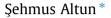
#### Fuel 117 (2014) 450-457

Contents lists available at ScienceDirect

### Fuel

journal homepage: www.elsevier.com/locate/fuel

## Effect of the degree of unsaturation of biodiesel fuels on the exhaust emissions of a diesel power generator



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#### HIGHLIGHTS

• The effect of the degree of unsaturation of biodiesels on diesel emissions was investigated.

• Biodiesels resulted in smoke opacity, with an increase in BSFC compared to ULSD.

• Saturated biodiesel had highest cetane number and lowest adiabatic flame temperature which was good to reduce NO<sub>x</sub> emission.

• The cetane number and adiabatic flame temperature appear to be the key properties that determined the emissions.

#### ARTICLE INFO

Article history: Received 1 August 2013 Received in revised form 6 September 2013 Accepted 10 September 2013 Available online 25 September 2013

Keywords: Biodiesel Iodine number Degree of unsaturation Diesel emissions

#### ABSTRACT

In this work, three biodiesel fuels with iodine numbers ranging from 59 to 185 were tested in a directinjection diesel engine powered generator set at constant speed of 1500 rpm under variable load conditions to investigate the effect of the degree of unsaturation of biodiesel fuels, which are quantified by the iodine number, on the performance and exhaust emissions of a diesel engine. The increase in unsaturation involved a decrease in cetane number, and therefore, allowed for the maximization of the effect of the cetane number, while other properties, such as oxygen content, heating value, and viscosity, varied within a small range. Experimental results showed that biodiesel fuels resulted in lower emissions of nitrogen oxides, carbon monoxide, and smoke opacity, with some increase in emissions of unburned hydrocarbons. With their low energy content, neat biodiesel fuels resulted in an increase in fuel consumption compared to the conventional diesel fuel (ultra-low sulphur diesel). The degree of unsaturation of biodiesel fuels had effects on engine emissions via its effect on the cetane number and adiabatic flame temperature while engine performance was not significantly affected by the type of biodiesel fuel or its degree of unsaturation. The biodiesel having lowest iodine number had highest cetane number, and lowest density and adiabatic flame temperature, which was good to reduce NO<sub>x</sub> emissions, as it agreed with experimental results. Additionally, more unsaturated biodiesel fuels showed higher NO<sub>x</sub> emissions, smoke opacity, and lower HC emissions. It can be said that cetane number and adiabatic flame temperature are responsible for such results.

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#### 1. Introduction

As a consequence of the increasing concern about environmental pollution and more stringent regulations on exhaust emissions, reduction in engine emissions have become a major subject in engine studies. In addition, much effort has been made to reduce dependence on the petroleum as it is obtained from limited reserves. These concerns have led to much research on alternative renewable fuels in the last decade. Among the proposed alternative fuels, biodiesel has received much attention for using in diesel engines in recent years [1,2]. Biodiesel is typically produced by transesterification reaction of vegetable oils or animal fats with methanol in the presence of a catalyst to yield glycerin and methyl esters, and it can be used directly or blended with fossil diesel fuels

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*Abbreviations:* ASTM, American Society for Testing and Materials; US EPA, United States Environment Protect Agency; GC, gas chromatograph; FID, flame ionization detector; LHV, lower heating value (kJ/kg); ppm, parts per million; rpm, revolution per minute; CO, carbon monoxide; HC, hydrocarbons; NO<sub>x</sub>, nitrogen oxides; BSFC, brake specific fuel consumption (g/kW h); BTE, brake thermal efficiency (%); IN, iodine number (g of  $I_2/100$  g); ULSD, ultra-low sulphur diesel; POME, palm oil methyl ester; CSOME, cottonseed oil methyl ester; WFOME, waste fish oil methyl ester.

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in diesel engines with no or little modifications. However, some diesel engine manufacturers do not allow using neat biodiesel or its blends instead of fossil diesel fuels. Warranties are often applied to only biodiesel that fulfills the ASTM D 6751-03 for USA and EN 14214 for European Union standards [3,4], and in Europe in concentrations below 7%, as specified by standard EN-590.

Although the fuel properties of biodiesel can vary with production technologies and feedstock, it has some fuel advantages over fossil diesel fuel, including renewability, biodegradability, better lubricity, and high flash point and oxygen content [5]. Lapuerta et al. [6] concluded in their review study that using biodiesel fuels in diesel engines result in reductions in CO, HC and particulate emissions due to the higher oxygen content of biodiesel compared to fossil diesel fuel. However, in the case of nitrogen oxides (NO<sub>x</sub>), despite the highest consensus lies in an increase of NO<sub>x</sub> emissions with biodiesel, some contradictory trends have also been reported. Some of the researchers found increases in NO<sub>x</sub> emissions: some others did not find any differences between diesel and biodiesel fuels, and others found decreases in NO<sub>x</sub> emissions while using biodiesel. This is mainly attributed to differences in physicochemical properties of biodiesel, its effect on injection timing, ignition delay, adiabatic flame temperature, radiative heat loss, and other combustion phenomena, also varies with engine technology and operating conditions [7,8]. However, several researchers indicate that NO<sub>x</sub> formation in biodiesel-fueled diesel engines is highly dependent on the degree of unsaturation and cetane number of biodiesel [9,10]. In general, higher degrees of saturation correlate with higher cetane numbers, and saturated biodiesel fuels (i.e. without double bonds) produce lower amounts of  $NO_x$  than unsaturated fuels [11]. In a study done by US EPA (United States Environment Protect Agency) [12], it was confirmed the direct relationship between  $NO_x$ emissions and molecular unsaturation. It was observed in the study that on average, biodiesel obtained from soybean oil provided a 15% increase in NO<sub>x</sub> emissions as compared to those with fossil diesel fuel, rapeseed oil based biodiesel provided a 12% increase, while biodiesel produced from animal fats led to only a 3% increase. The study of Wyatt et al. [13] also showed that the animal fat-based biodiesel fuels, which are highly saturated, had lower NO<sub>x</sub> emission levels than did the soybean oil based biodiesel fuel (unsaturation ones). In the same way, Wang et al. [14] found a measurable reduction in NO<sub>x</sub> emissions with biodiesel obtained from high oleic soybean oil compared to normal soybean oil based biodiesel which contains 25% oleic acid in its fatty acid composition. In another study by Ng et al. [15], NO emission was found to decrease with increasing palm and coconut oil biodiesels content in the fuel when compared with fossil diesel, opposite to the emissions of the highly unsaturated ones (soybean oil based biodiesel), where NO level are higher in relation to that of fossil diesel.

Table 1		
Speciation	of tested	fuels

However, the effect of the degree of unsaturation of biodiesel on opacity and particulate emissions is much less known. There is no consensus about whether or not the degree of unsaturation of biodiesel fuels affects smoke opacity and/or particulate emissions. Although a few authors found a slight dependency [16], there are also others who found no effect of the biodiesel feedstock on exhaust opacity and particulate emissions [17].

In this work, effect of the degree of unsaturation of biodiesel fuels, which are quantified by the iodine number, on the characteristics of the engine was investigated experimentally in a diesel engine powered generator set. Biodiesel fuels were produced from different feedstock such as palm oil, cottonseed oil and waste anchovy fish oil via transesterification process, and consequently their iodine values were different (from 59 to 185). The increase in unsaturation involved a decrease in cetane number, and therefore, allowed for the maximization of the effect of the cetane number, while other properties, such as oxygen content, heating value, and viscosity, varied within a small range.

#### 2. Experimental section

#### 2.1. Test fuel characterization

A conventional diesel fuel (Ultra-Low Sulphur Diesel (ULSD)) was provided from Shell fueling station located in Batman, Turkey, and used as the reference fuel in this work. Biodiesel fuels were produced from different feedstock such as palm oil, cottonseed oil and waste anchovy fish oil through transesterification reaction using methanol in the presence of an alkali catalyst. Biodiesel fuels were selected to have different values of iodine number, from 59 to 185. Among the biodiesels tested, palm oil is the most saturated one, and consequently, it has a high cetane number and low density. Cottonseed oil is available abundantly in Turkey, and waste anchovy fish oil is also taken into account as a promising alternative feedstock for biodiesel production [18]. In addition to these, they have more unsaturated fatty acids than palm oil. For transesterification reaction, methanol and sodium hydroxide with purity of 98% were provided from Refinery and Petro-Chemistry laboratory at Batman University, Batman, Turkey. After solving the NaOH catalyst in methanol at room temperature in a magnetic stirrer, the moisture-free oils were added to the reaction tank to start the transesterification reaction. The mixture was agitated throughout at 60 °C. After glycerol separation, the ester phase was washed with warm distilled water. After washing process, the methyl ester was subjected to a heat at 110 °C to remove excess alcohol and water, and then filtered. To determine the fatty acid profile, GC analyses were carried out on a Shimadzu GC2010 plus Gas

Fatty acid type	Carbon chain	Palm oil	Cottonseed oil	Waste anchovy fish oil
Linoleic	C18:2	11.8155	57.1	4.43
Palmitic	C16:0	39.7834	20.9	20.20
Oleic	C18:1	43.5639	17.9	19.71
Stearic	C18:0	3.1628	2.43	4.2
Miristic	C14:0	1.3810	0.65	6.71
Palmitoleic	C16:1	-	0.46	6.59
Trideconoic	C13:0	-	0.29	_
Linolenic	C18:3	0.2933	0.18	1.64
Eicosatetraenoic	C20:4	-	-	0.79
Eicosapentaenoic	C20:5	-	-	10.41
Docosapentaenoic acid	C22:5	-	_	0.82
Docosahexaenoic	C22:6	-	-	21.58
Others		-	_	1.53
Total unsaturated		55	75	69

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