1 **Effect of oxygenates addition on the flame characteristics and soot**
2 **formation during combustion of single droplets of a petroleum**
3 **diesel in air**

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Abstract

The effect of methyl oleate and ethanol addition on the combustion characteristics and soot emission of single droplets of diesel was studied by means of experimentation and kinetic modelling. The experiments were performed using a high-temperature tube furnace operating at 973K and the soot intensity indicated by the soot KL factor, and flame temperature were simultaneously measured using a two-colour pyrometry technique and a colour CCD camera. A detailed chemical kinetic calculation was performed using Chemkin-Pro. The experimental results showed that adding methyl oleate to diesel significantly suppressed the soot formation. The burning rate and flame temperature of the droplets decreased with increasing methyl oleate addition up to 20% vol and slowly increased again at methyl oleate addition exceeding 20% vol. Ethanol addition up to 10% vol in the diesel also led to less soot formation, lower flame temperature and burning rate. Kinetic modelling showed satisfactory agreement with the experimental results: the effectiveness of ethanol and methyl oleate in soot abatement was linear with the oxygen content in the fuel mixtures with ethanol being more effective than methyl oleate. The kinetic analysis also showed that ethanol utilised its oxygen atoms more efficiently than methyl oleate in suppressing the formation of soot precursors.

Keywords: Combustion characteristics; Diesel; Droplets; Oxygenated fuel; Soot

1. Introduction

Adding oxygenates into petroleum diesel fuel has been known to reduce particulate matter emissions in CI engines [1-3]. Among all oxygenated fuels reported in the literature, biodiesel and ethanol have emerged as strong candidates [2,3]. Both biodiesel and ethanol have lower tendencies than diesel to produce soot [4]. It has been widely reported in the literature that the additions of biodiesel and ethanol, respectively, into diesel reduced the total amount of particulate matter in the exhaust [4-10]. However, the working mechanisms of ethanol and biodiesel in diesel combustion processes and soot production process are not well understood [9,10].

Literature reports suggest that the overall oxygen content in an oxygenated fuel is the only parameter determining the capability of the fuel in suppressing soot emission [5, 6]. Miyamoto et al [5] found that oxygenated fuels, including di-n-butyl ether, ethylhexyl acetate, ethylene glycol mono-n-butyl ether, and diethylene glycol dimethyl ether, had the same effectiveness in reducing the Bosch Smoke number of the exhaust from a diesel engine when measured by the total oxygen mass fraction added into the base diesel [5]. Albeit interesting, this finding was challenged by many other diesel engine tests results, in which the molecular structure of the oxygenated compounds was also found to have some impacts on the soot emission [7-14]. Some engine experiments suggested that alcohols were more effective than ethers and esters in reducing soot [8,9]. Westbrook et al [15] performed a detailed chemical kinetic simulation to investigate the effect of various oxygenated hydrocarbons on soot precursors in rich premixed homogeneous mixtures of n-heptane and oxygenates and found that all the oxygenated fuels tested reduced soot precursors but the extent of these reductions depended on the molecular structure of the oxygenates in the fuel mixtures [15]. However, experimental validation of the model simulation results would help understanding the mechanisms involved. The diverse experimental data from the widely varying diesel engine

tests also makes it difficult to obtain the working mechanisms of biodiesel and ethanol in diesel combustion processes, particularly the kinetics involved in reducing the soot emission. The present work investigated the potential of biodiesel and ethanol addition in petroleum diesel on the combustion characteristics and soot formation using droplets combustion experiments and whether the molecular structure of the oxygenated compounds have some impact in the soot formation. The single droplet experimentation approach has been adopted by many researchers to study the ignition and combustion characteristics of liquid fuels because of its simplicity and capability of providing fundamental perspectives into the combustion processes [16-22]. Detailed kinetic modelling was also carried out in order to understand the working mechanisms of the ethanol and biodiesel additions, respectively, in diesel soot precursor formation process.

2. Experimental

2.1 Materials

A commercial diesel (Caltex No.2 diesel) and pure ethanol were used for the experimentation. A technical grade methyl oleate (70% vol methyl oleate with 10% vol methyl linoleate, 5% vol methyl palmitate and 5% vol methyl palmitoleate and other fatty acid methyl esters in balance) was used to represent biodiesel. Justifying the use of methyl oleate, it is a common component of most biodiesel fuels and the kinetic mechanisms of some methyl esters, which have similar chemical structure to methyl oleate, are available. This will make it possible to investigate the kinetic effect of the methyl ester group addition on diesel soot production process without the computational complexity of the actual biodiesel fuel. The thermochemical properties of the methyl oleate together with those of diesel and ethanol are listed in Table 1. For the convenience of discussion in this paper, the blends of biodiesel and diesel or ethanol and diesel are designated by their volume fractions. For instance, D90B10

means 90% vol diesel and 10% vol biodiesel and D90E10 means 90% vol diesel and 10% vol ethanol.

2.2 Experimental procedures

Single droplet combustion experiments of diesel and biodiesel were carried out using the experimental apparatus as schematically illustrated in Figure 1. Briefly, the experimental rig consisted of a horizontal tube furnace (600mm in length and 40mm in diameter) with temperature control for providing a hot air environment, a droplet suspension system, a step motor for delivering the droplet into the furnace and a CCD camera for measuring flame temperature.

In a typical experiment, the tube furnace was heated to and maintained at 973K, in which a droplet was ignited and combusted. The droplet was produced by a 10 μ L micro-syringe and deposited on the tip of a silicon carbide fibre of 142 μ m in diameter. A high speed CCD camera (Basler PIA-210gc) with exposure time of 20ms was used to capture the images of the entire process from the moment when the droplet entered the furnace until it burned out. The video images taken on the colour CCD camera were subsequently analysed to obtain the flame temperature, soot intensity and burning rate of the burning droplet, following the procedures detailed in Section 2.3. To determine the burning rates from the changing droplet size during combustion, the burning droplet was backlit with a 50W halogen lamp while being recorded on the CCD camera. A computer was used to operate the step motor and the CCD camera.

2.3. Data analyses

Using the optical images taken on the CCD camera, the soot intensity and the flame temperature were determined using the two-colour pyrometry [23-26]. The CCD camera

operating with an RGB pattern records three sets of signals, Red, Green and Blue, simultaneously. Since the camera sensor response is almost linear with respect to the source intensity, the pixel intensity of each signal is the product of the emissive power and spectral response [23,24]. The ratios of any two of the three colours give two independent measures of the temperature and soot intensity:

$$r_{RB} = \frac{\int_{\lambda_{R1}}^{\lambda_{R2}} S_R(\lambda) \cdot \varepsilon_\lambda \cdot \frac{2C_1}{\lambda^5 [\exp(C_2 / \lambda T) - 1]} d\lambda}{\int_{\lambda_{B1}}^{\lambda_{B2}} S_B(\lambda) \cdot \varepsilon_\lambda \cdot \frac{2C_1}{\lambda^5 [\exp(C_2 / \lambda T) - 1]} d\lambda} \quad (1)$$

$$r_{GB} = \frac{\int_{\lambda_{G1}}^{\lambda_{G2}} S_G(\lambda) \cdot \varepsilon_\lambda \cdot \frac{2C_1}{\lambda^5 [\exp(C_2 / \lambda T) - 1]} d\lambda}{\int_{\lambda_{B1}}^{\lambda_{B2}} S_B(\lambda) \cdot \varepsilon_\lambda \cdot \frac{2C_1}{\lambda^5 [\exp(C_2 / \lambda T) - 1]} d\lambda} \quad (2)$$

where r_{RB} is the ratio of the pixel intensities of red and blue, r_{GB} the ratio of the pixel intensities of green and blue, T the soot temperature, λ the wavelength, C_1 the first radiation constant, C_2 the second radiation constant, $S(\lambda)$ the spectral response and ε_λ the soot emissivity.

The soot emissivity can be modelled by the widely used empirical correlation proposed by Hottle and Broughton [27]:

$$\varepsilon_\lambda = 1 - \exp(-KL / \lambda^\alpha) \quad (3)$$

where K is the absorption coefficient of soot particles, L the optical path length of measurement, and α is 1.39 in the visible wavelength range [27,28]. In the present study, the so-called KL factor, which measures the number density of soot particles in the flame, was used to represent the soot intensity [29]. A higher KL factor means a higher soot intensity. It has been found the KL factor for glowing soot with temperatures ranging from about 1900 to 2600K varies between 0.2 and 1.4 [28].

For a given CCD camera, the spectral response of the camera's sensor is known. The colour

ratios are only a function of the soot temperature and intensity. For instance, supposing the soot is glowing at 2000K and has a KL of 0.5, the r_{RB} and r_{GB} ratios are 10.21 and 3.13, respectively, with the camera used in the current study. A computer program was written to repeat the process for temperatures ranging from 1300K to 2500K at a 10K increment and KL from 0 to 1.4 at an increment of 0.01. This provides a look-up table from which every pixel in an image is compared and its temperature and soot intensity are estimated. Figure 2 shows an example of the calculated r_{RB} and r_{GB} in the look-up tables created with the interpolation method. When calculating the soot temperature and intensity for every pixel, the colour ratios were matched to those in the look-up table. The matching algorithm used an error function to decide the best match [23,24]. The use of the CCD camera for the temperature measurement was calibrated against a blackbody furnace operating from 1273 to 1573K and it was found that the absolute errors of the temperature and soot intensity measurements using this method were within 50K and 0.01, respectively. It has also been reported in the literature [23,24] that the absolute errors of the same temperature measurement technique at high temperature up to 2500K were within 50K.

The backlit images of a droplet surrounded by luminous flame were recorded and post-processed so that the evolution of the droplet size (d_s) during combustion was determined using Matlab [30]. The actual shape of the suspended droplet in the present experimentation was elliptical due to the influence of gravity and the stated droplet size referred to an equivalent value determined as the cubic root of the product of the droplet width squared and the droplet length [20]. Once the time history of the droplet size was known, the burning rate was determined based on the classical d^2 -law of droplet combustion [21].

3 Kinetic Modelling

It is hypothesised that the oxygenated fuels affect the chemical reactions and kinetics of the

formation of the primary precursors of soot. Therefore, a detailed kinetic modelling was deployed in the present study to reveal the reaction pathways of the oxygenated fuels in reducing soot formation and assist the interpretation of the experimental observations. The kinetic modelling was performed using CHEMKIN-Pro with a closed homogeneous batch reactor model [15], in which the fuel and air were assumed to be perfectly premixed. N-heptane was used to represent diesel as it has a similar Cetane number to diesel and the methyl-9-decenoate was chosen to represent methyl oleate [31] in the kinetic modelling. Detailed reaction mechanisms of n-heptane, ethanol and methyl-9-decenoate used in the simulation, including about 3500 species and 17000 reactions, were developed by Herbinet et al [31], available on the official website of Lawrence Livermore National Laboratory.

It is well known that diesel droplet combustion is characterised as diffusion combustion with a flame enveloping the droplet [20,32,33]. During the steady state combustion, the fuel evaporates, decomposes and diffuses to the flame front where combustion occurs. Soot precursors and primary soot particles are mainly formed in the region between the droplet surface and the flame front [33-35], which was confirmed as discussed in the following sections. In this region, the equivalence ratio of the fuel/air mixture is very high as most of the oxygen diffused from the ambience to the flame is consumed in the flame zone. Therefore, the current modelling was performed in the fuel-rich regime with the equivalence ratio varying from 3 to 10 to examine the effect of equivalence ratio on the computed results. The initial temperature was taken as the average temperature between the fuel boiling temperature and the flame temperature while the total pressure was kept constant at 1 atm. In each calculation, there was an ignition period and, after a very short ignition delay, a rapid ignition occurred during which the reactants were completely consumed, the temperature increased, the soot precursors were formed, and reached levels that remained constant. The baseline calculation was the combustion of n-heptane and then the calculation was repeated by gradually replacing

the n-heptane with the ethanol or methyl-9-decenoate at various volumetric percentages corresponding to the experimental data. In the calculation, the concentration of acetylene (C_2H_2) was used to represent the soot intensity as C_2H_2 is known as the soot precursor of hydrocarbons combustion [15,16,34].

4. Results and Discussion

4.1 Soot intensity and flame temperature of a burning diesel droplet

Figure 3 shows the images of typical flames of a burning droplet of pure diesel at 0.25s after ignition with and without the backlight. It is clear that the droplet was elliptical and surrounded by a flame envelope. The flame, rather than in a spherical shape, is elongated in the opposite direction of the gravitation due to natural convection. Figure 4 shows the calculated distributions of 2-D soot intensity and flame temperature of the burning droplet. Note that the calculations of the soot intensity and flame temperature were carried out on a pixel by pixel basis and the smoothing technique, namely neighbourhood average method [25], has been applied during the data processing to mitigate the errors associated with noises. It is evident from Figure 4 that the distributions of the soot intensity (KL) and flame temperature were non-uniform. As shown in Figure 4(a), the soot intensity near the droplet surface and at the top tip of the flame was high while it was relative low in the flame zone. This suggests that the soot precursors and aggregates tend to form between the droplet surface and flame front, which then travelled upwards due to the natural convection, resulting in a high soot concentration at the top of the flame. The flame temperature shown in Figure 4(b) indicates that the flame temperature was the highest at the flame front but decreased as the flame moved upwards due to the gravitation-induced natural convection. The trend in the experimental observations shown in Figure 4 is consistent with the literature report [36] where the flame temperature was measured using fine thermocouples and the soot

concentration measured using a laser technique. The method used in the current study proved to be simple and useful for qualitatively measuring the soot intensity and flame temperatures. The flame temperature and soot intensity used for the following discussion refer to the average temperature and soot intensity of the flame, respectively.

4.2 Effect of methyl oleate

Figure 5 shows the effect of methyl oleate addition on the soot intensity and flame temperature of the burning diesel droplets with error bars showing the standard deviations. It is clear that adding methyl oleate to diesel significantly reduced the soot concentration and the reduction level of soot intensity increased with increasing amount of methyl oleate dosed in diesel, consistent with the literature [5-11]. The flame temperature decreased as the methyl oleate addition increased before it started to slowly increase again at 20% vol methyl oleate addition. In general, flame temperature is determined by the heating value of the fuel, burning rates and heat loss through radiation by the gas and soot in the flame. In the present study, the effect of methyl oleate addition on flame temperature was essentially a trade-off between the heating value of the fuel and heat loss by soot radiation. On one hand, increasing methyl oleate addition reduced the heating value of the diesel/methyl oleate mixture, which in turn reduced the flame temperature. However, due to the lower soot intensity with the methyl oleate addition, the overall soot radiation loss was suppressed, and this would increase the flame temperature. The results shown in Figure 5 indicate the important role of soot radiation in the droplet combustion processes, which has been revealed in some modelling studies. The temporal changes in the normalised square of the burning droplet size of diesel with methyl oleate addition and the calculated droplet burning rates of the mixtures are shown in Figure 6. It is evident from Figure 6(a) that the d^2 – law was well conformed to by the burning droplets after an initial period of heating. Therefore, the linear fitting method was used to fit the data with the slope being the burning rate and the standard deviation of the fitting being the errors

of the burning rate, as shown in Figure 6(b). It is seen from Figure 6(b) that the addition of methyl oleate decreased the burning rate of diesel, reaching the minimum at about 20% vol methyl oleate addition and then slowly increased again. The burning rates of the diesel/methyl oleate mixtures depended on the ratio of methyl oleate in the mixtures. Based on the classic droplet burning theory [31,34], the burning rate of a pure fuel increases with: (1) increasing flame temperature and (2) decreasing latent heat of evaporation, density and fuel boiling point. Increasing the methyl oleate addition in the diesel/methyl oleate mixtures not only increased the density but also decreased flame temperature, the latent heat and boiling point of the mixture as methyl oleate has a lower latent heat of evaporation, a lower boiling point and a higher density than diesel, as seen in Table 1.

4.3 Effect of ethanol

Figure 7 shows the effect of ethanol addition on the soot intensity and flame temperature of burning diesel droplets. The current experimentation found that ethanol and diesel were not miscible when the ethanol addition was more than 10% vol. Ethanol itself burned in an almost invisible flame with no observable soot formation. The addition of ethanol in diesel reduced the soot intensity and flame temperature and the levels of reduction in both soot intensity and flame temperature were almost linearly proportional to the percentage of ethanol addition. The temporal changes in the normalised square of the burning droplet sizes of diesel with ethanol addition and the calculated burning rates are presented in Figure 8. Ethanol burned at a much lower burning rate than diesel and the addition of ethanol up to 10% vol reduced the burning rates of the diesel/ethanol mixtures. This is mainly due to the fact that the addition of ethanol in diesel reduced the flame temperature (as shown in Figure 5) and the latent heat of the fuel mixtures [3,31].

4.4 Mechanisms of methyl oleate and ethanol in diesel soot formation

The preceding discussion has shown that the addition of methyl oleate and ethanol reduced

the soot intensity from the combustion of diesel droplets. In order to understand the mechanisms of the two oxygenated fuels in the soot formation processes, kinetic modelling was carried out.

Literature reports have suggested that the chemical mechanism of the oxygenated fuels in reducing soot emission from diesel combustion in diesel engines was related to the oxygen mass fraction in the fuel mixtures, while the oxygenate molecular structures had little effect [5,6]. The influence of ethanol and methyl oleate on soot reduction as a function of oxygen mass content in the present experimental work is shown in Figure 9. Figure 9 also includes the modelling results of the ethanol and methyl-9-decenoate (representing methyl oleate) effects, respectively, on the reduction profiles of soot precursor (C_2H_2) for comparison. The modelling results were obtained for the equivalence ratio of 5. The calculations were repeated by varying the equivalence ratio from 3 to 10 and the relative rates of soot reduction by the two oxygenated fuels under different equivalence ratios showed a similar trend. It is important to note that the comparison between the experimental data and modelling results was qualitative and only the trend was of relevance. The main purposes of this kinetic modelling were: 1) to reveal the reaction pathways, i.e. how ethanol and methyl-9-decenoate reduced soot production; and 2) to interpret the observed trends with the improved understanding of the reaction pathways. The same trend between the experimental data and predicted results with regards to the soot reduction level (Figure 9) suggests that the mechanism employed in the current study was capable of capturing the kinetic effect of the oxygenates added to diesel on soot precursor formation.

It is evident from Figure 9 that the addition of ethanol and methyl oleate, respectively, reduced soot intensity and the reduction level was linearly proportional to the mass fraction of oxygen in the fuel mixtures. Ethanol was slightly more effective in reducing the level of soot formation than methyl oleate. This suggests that ethanol has a higher capability to utilise the

295 oxygen atoms to suppress the formation of soot precursor than methyl oleate [15]. Figure 10
296 illustrates the reaction pathways of oxygen atoms present in ethanol and methyl-9-decenoate.
297 Close examination of the kinetic pathways associated with oxygen atoms showed that nearly
298 all of the oxygen atoms initially present in the two oxygenated fuels dissociated directly to
299 produce CO or CO₂, which hardly participated in the process of soot precursor formation [15].
300 The addition of ethanol to diesel replaced the carbon atoms bonded to hydrogen only in the
301 diesel with carbon atoms bonded to oxygen and this bond remained intact during the reaction.
302 In other words, the carbon atoms in diesel that can produce soot precursors were displaced by
303 the carbon atoms that cannot contribute to the formation of soot precursors. In this case, one
304 oxygen atom removed one carbon atom from the pool of diesel combustion radicals that
305 potentially produce soot precursors. On the other hand, the kinetic pathway involving the
306 oxygen present in methyl-9-decenoate showed that the initial oxygen can be converted to CO
307 or CO₂ and the relative reaction contribution analysis indicated that the reaction rates for
308 CH₃OCO to produce CO and CO₂ are of the same order. This is also consistent with the
309 experimental observation by Szybist et al [9], in which both CO and CO₂ were found in a
310 motored engine with premixed charges of diesel added with methyl decanoate [9]. This
311 suggests that when CO₂ is the product, the two oxygen atoms presented in the
312 methyl-9-decenoate removed only one carbon atom from the pool of reactive hydrocarbon
313 radicals that could potentially produce soot precursors. As a result, methyl-9-decenoate is less
314 effective in utilising its oxygen to remove soot precursors than ethanol. This explains why
315 ethanol was more effective in suppressing soot formation than methyl oleate as supported by
316 the present experimental results. Some literature reports also suggest that the decomposition
317 of CH₃OCO is dominated by the pathway producing CO₂ [37,38]. However, this would not
318 change the working mechanism of the methyl oleate addition in suppressing soot formation as
319 discussed above. The differences in the reaction rates of the decomposition of CH₃OCO to

produce CO₂ in the different mechanisms will only make slight differences in the absolute concentrations of the soot precursors formed

4. Conclusions

The effect of methyl oleate and ethanol addition on the combustion characteristics and soot formation of single diesel droplets was investigated. The two-colour pyrometry method using a colour CCD camera proved to be a simple and useful tool to simultaneously measure soot intensity and flame temperature. The addition of methyl oleate significantly suppressed the soot intensity of diesel droplets. The burning rate and flame temperature of diesel droplets decreased with increasing methyl oleate addition at low level (below 20% vol) and increased slowly again when methyl oleate addition was higher than 20% vol, suggesting that the role of radiation from the soot particles in determining the flame temperature is not negligible. Ethanol addition up to 10% vol also reduced the soot formation, the flame temperature and burning rate. Ethanol was slightly more effective in suppressing soot formation than methyl oleate, due to its higher efficiency in utilising the oxygen atoms to remove the soot precursors forming carbon atoms.

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Table 1 Major physical properties of diesel, ethanol and methyl oleate

Fuels	Composition	Density (gml^{-1})	Boiling Point (K)	LHV (MJkg^{-1})	Latent Heat of Vaporisation at boiling point (KJkg^{-1})
Diesel	C10-C18	0.845	473-673	43.4	250
Ethanol	$\text{C}_2\text{H}_6\text{O}$	0.789	351	29.7	841
Methyl Oleate	$\text{C}_{19}\text{H}_{36}\text{O}_2$	0.874	491	40.1	230

Figure Captions

- Figure 1 A schematic diagram of the apparatus for the droplet combustion experiments
- Figure 2 Calculated r_{RB} and r_{GB} ratios of the camera with different KL values
- Figure 3 Typical images of a burning droplet of pure diesel in air at 973K (a) without backlight and (b) with backlight
- Figure 4 Typical 2-D distributions of (a) soot intensity and (b) flame temperature of a burning droplet of pure diesel in air at 973K
- Figure 5 Effect of methyl oleate addition on soot intensity and flame temperature of burning droplets of diesel/methyl oleate mixtures
- Figure 6 Temporal variation of (a) the square of the normalised droplet diameter and (b) burning rates of diesel with methyl oleate addition
- Figure 7 Effect of ethanol addition on soot intensity and flame temperature of burning droplets of diesel/ethanol mixtures
- Figure 8 Temporal variation of (a) the square of the normalised droplet diameter and (b) burning rates of diesel with ethanol addition
- Figure 9 Comparisons between experimental and modelling results of reductions in soot intensity with the addition of methyl oleate and ethanol
- Figure 10 A schematic representation of the reaction pathways of oxygen atoms in (a) ethanol and (b) methyl-9-decenoate added into n-heptane in the fuel-rich combustion

Figure 1

Figure 1 A schematic diagram of the apparatus for the droplet combustion experiments

Figure 2

Figure 2 Calculated r_{RB} and r_{GB} ratios of the camera with different KL values

Figure 3

Figure 3 Typical images of a burning droplet of pure diesel in air at 973K (a) without backlight and (b) with backlight

Figure 4

Figure 4 Typical 2-D distributions of (a) soot intensity and (b) flame temperature of a burning droplet of pure diesel in air at 973K

Figure 5

Figure 5 Effect of methyl oleate addition on soot intensity and flame temperature of burning droplets of diesel/methyl oleate mixtures

Figure 6

Figure 6 Temporal variation of (a) the square of the normalised droplet diameter and (b) burning rates of diesel with methyl oleate addition

Figure 7

Figure 7 Effect of ethanol addition on soot intensity and flame temperature of burning droplets of diesel/ethanol mixtures

Figure 8

Figure 8 Temporal variation of (a) the square of the normalised droplet diameter and (b) burning rates of diesel with ethanol addition

Figure 9

Figure 9 Comparisons between experimental and modelling results of reductions in soot intensity with the addition of methyl oleate and ethanol

Figure 10

Figure 10 A schematic representation of the reaction pathways of oxygen atoms in (a) ethanol and (b) methyl-9-decenoate added into n-heptane in the fuel-rich combustion