temperatures. However, the CP of a biodiesel fuel is not the same as the melting point of the highest melting point substance due to the interference or interaction between the different substances in the resulting mixture. Table 4 lists the melting point temperatures of some fatty acid esters commonly seen in biodiesel.

It is generally accepted that unsaturated fatty esters are preferred in terms of better cold flow properties of biofuels. This is contradictory to requirements for better ignition

quality or cetane number and fuel oxidative stability, where low levels of unsaturation are expected. On the other hand, when a branched alcohol, such as *iso*-propanol, is used, the fatty alkyl ester has a low melting point in the neat form (table 4). This is in agreement with the requirements for better ignition quality and fuel oxidative stability.

Different enhancers for improving cold flow properties of diesel and/or biodiesel are commercially available. Generally, these enhancers are marketed to reduce gelling temperature and improve fuel operability at low temperatures. Research indicated that such enhancers demonstrated less effectiveness with biodiesel than with fossil diesel (Shrestha et al., 2005). To achieve the same effect, biodiesel required much higher amounts of the enhancers than what was normally recommended. The enhancers reacted differently depending on the biodiesel feedstocks for and blending levels. In optimum conditions, PP was decreased by as much as 14°C but CP was decreased by only 2.2°C. Therefore, enhancers may not achieve a significant improvement in biodiesel cold flow properties due to their being less effective in biodiesel.

HEALTH VERSUS FUEL ATTRIBUTES OF OILS AND FATS

The above descriptions of the desirable characteristics of vegetable oils and animal fats for food and health and for fuel highlight some differences as well as some overlap. Table 5 summarizes the attributes of oils in terms of fatty acids. For human health, saturated fats are undesirable; however, for fuel, they have a positive effect on cetane number and oxidative stability but a negative effect on cold weather properties. Polyunsaturates are beneficial for health but are generally undesirable in fuels, except in the case of cold weather application. Monounsaturates appear to be beneficial for both health and for fuel. In the case of fuel, even though they cause a lower cetane number and lower oxidative stability than the saturated stearic acid, the resulting properties are still regarded as

Table 5. Health versus fuel effects of fatty acids.

		Lauric ($C_{12:0}$)	Myristic ($C_{14:0}$)	Palmitic ($C_{16:0}$)	Stearic ($C_{18:0}$)	Oleic ($C_{18:1}$)	Linoleic ($C_{18:2}$)	Linolenic ($C_{18:3}$)
Health effects	HDL cholesterol	Negative	Negative	Negative	Neutral	Very positive	Positive	Positive
	LDL cholesterol	Very negative ————	Increasing	————→ Neutral		Positive	Positive	Positive
Fuel effects	Cetane number	Low	Increasing	————→	High	Rapidly decreasing ————→		Very low
	Oxidative stability	High	High	High	High	Rapidly decreasing ————→		Very low
	Cold weather (melting point)	Low	Increasing	————→	High	Rapidly decreasing ————→		Very low

acceptable. A benefit of oleic acid in fuel is a lower melting point compared to stearic acid. Hence, if the fuel is to be used in a relatively warm climate, there will be a greater tolerance of saturated fatty acid components, which will in fact be beneficial in raising the cetane number and improving oxidative stability. If the fuel is to be used in a colder climate, then it will be important to minimize the saturated fatty acids. Overall, it can be said that the relative proportions of fatty acids for an ideal edible oil specified by Beardsell et al. (2002), namely about 80% to 90% oleic acid and the remainder polyunsaturates with a ratio of about 4-10 to 1 of linoleic acid to linolenic acid, should also satisfy the desirable attributes for fuel.

SUMMARY AND CONCLUSIONS

The fatty acid composition of vegetable oils and animal fats has a big impact on the properties and quality of the food or fuel derived from such feedstocks. In the case of biodiesel produced from oils and fats via transesterification, key properties that are affected are the ignition quality, oxidative stability, and cold flow properties. Saturated fats contribute to higher ignition quality and oxidative stability, but they have a negative effect on cold flow properties. Polyunsaturates improve the cold flow properties of biodiesel. However, they reduce both ignition quality and oxidative stability. Monounsaturates have characteristics that make them the best compromise in achieving acceptable properties. Relative to health effects, monounsaturates are beneficial, but saturated fats are regarded as detrimental. Contrary to the above for fuel, polyunsaturates are desirable for health. Hence, it can be expected that a vegetable oil or animal fat that has a high content of monounsaturated fats may be acceptable for both food and fuel production, although small amounts of saturated fats may have a negative impact on health.

REFERENCES

Abbott, S. K., P. L. Else, and A. J. Hulbert. 2010. Membrane fatty acid composition of rat skeletal muscle is most responsive to the balance of dietary n-3 and n-6 PUFA. *British J. Nutrition* 103(4): 522-529.

Ascherio, A., M. B. Katan, P. L. Zock, M. J. Stampfer, and W. C. Willett. 1999. Trans fatty acids and coronary heart disease. *New England J. Med.* 340(25): 1994-1998.

ASTM. 2005. D613-05: Standard test method for cetane number of diesel fuel oil. West Conshohocken, Pa.: ASTM International.

ASTM. 2007a. D6751-07b: Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels. West Conshohocken, Pa.: ASTM International.

ASTM. 2007b. D975-07b: Standard specification for diesel fuel oils. West Conshohocken, Pa.: ASTM International.

ASTM. 2007c. D6890-07b: Standard test method for determination of ignition delay and derived cetane number (DCN) of diesel fuel oils by combustion in a constant volume chamber. West Conshohocken, Pa.: ASTM International.

Beardsell, D., J. Francis, and D. Ridley. 2002. Health-promoting constituents in plant-derived edible oils. *J. Food Lipids* 9(1): 1-34.

BLT. 2003. Stability of biodiesel: Used as a fuel for diesel engines and heating systems. Presentation of the BIOSTAB project results. Wieselburg, Austria: Federal Institute of Agricultural Engineering (BLT).

CEN. 2003a. EN 14112: Fat and oil derivatives. Fatty acid methyl esters (FAME). Determination of oxidation stability (accelerated oxidation test). Brussels, Belgium: European Committee for Standardization CEN).

CEN. 2003b. EN 14214: Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods. Brussels, Belgium: European Committee for Standardization CEN).

Chao-Liang, X., and K. Schwarzer. 1998. Comparison of four accelerated stability methods for lard and tallow with and without antioxidants. *JAOCS* 75(10): 1441-1443.

Cheenkachorn, K. 2004. Predicting properties of biodiesels using statistical models and artificial neural networks. In *Proc. Joint Intl. Conf. on Sustainable Energy and Environment (SEE)*, 176-179. Sponsored by Joint Graduate School of Energy and Sustainability, King Mongkut's University of Technology, Thailand.

Chiu, C. W., L. G. Schumacher, and G. J. Suppes. 2004. Impact of cold flow improvers on soybean biodiesel blend. *Biomass and Bioenergy* 27(5): 485-491.

Dunford, N. 2008. Formulating food products with low trans fats. Fact sheet FAPC 134. Stillwater, Okla.: Oklahoma State University, Food and Agricultural Products Research and Technology Center.

Dunn, R. 2005. Cold weather properties and performance of biodiesel. In *The Biodiesel Handbook*, 83-121. G. Knothe, J. Van Gerpen, and J. Krahl, eds. Champaign, Ill.: AOCS.

Dunn, R., and M. Bagby. 1995. Low-temperature properties of triglyceride-based diesel fuels: Transesterified methyl-esters and petroleum middle distillate/ester blends. *JAOCS* 72(8): 895-904.

Emken, E. A., R. O. Adlot, and R. M. Gulley. 1994. Dietary linoleic acid influences desaturation and acylation of deuterium-labeled linoleic and linolenic acids in young adult males. *Biochim. Biophys. Acta* 1213(3): 277-288.

Grundy, S. M. 1994. Influence of stearic acid on cholesterol metabolism relative to other long-chain fatty acids. *American J. Clinical Nutrition* 60(6): 986S-990S.

Gunstone, F., and T. Hilditch. 1945. The union of gaseous oxygen with methyl oleate, linoleate, and linolenate. *J. Chem. Soc.* (1945): 836-840.

Harrington, K. J. 1986. Chemical and physical properties of vegetable oil esters and their effect on diesel fuel performance. *Biomass* 9(1): 1-17.

He, B., J. H. Van Gerpen, and J. C. Thompson. 2009. Sulfur content in selected oils and fats and their corresponding methyl esters. *Trans. ASABE* 25(2): 223-226.

Kalnes, T., T. Marker, and D. R. Shonnard. 2007. Green diesel: A second-generation biofuel. *Intl. J. Chem. Reactor Eng.* 5: A48.

Knothe, G. 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Proc. Tech.* 86(10): 1059-1070.

Knothe, G., R. Dunn, and M. Bagby. 1996. Biodiesel: The use of vegetable oils and their derivatives as alternative diesel fuels. Jefferson City, Mo.: National Biodiesel Board. Available at: www.biodiesel.org/resources/reportsdatabase/reports/gen/19961 201_gen-162.pdf. Accessed 9 July 2010.

Knothe, G., A. Matheaus, and T. Ryan III. 2003. Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester. *Fuel* 82(8): 971-975.

Klopfenstein, W. E. 1985. Effect of molecular weight of fatty acid esters on cetane numbers as diesel fuel. *JAOCS* 62(6): 1029-1031.

Lui, K. 1999. Soy oil modifications: Products and applications. *Inform* 10(9): 868-877.

Mattson, F. H., and S. M. Grundy. 1985. Comparison of effects of dietary saturated, monounsaturated, and polyunsaturated fatty acids on plasma lipids and lipoproteins in man. *J. Lipid Res.* 26(2): 194-202.

Mensink, R. P., and M. B. Katan. 1990. Effect of dietary trans fatty acids on high-density and low-density lipoprotein cholesterol levels in healthy subjects. *New England J. Med.* 323(8): 439-445.

Mozaffarian, D., M. B. Katan, A. Ascherio, M. J. Stampfer, and W. C. Willett. 2006. Trans fatty acids and cardiovascular disease. *New England J. Med.* 354(15): 1601-1613.

NAS. 1976. *Fat Content and Composition of Animal Products: Proceedings of a Symposium*. Washington, D.C.: National Academy of Sciences.

NIH. 2001. High blood cholesterol: What you need to know. National cholesterol education program brochure. Publication No. 01-3290 (May 2001). Bethesda, Md.: National Institutes of Health, National Heart, Lung, and Blood Institute.

Shrestha, D. S., J. Van Gerpen, J. Thompson, and A. Zawadzki. 2005. Cold flow properties of biodiesel and effect of commercial additives. ASABE Paper No. 056121. St. Joseph, Mich.: ASABE.

Simopoulos, A. P. 1999. Essential fatty acids in health and chronic disease. *American J. Clinical Nutrition* 70(3): 560S-569S.

Talbot, G. 2006. Independent advice on possible reductions for saturated fat in products that contribute to consumer intakes. Summary report prepared for Food Standards Agency. Bedford, U.K.: The Fat Consultant.

USDA. 2009. Oilseeds: World markets and trade. Circular Series FOP 1-09. Washington, D.C.: USDA Foreign Agricultural Service, Office of Global Analysis.

Van Gerpen, J. H. 1996. Cetane number testing of biodiesel. In *Proc. 3rd Liquid Fuel Conf.*, 197-206. St. Joseph, Mich.: ASAE.

Waynick, J. A. 2003. Characterization of biodiesel oxidation and oxidation products. Technical literature review. Golden, Colo.: National Renewable Energy Laboratory.

Wikipedia. 2006. Fatty acid. In *Wikipedia, The Free Encyclopedia*. Available at: http://en.wikipedia.org/wiki/Fatty_acid. Accessed 9 July 2010.