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Biodiesel fuels

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ABSTRACT

The mono-alkyl esters, most commonly the methyl esters, of vegetable oils, animal fats or other materials consisting mainly of triacylglycerols, often referred to as biodiesel, are an alternative to conventional petrodiesel for use in compression-ignition engines. The fatty acid esters that thus comprise biodiesel largely determine many important fuel properties. In turn, the composition of the biodiesel depends on the composition of the parent feedstock because feedstocks with widely varying fatty acid composition can be used for biodiesel production. The use of different feedstocks is also significant under aspects of increasing biodiesel supply and socio-economic issues. In this article, biodiesel production is briefly described, followed by a discussion of biodiesel fuel properties and the influence of varying fatty acid profiles and feedstocks. It is shown that the properties of biodiesel least influenced by minor components can be determined by a straightforward equation in which the properties of the biodiesel fuel are calculated from the amounts of the individual component fatty esters and their properties. Optimizing biodiesel composition is also addressed.

Contents

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1. Introduction

The search for a variety of energy sources is nearly as old as mankind's need for energy. Increasing industrialization commencing in the 19th century, spurred by the development of machines converting the energy stored in a variety of resources to power, caused this search to intensify. The internal combustion engine, in its two major variations, the spark-ignition and compression-ignition (diesel) engines, is a prime example. While fuels obtained from fossil sources were investigated from the onset of these engines, biogenic materials also found some interest, primarily ethanol in the case of the spark-ignition engine [1] and vegetable oils in the case of the compression ignition engine [2]. Due to a variety of factors, petroleum became the major source of fuels for both engines, although research, testing and some use of the "alternative" biogenic fuels continued for many years through approximately World War II and then resumed with ever-increasing intensity, in the late 1970s and early 1980s as a result of the energy crises of the 1970s.

That operational problems were associated with the use of vegetable oils in a diesel engine was recognized early [2], with high viscosity being defined as a major cause of these problems. While one paper states [3] that it is "academically necessary to split off the glycerides and to run on the residual fatty acid," other work goes a step further by interchanging glycerol for ethanol by preparing the ethyl esters of palm oil through a transesterification reaction, with the Belgian patent 422877 probably being the first report of what is termed biodiesel today [4,5] and testing them in an urban bus [6]. This is probably the first documented use of what is now termed biodiesel [7,8], namely the mono-alkyl esters of vegetable oils or animal fats or other triacylglycerol-containing feedstocks. This approach was then rediscovered approximately forty years later [9] in the early stages of renewed interest in vegetable oils and their derivatives as diesel fuel.

Besides preparing biodiesel, several other approaches have been investigated over time with the objective of reducing the viscosity of triacylglycerol-containing materials. These approaches are dilution with petrodiesel, microemulsification, and pyrolysis [10]. Besides these four approaches, more recently another approach based on a catalytic reaction termed hydrodeoxygenation, which affords a mixture of hydrocarbons probably best called "renewable diesel" and simulating the composition of petroleum-derived diesel fuel (petrodiesel), has been developed [11,12]. The present article is, however, concerned with biodiesel and the other approaches are not discussed here.

With ever-increasing research interest as well as production and use of methyl esters of plant oils as biodiesel, especially since the mid- to late 1990s, standards were developed tailored largely toward these methyl esters. The first standard was established in Austria in 1991 followed by other European standards, most notably the German standard DIN 51606. Standards in individual European countries have been superseded by the European standard EN 14214 [13]. In the United States, concurrently the biodiesel standard ASTM D6751 [14] was developed. It may be noted that ASTM D6751 states that biodiesel meeting its specifications is to serve as blend stock for blends with petrodiesel and therefore is applied to neat biodiesel. Relatedly, the standard ASTM D7467 covers blends at levels of 6–20% biodiesel [15] and an ASTM specification WK52154 for blends >20% is under development [16]. Blends of up to 5% biodiesel with petrodiesel are covered by the petrodiesel standard ASTM D975 [17] with these blends required to meet the specifications for neat petrodiesel. The EN and ASTM standards now often serve as reference standards for other biodiesel standards world-wide. These standards address a variety of fuel quality issues caused by the properties of the major fuel components, the mono-alkyl esters of fatty acids, and by minor constituents (contaminants). It may be noted that viscosity, in the form of kinematic viscosity, as the major issue for using biodiesel instead of vegetable or plant oils, is limited in these standards to ensure that alkyl (usually methyl) esters are indeed used as biodiesel. Selected current specifications in the aforementioned two standards are listed in Table 1.

Besides overall favorable properties for use as transportation fuel, biodiesel has numerous other potential uses, although none of these uses can compete with fuel in terms of volume. These uses include heating oil [18,19], power generation [20], lubricants [21], plasticizers [22], high boiling absorbents for cleaning of gaseous industrial emissions [23], as well as various solvent applications, which are also discussed here briefly. It is biodegradable [24–26] and, relatedly, has also been tested as a possible oil spill remediation agent [27–31]. This application relates to the solvent properties briefly discussed at the end of this article. A detailed discussion of the applications

Table 1
Selected technical specifications in the biodiesel standards ASTM D6751 [14] and EN 14214 [13].

Specification	ASTM D6751		EN 14214	
	Limit	Method	Limit	Method
Kinematic viscosity	1.9–6.0 mm^2/s	D445	3.5–5.0 mm^2/s	EN ISO 3104
Cetane number	47 min	D613, D6890	51 min	EN ISO 5165
Cloud point	Report		–[b]	
Oxidation stability	3 h min	EN 14112	8 h min	EN 14112, EN 15751
Density	–	–	860–900 kg/m^3	
Free glycerol	0.02% mass max	D6584	0.02% mass max	EN 14105
Monoacylglycerols	0.4% mass max	D6584	0.7% mass max	EN 14105
Total glycerol	0.24% mass max	D6584	0.25% mass max	EN 14105
Acid value	0.5 mg KOH/g max	D664	0.5 mg KOH/g max	EN 14104
Na K combined	5 ppm (µg/g) max	EN 14538	5 mg/kg max	EN 14108, EN 14109
S	0.015 or 0.05% mass, max[a]	D5453	10 mg/kg	EN ISO 20846, EN ISO 20884
P	0.001% mass, max	D4951	4 mg/kg	EN 14107
Ca Mg combined	5 ppm (µg/g)	EN 14538	5 mg/kg	EN 14538

Max = maximum; min = minimum.
[a] Depends on the grade of petrodiesel to be blended with.
[b] Cold filter plugging point with varying limits depending on geography and time of year.