Fuel 124 (2014) 91–96

Contents lists available at ScienceDirect

Fuel

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

Effect of biodiesel on the autoxidation of lubricant base fluids

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HIGHLIGHTS

- Methyl linoleate & squalane were used to model biodiesel & engine oil degradation.
- Conditions of temperature used were comparable to those in engines.
- At low temperatures (below 160 °C) methyl linoleate promotes lubricant oxidation.
- At higher temperatures (above 160 °C) methyl linoleate shows antioxidant character.
- This is due to O_2 addition to doubly allylic radicals being reversible above 160 °C.

ARTICLE INFO

Article history:
Received 21 November 2012
Received in revised form 15 November 2013
Accepted 8 January 2014
Available online 10 February 2014

Keywords:
Biodiesel
Oxidation
Lubricant
Kinetics

ABSTRACT

The effect of low concentrations of methyl linoleate on the autoxidation of squalane (2, 6, 10, 15, 19, 23 hexamethyltetracosane) was investigated at temperatures 100 to 170 °C as a chemical model of the effect of biodiesel on the degradation of hydrocarbon lubricants during use. Below 158 ± 5 °C, methyl linoleate behaves as a pro-oxidant, whilst above 158 °C, it inhibits alkane autoxidation. This change of mechanism is consistent with the addition of oxygen molecules to doubly allylic carbon centred radicals formed by hydrogen abstraction from methyl linoleate becoming reversible above 158 °C.

1. Introduction

The effects of biodiesel on engine lubricants have been studied since their planned entry into the market in the 1980s. Although Rudolf Diesel's original ignition engine was designed to run on vegetable oil [1], subsequent changes in the engine to cope with mineral diesel, as well as both consumer demand and environmental legislation has meant that the use of neat vegetable oils can no longer be considered a viable option as a renewable fuel. This is due to a number of factors both physically, such as high freezing points and viscosities [2], but also chemically, particularly with regards to the contamination of the engine lubricant [3,4], causing enhanced oxidation – especially when using oils with high levels of unsaturation [5,6] in engines. This has been particularly noted in those engines utilising direct-injection methods, which will become common in Europe due to legislation on Particulate Matter - EC Regulation No. 595/2009. Studies of the oxidised lubricating oil taken from the engine after use have shown oxidised biodiesel amongst the components, suggesting that biodiesel could be chemically interacting with the lubricant by increasing its rate of oxidation [7] and hence viscosity.

This theory was examined in this study using single chemicals to model the system. Methyl linoleate was used to model biodiesel as it is doubly unsaturated and a major component of many common Fatty Acid Methyl Ester (FAME) biodiesels [8,9], whilst squalane (2, 6, 10, 15, 19, 23 hexamethyltetracosane)was the oil used for the lubricant as its physical properties have already made it suitable for other work on lubricants [10–14], but crucially for this work it elutes as a single peak in GC, meaning its rate of decay was easily monitored. The two species were reacted together under oxygen at temperatures between 100 and 170 °C to represent the various temperatures found in an engine from the sump (lowest) to the piston ring assembly and combustion chamber (highest) [15,16] with methyl linoleate being added in concentrations of 0 to 10% to encompass the typical levels of fuel dilution, especially in the sump where biodiesel accumulates [17] with the aim of identifying any interactions between methyl linoleate and squalane and the chemical mechanisms behind them.

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http://dx.doi.org/10.1016/j.fuel.2014.01.039
0016-2361/

2. Experimental

Squalane (2,6,10,15,19,23 hexamethyl tetracosane), methyl linoleate (methyl 9,11-octadec-*cis*, *cis*-dienoate) (Sigma Aldrich, 99% pure), oxygen and nitrogen (BOC, 99.9% pure) were used. A volume of 5 cm^3 of substrate was introduced into a stainless steel reactor with internal volume 65 cm^3 and heated to the required temperature under a flow of nitrogen to ensure no oxidation occurred before the desired temperature was reached, with the temperature of the liquid measured via a K-type thermocouple, accurate to ± 0.1 °C. Once the correct temperature was reached, a flow of oxygen was introduced at a pressure of 1.05 bar with the flow rate chosen so that oxygen consumption was comparatively low, so that there was an approximately constant oxygen concentration in the reactor headspace (the oxygen level during the reaction did not drop below 95% of the starting concentrations), and hence dissolved in the reaction mixtures. The gas output from the reactor was passed through a cold trap to condense any volatile oxidation products and the oxygen content of the exhaust gas was measured with an oxygen sensor (Teledyne Analytical ClassR-17MED). The reaction was initiated by stirring using a magnetic PTFE stirrer bar to ensure thorough oxygenation of the liquid. The temperature and pressure inside the reactor, as well as the oxygen content of the output gas flow, were recorded on a PC using an analogue to digital converter (Picotec ADC-20). 0.5 ml liquid samples were also withdrawn via a cannula at regular intervals and stored at −10 °C prior to analysis. To stop the reaction, stirring was ceased and the reactor was purged with nitrogen to prevent further oxidation.

Chemical analysis was performed using Gas Chromatography. An injection volume of 0.3 µl of all samples were analysed via a Varian 3380 GC-FID equipped with a 1079 injector and a Phenomenex Zebron ZB-5HT column, of 30 m length 0.25 mm internal diameter and 0.25 µm film thickness and a split ratio of 50:1. The injector and detector were set to 350 °C, the column started at 50 °C and was ramped up to 340 °C at a rate of 5 °C min^{-1}, then held for 22 min giving a total run time of 80 min. Authentic samples of squalane and methyl linoleate were injected to verify retention times and calibrate to allow for calculation of concentration. The data was collected using JCL6000 integration with the sample rate of 2 per second.

The viscosity (KV40 – kinematic viscosity at 40 °C) was also measured for each of samples collected (where possible – i.e. if enough material was collected; some mixtures were too viscous to be withdrawn effectively though the cannula), using a Cannon-Manning Semi-Micro viscometer, Extra Low Charge at 40.000 °C ± 0.001 °C.

3. Results

The concentration of squalane and methyl linoleate in samples withdrawn at different times of reaction were measured by integrating the peak areas on the GC traces. Plotting the peak areas vs time showed that the consumption of squalane and methyl linoleate at temperatures from 100 to 170 °C was approximately pseudo-first order with respect to squalane, (shown for the example of squalane being consumed in the absence of methyl linoleate in Fig. 1). The pseudo-first order rate constants for squalane consumption in the absence of methyl linoleate, indicated here by $k_{squalane}0$ and given in Table 1, can then used as the basis for examining how the rate of consumption of squalane changes as methyl linoleate is added. In addition to Fig. 1 showing the consumption of squalane, from the GC peak areas, the traces also showed other minor products with the retention times matching those of squalane oxidation products observed from previous work [18]. These peaks were also noted in all further co-oxidation studies with methyl linoleate.

Fig. 2 shows $\Delta k_{squalane}$, which is the pseudo first order decay rate constant for the removal of squalane ($k_{squalane}x$, where x is the concentration of methyl linoleate in the initial reaction mixture) during its co-oxidation with 0 to 10% methyl linoleate, normalised against the rate of consumption of squalane in the absence of methyl linoleate ($k_{squalane}0$) to show the effect of methyl linoleate on the decay of squalane, as defined in Eq. (1).

$$\Delta k_{squalane} = \frac{k_{squalane}x}{k_{squalane}0} \quad (1)$$

This figure shows that increasing methyl linoleate concentration increased the rate of squalane autoxidation, $k_{squalane}$, at 100 and 130 °C, but reduced it at 170 °C. Plotting the rate of change of the equivalent pseudo-first order rate constants for methyl linoleate consumption (k_{ML}) v temperature it can be seen that, unlike for squalane, the rate of k_{ML} increase per addition of methyl linoleate increases across all temperatures (Fig. 3).

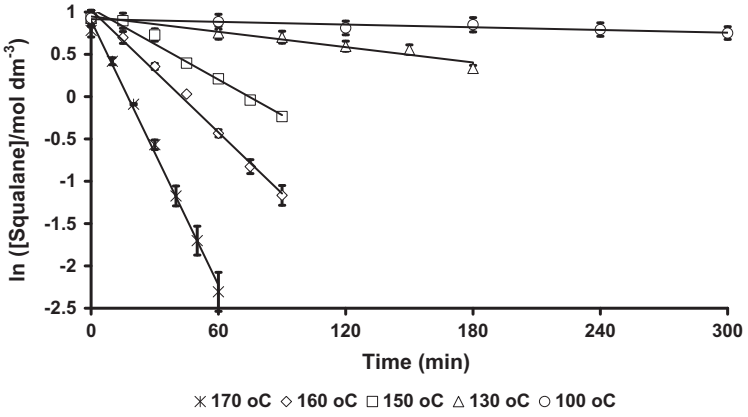

Fig. 1. Decay of squalane over time between 100 – 170 °C.

Table 1
The pseudo-first order rate of autoxidation of squalane between 100 and 170 °C under oxygen with no methyl linoleate present.

Temperature (°C)	100	130	150	160	170
$k_{squalane}0$ (h^{-1})	0.031 ± 0.008	0.18 ± 0.02	0.84 ± 0.06	1.44 ± 0.05	3.13 ± 0.50