Renewable Energy 36 (2011) 2918–2924

Contents lists available at ScienceDirect

Renewable Energy

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

Biodiesel improves lubricity of new low sulphur diesel fuels

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ARTICLE INFO

Article history:
Received 18 January 2010
Accepted 7 April 2011
Available online 6 May 2011

Keywords:
Biodiesel lubricity
Low sulphur diesel fuel
Diesel engine performance
Diesel engine emissions

ABSTRACT

In this work, biodiesel from waste vegetable oil was used as an additive in low sulphur diesel fuel in automobile engines. The result was a fuel mixture with high lubricating power. According to the lubrication trials, the experimental mixtures complied with lubricity conditions established by European regulations, even when only a small quantity of biodiesel was used. It was also found that the mixtures were compatible with different engine gaskets and engine lubricant. Lastly, bench tests were performed using an automobile engine with mixtures of diesel fuel without conventional lubricant additive and biodiesel. The results showed that engine performance curves were very similar to those obtained with diesel fuel and that contaminating emissions from the engine decreased substantially by including biodiesel in the fuel, except for nitrogen oxides.

1. Introduction

Due to environmental concerns, the sulphur content in new fuel formulations is to be decreased. However, that measure decreases fuel lubricity. The EURO IV regulation from 2005 established a limit of 50 ppm of sulphur in automobile fuels [1]. The new limits for contamination emissions are difficult to obtain using current engine technologies and fuel formulations. Among other innovations, it will be necessary to increase the injection pressure and to improve control over the combustion process. The tendency to increase injection pressure in engines can cause problems regarding inadequate lubricity, stimulating the search for new fuel formulations, among which biodiesel is an important alternative [2–5].

Important environmental, social and economic benefits can be obtained by using biodiesel from agro-alimentary wastes (such as used vegetable oil, fish oil and animal fats) as a lubrication additive in diesel fuels. In this paper the possibility to obtain good results using biodiesel produced from those wastes as a lubrication additive in fuels with low sulphur content is proved.

Starting from a quality biodiesel obtained from used vegetable oils, this paper aims to cover the following objectives:

- Obtain special mixtures of biodiesel–diesel without conventional lubrication additive that had high lubrication capabilities and was compatible with gaskets and engine lubricants.
- Determine the performance and emissions of an automobile engine in bench tests using the experimental mixtures.

Table 1 summarises the characteristics of the biodiesel used for the tests. It was obtained from an experimental reactor, starting from vegetable oil previously used for frying, and purified in the laboratory. The characteristics of the used oil are shown in Table 2 as well as the specifications for the special diesel fuel used in this work with a low content in lubricity additive (supplied by REPSOL S. A.).

2. Lubricity analysis

Before starting the tests for lubricity, compatibility and engine performance, a study on the miscibility of the different biodiesel-diesel special fuels without the lubrication additive was carried out, following the regulation [6]. For that purpose, four mixtures with 0.5%, 2%, 5% and 10% biodiesel were prepared. Those mixtures were maintained at 50 °C for seven days. During that time, no precipitation or opacity was observed to describe any differences in stability and miscibility between the two fuels considered.

Next, the lubricity of the biodiesel and the corresponding mixtures with the diesel fuel was determined. Lubricity is defined as the capacity of a fluid to prevent wear due to adhesion between surfaces in contact. The capacity of a liquid to avoid wear is intimately related with its composition.

Fuel lubricity is studied by observing the wear in different parts in contact when submerged in the fuel, and based on methods established for lubricating oils. Since those methods are quite strict, they were adapted slightly to be able to discriminate among values with comparatively lower lubricity. Among the different standardized tests to measure diesel fuel lubricity, the HFRR method (High Frequency Reciprocating Wear Rig) was used at different

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doi:10.1016/j.renene.2011.04.007

Table 1
Fuels quality parameters.

Property	D_l	B	B5	B10	Test method
Density (15 °C) (kg/m^3)	823.5	886.0	826.5	829.5	ASTM D1298
Viscosity (40 °C) (Cst)	2.44	4.94	2.51	2.60	ASTM D445
Flash point (°C)	81	178	82	82	ASTM D93
Sulphur content (%)	0.005	<0.01	<0.01	<0.01	ASTM D5185
Carbon Conradson (%)	0.0027	0.21	0.0046	0.0055	ASTM D189
Ash content (%)	0.014	0.003	0.006	0.007	ASTM D482
Water content (ppm)	47.7	268.2	125.7	205.2	ASTM D1533
Total acidity (mg KOH/g)	0.05	0.45	0.05	0.05	ASTM D2896
Phosphorus content (ppm)	0	0	0	0	ASTM D5185
Sodium content (ppm)	2.2	4.3	2.2	2.3	ASTM D5185
Potassium content (ppm)	0	157	11	25	ASTM D5185
Cetane number	53.7	54.1	53.1	52.5	ASTM D976
Methanol (% peso)	–	0.020	–	–	GC
Monoglycerides (%)	–	0.205	–	–	GC
Diglycerides (%)	–	0.176	–	–	GC
Triglycerides (%)	–	0.126	–	–	GC
Free glicerine (%)	–	0.01	–	–	GC
Iodine number (g I_2/100 g)	–	93	–	–	Titrimetric method
Distillation	65% (262.2 °C)	–	65% (265.9 °C)	65% (269.3 °C)	ASTM D86
	85% (276.8 °C)	–	85% (288.3 °C)	85% (295.5 °C)	
	95% (306.4 °C)	–	95% (332.5 °C)	95% (330.2 °C)	

prepared mixtures (see Fig. 1) to compare the wear scars [7]. In that way the capacity of the fuel to minimize the wear in the injection set of diesel engines was determined. Those values of the wear scar were compared with others described by the European regulation [8], which establishes a maximum scar of 460 μm.

The lubricity trial was carried out using a mechanism where a load is applied onto a 6 mm ball, which is moved with a reciprocal movement on a static steel disc. The surface areas in contact are covered by the fuel. The trial conditions defined by the fluid temperature, the load applied, frequency, and amplitude of the oscillation, environmental conditions and metallurgic characteristics are specified in the regulation [7].

Once the trial was completed, using a graduated microscope the diameter of the wear scar of the ball at 0° and 90° on the scar lines (X and Y) was measured. Then, the mean diameter of the wear scar without correction, WSMD = (X + Y)/2, was obtained. Since the absolute humidity of the air affects the results of the trial, it was necessary to calculate the average value of the vapour pressure at the beginning and at the end of each trial and to apply the uncorrected wear scar (WSMD), the correction factor of the humidity that normalized the results to a vapour pressure of 1.4 kPa. That corrected wear scar is called WS1.4. Table 3 presents the results obtained for the different mixtures.

Fig. 1 shows the mean values of the wear scar diameter normalized to a vapour pressure of 1.4 kPa. Note how the diesel fuel without the lubrication additive (D_l) has an approximate wear scar of 600 μm, much higher than the maximum value (460 μm) established by the European regulation. Nonetheless, when D_l includes small percentages of biodiesel, the lubricity gets closer to conventional diesel fuel (wears cars of 283 μm and 312 μm with 10% (B10) and 5% (B5) biodiesel, respectively, compared with 314 μm with conventional diesel fuel).

Two mixtures with two very small quantities of biodiesel were also tested to quantify what happens when the quantity of biodiesel used is similar to the lubrication additive used normally in diesel fuel. As seen in Fig. 1, adding D_l at 100 ppm of biodiesel a mixture (B001) with good lubricating properties is obtained, since the wear scar is 338 μm. Nonetheless, adding 10 ppm of biodiesel (B0001) the wear scar was 543 μm (above the maximum limit).

Thus, the lubricity trials demonstrate that incorporating small percentages of biodiesel (5–10%) in the diesel fuel, without a conventional lubricity additive, the lubricating characteristics of the fuel is equivalent to automobile diesel fuel (a wear scar value around 300 μm). Even by including biodiesel in very small quantities (not less than 100 ppm), wear scar values were within the limits allowed by the EU regulation, although slightly higher than conventional automobile diesel fuel.

Table 2
Waste oil used as raw material for biodiesel (no information on the original *source available)* ND: No detected. GC: Gas chromatography. FID: Flame ionization detector.

Property	Used frying oil	Test method
Fatty acid composition (%)		GC/FID
C16.0 Palmitic	10.01	
C16.1 Palmitoleic	0.37	
C18.0 Stearic	4.44	
C18.1 Oleic	39.45	
C18.2 Linoleic	42.6	
C18.3 Linolenic	0.30	
C20.5 EPA	ND	
C22.6 DHA	ND	
Iodine number (g I_2/100 g)	109	Wijs Method
Water content (ppm)	1000	ASTMD 1533
Viscosity (40 °C) (Cst)	44	ASTMD 445
Total acidity (mg KOH/g)	4.23	ASTMD 664
Carbon Conradson (%)	0.25	ASTM 189
Ash content (%)	0.030	ASTM 482

3. Compatability study

Some rubber elements in engines, such as gaskets and seals, can be exposed to oil, fuel, and other types of fluids. The characteristics of the elastomeric materials can deteriorate during exposure to those fluids, affecting their physical, chemical and mechanical properties. The use of biodiesel in diesel fuel can create unforeseeable problems with some elastomeric components due to inevitable changes in fuel composition. For that reason, the interaction of different fuel mixtures with elastomeric elements normally used in automobile diesel engines was analysed.

3.1. Compatibility with elastomers

Three components used in automobile engines were analysed (characteristic in Table 5), including a gasket for the protective cover of the camshaft (composed of nitrilic rubber; Material 1), a camshaft seal made up of fluoroelastomer on steel (Material 2) and a crankshaft seal of fluoroelastomer on steel (Material 3).

Using those three elastomers, laboratory trials were performed to evaluate compatibility with four types of fuel: D_l, B10, B40 and B.

The influence of the liquids on elastomeric materials is normally studied using laboratory trials based on the international regulation ASTM D471 [9]. That trial consists in a standardized immersion test, carried out in the absence of direct light and under specific temperature and time conditions. The resulting deterioration of the elastomer is determined by measuring the changes in the properties before and after immersion. The time of immersion and the temperature of the trial are established in terms of the real service conditions of the elastomer. The trial temperature has to be compatible with the real temperature supported by the elastomeric