Determination of biodiesel properties from residual feedstock

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Abstract

The current work examined how biodiesel produced by frying oils affects the physicochemical properties of its mixtures with conventional diesel heating oil. Through the characterization of biodiesel blends and heating oil, the purpose is to promote the optimum mixture; the one that will continue to meet the requirements of the existing legislation for heating oil, while positively contributes in reducing the production of pollutants. The percentage of biodiesel added to a conventional diesel fuel helps to reduce pollutants produced during combustion. The examined biodiesel is considered the corrupted product that produced at a factory in Cyprus, which is deemed unsuitable for export, because it does not meet the legal requirements. Using specific volumes of these mixtures, cetane index after distillation, oxidation stability, and cold filter plugging point, were determined in order to investigate the effect of the mixtures. Taking everything into consideration, an efficient potential utilization of a residual domestic product is proposed. Furthermore, the pollutants that accumulate on the urban atmospheres during the winter months, due to increased heating needs of homes and other public or private buildings, will be significantly reduced.

Keywords: biodiesel; heating oil; blends; legal requirements; pollutants

1. Introduction

Biodiesel is a methyl ester product (FAMEs: fatty acid methyl esters) derived by the transesterification of vegetable oils with methanol. The transesterification includes the splitting of vegetable oil molecules in three chains of fatty acids and one glycerol molecule, separately. These alkyl chains are called biodiesel. Many raw materials are used in the production of biodiesels; the most known in Europe are rapeseed oil (rape methyl ester, RME) and in USA soybean oil (methyl soy, SME), whereas many other oils exist, such as sunflower, palm oil, etc. Initially, diesel engine was designed to run on with vegetable oil, but because of weakness in the operation, a modification of vegetable oils was performed by transesterification, so that vegetable oils to become compatible with existing diesel engines (Ghannam *et al.*, 2016; Cheung *et al.*, 2015; da Silva *et al.*, 2017). The data about the biodiesel production costs vary depending on the feedstock used and the production process. Biodiesel can be used in engines, either pure (B100, when the manufacturer accepts such usage), or as a blend with diesel. However, biodiesel has lower energy content than diesel, due to the oxygen content, and as a result the performance and fuel consumption can be influenced. Moreover, it shows the highest NOx emission levels, lowers the oxidation stability of diesel (Kokkinos *et al.*, 2015) and potentially favors bacteria to grow. Furthermore, unsaturated fatty acids react with oxygen to form peroxides; this leads to degradation by-products that can cause sludge and varnish in the fuel system. Also, FAMEs can cause corrosion of the fuel injector, block the low-pressure fuel system, increase dilution and polymerization of the oil sump, clogging the pump due to high fuel viscosity at low temperature, increase injection pressure, elastomeric gaskets failures and blockage of the fuel injection (da Silva *et al.*, 2017; Xue *et al.*, 2011; Karavalakis *et al.*, 2009). Nevertheless, biodiesel usage presents a growing trend worldwide (Papadopoulos *et al.*, 2009). Biodiesel is highly biodegradable, has low toxicity and can replace diesel fuel; it is an alternative fuel for diesel engines. The use of biodiesel as fuel results to the reduction of major exhaust pollutants (SO_x, CO, Particulate Matter-PM, Volatile Organic Compounds-VOCs). Therefore, the negative environmental and health effects of diesel use are severely improved (Xue *et al.*, 2011; Karavalakis *et al.*, 2009; Chiatti *et al.*, 2016).

2. Materials and Methods

2.1. Blend preparation

In the present study, four different heating oils and biodiesel (B100) were used. The properties of biodiesel are presented in Table 1. Diesel fuels were blended with biodiesel at percentages 10%, 20%, and 50% in biodiesel at ambient temperature. For sample 1, the heating oil was mixed with biodiesel in a ratio of 2.5%, 7%, 10%, 20% and 50% v/v biodiesel. Because the results in the ratios 2.5% and 7% were quite close, the rest samples (sample 2, 3 and 4), were mixed at higher ratios, as shown in Table 2.

Table 1. Properties of biodiesel (B100)

Parameter	Result	Units	EN 14214 value
Visual Chracteristics			
Appearance	clear liquid		
Colour	yellow		
Chemical Chracteristics			
Density at 15 ^{0}C	881	kg/m^3	860 - 900
Water content	325	mg/kg	500 max
Oxidation Stability (110^{0}C)	7.1	hrs	6.0 min
Acid value	0.27	mg KOH/g	0.50 max
Potassium	1.0	mg/kg	5.0 max (as K & Na)
Iodine value	81.2	g I_2/100g	120 max
Total glycerol	0.11	% mass	0.25 max
Linolenic acid methyl ester	2.02	% mass	12 max
Total Contamination	3	mg/kg	24 max
Phosphorous	1.8	mg/kg	10 max

2.2. Materials

A residual product (biodiesel B100), which did not satisfy the specifications for placement in the market, was purchased from a local industrial plant in Cyprus. Also, four different oils were mixed with B100 (S1: heating oil with destination outside Europe, S2: heating oil with destination within Europe, S3: heating oil for Cyprus trade and S4: rural Cyprus oil). The reagents used in the synthesis and purification procedures were: hexane (≥96.0%, Merck), acetone (≥99.5%, Merck), propane (≥ 99.5%, Merck), distilled water (Water Purification System, Elga Purelab Option Q7) and heptane (≥ 99.0%, Merck).

2.3. Methods

2.3.1. Measurement of cetane index

ASTM standard D86-12 was used to measure cetane index of diesel fuel and its mixtures with biodiesel. The cetane index was obtained in an automated manner by calculation after distillation of fuel from the distillation measurement instrument (Automated Distillation Analyzer, Optidist Herzog, Pac). It was calculated using the density measurements and boiling point curves of distillation according to ASTM standard D86-12.

2.3.2. Measurement of oxidation stability

The methods described in standards EN 14112 for biodiesel and EN 15751 for diesel and biodiesel blends, were used to measure the oxidation stability of biodiesel, diesel fuels and their mixtures. The results were obtained in the constant temperature of 110.9^{o}C and at an air flow of 10L/h by the measuring instrument (893 Professional Biodiesel Rancimat, Metrohm).

Table 2. Preparation of mixtures by volume ratio of biodiesel with heating oil

Samples	Volume ratio (%)				
S1	**2.5%**	**7%**	**10%**	**20%**	**50%**
Biodiesel (gr)	2.20	6.17	8.82	17.64	44.10
Diesel (gr)	81.98	78.19	75.67	67.26	42.04
S2			**10%**	**20%**	**50%**
Biodiesel (gr)			8.82	17.64	44.09
Diesel (gr)			75.77	67.35	42.09
S3			**10%**	**20%**	**50%**
Biodiesel (gr)			8.82	17.64	44.09
Diesel (gr)			76.68	68.16	42.60
S4			**10%**	**20%**	**50%**
Biodiesel (gr)			8.82	17.64	44.09
Diesel (gr)			74.56	66.27	41.42

2.3.3. Measurement of cold filter plugging point (CFPP)

The method described by ASTM standard D 6371-05 was used to measure the cold filter plugging point (CFPP) of the diesel heating oil and its mixtures with biodiesel fuels. The cold filter plugging point was obtained in an automated way by the CFPP measurement instrument (Normalab).

3. Results and Discussion

3.1. Cetane index

The measurement of cetane number indicates the quality of diesel fuel. The calculated cetane index (CCI) is used for the calculation of the fuel ignition quality (Aburudyna *et al.*, 2014). It is an attempt to predict cetane number (CN) by simpler tests, such as the density and distillation curve. The CN affects the length of time from the start of fuel injection to the start of combustion in a diesel engine. The higher is the CN, the shorter will be the period of ignition delay. The CN affects the ease of starting, combustion noise and exhaust emissions of diesel engines (Bezaire *et al.*, 2010; Candeia *et al.*, 2009). As presented in Table 3, no noticeable behavior was observed for diesel sample 1, as all measurements were approximately equal. For diesel sample 2, a reduction in cetane index was observed as percentage of FAMEs was increased. Cetane index in diesel sample 3 increased, as percentage of FAMEs was also increased. For sample 4, there was a small increase in the cetane index. The cetane index of the fuels blends showed only marginal differences from the cetane index of the base fuel; it can be concluded that the addition of biodiesel to diesel fuels has an insignificant effect on the cetane index of the base fuels.

Table 3. Experimental results of cetane index for the tested samples

Cetane index	Sample 1	Sample 2	Sample 3	Sample 4
Diesel (heating oil)	52.6	51.8	47.6	57.1
Fame content 2.5%	52.5	[2] n.m.	n.m.	n.m.
Fame content 7%	52.8	n.m.	n.m.	n.m.
Fame content 10%	52.7	51.8	48.2	57.5
Fame content 20%	53.0	51.6	48.5	57.5
Fame content 50%	52.6	50.9	49.1	55.4

Europeans specifications for diesel (heating oil): min 46.0; max: --, Cyprus and Greek specifications: min 40.0; max: --[2] n.m. = not measured

3.2. Oxidation stability

The oxidation stability is a measurement of fuel resistance to degradation by oxidation. The oxidation of diesel fuel can lead to the formation of gums and sediments, causing blockage of filters and engine deposits. It can also lead to darkening of the fuel color, although this is not a significant problem (Xue *et al*., 2011). Determination of the oxidation stability is applied for use to biodiesel, as pure fuel or as a blending component for diesel fuel and biodiesel and gas mixtures, based on oil containing minimum 2% by volume of the biodiesel. As shown in Table 4, oxidation stability of diesel samples decreased as the percentage of FAMEs was increased. Compared to all diesel samples, it seems that sample 2 is the most stable to oxidation, while sample 4, the less stable. Finally, it was noted that oxidation stability for sample 1 was increased over time and is within the specification limits (> 25h).

3.3. Cold filter plugging point (CFPP)

CFPP is the lowest temperature at which fuel can pass through a standard test filter under standard conditions. The price of cold filter plugging point calculated in ^{o}C, records the first temperature at which the sample fails to reach the 20 mL mark in less than 60 s or fails to flow back into the test vessel. Improving additives reduce the cold filter plugging point by changing the size and shape of the wax crystals formed at cold temperatures. The method is applicable to distillate fuels, including those that contain improved flow or other additive, intended for use in diesel and domestic heating installations (Yuan *et al*., 2017).

Table 4. Experimental results for the oxidation stability of the tested samples

CFPP	Units: ^{o}C			
	Sample 1	Sample 2	Sample 3	Sample 4
Diesel	-4	-10	0	-5
Fame content 10%	-3	-12	-1	-4
Fame content 20%	-3	-12	0	-7
Fame content 50%	-10	-10	-6	-11

* Sample $1_{t = 0}$ / Sample $1_{t = 4 \text{ months}}$

[1] Europeans specifications for biodiesel: min 6.0 h; Diesel heating oil: min 20 h

[2] n.m. = not measured

Table 5. Experimental results for cold filter plugging point of diesel samples.

Oxidation stability	Units: h			
	Sample 1/ *after 4 months	Sample 2/ *after 4 months	Sample 3/ *after 4 months	Sample 4/ *after 4 months
Biodiesel	0.07/ n.m.	0.03/ 14.45	0.03/ 14.45	0.03/ 14.45
Diesel (heating oil)	125.67/ 140.90	141.90/ 210.34	110.87/ 190.54	50.97/ 60.75
Fame content 2.5%	>90/ n.m.	n.m./ n.m.	n.m./ n.m.	n.m./ n.m.
Fame content 7%	>90/ n.m.	n.m./ n.m.	n.m./ n.m.	n.m./ n.m.
Fame content 10%	110.43/ 134.55	112.81/ 226.79	75.02/ 181.02	17.33/ 25.78
Fame content 20%	88.30/ 111.64	112.41/ 135.65	46.99/ 64.85	11.16/ 16.70
Fame content 50%	39.81/ 37.47	11.14/ 10.31	0.03/ 0.03	0.03/ 0.03

[1] Category A (summer season): European/Cyprus/Greek specifications: max: +5 ^{o}C, from 1/4 to 30/9 each year.

[2] Category B (winter season): European/Cyprus/Greek specifications: max: -5 ^{o}C, from 1/10 to 31/3 each year.

According to Table 5, test sample 2 seems to belong to winter oils based on the specification limits (5 ^{o}C max. for summer, winter -5 ^{o}C), whereas samples 1, 3, and 4 appear to be summer oils.

4. Conclusions

Biodiesel prepared at different ratios (2.5%, 7%, 10%, 20% and 50% FAMEs), cetane index, oxidation stability and CFPP of biodiesel-diesel blend values were investigated according to EN and ASTM standards. The aim was to explore, whether these properties are improved after mixing, so that the final product to be used at fuel engines. The use of a residual product to produce a fuel that meets the specifications resulted to a product with better properties (e.g. improved oxidation stability and higher cost value). This is also in accordance to the requirement set by the European Union for using a specific 3% of biodiesel fuel. Increasing the percentage of biodiesel in fuels will result to the reduction of exhaust gases produced by the combustion of oil, since it is a natural product. Such efforts contribute to the wider use of biodiesel as a renewable energy source and further assist to adopt a wider fuel strategy.

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