An investigation into the conversion of specific carbon atoms in oleic acid and methyl oleate to particulate matter in a diesel engine and tube reactor

Aaron Eveleigh [a,*], Nicos Ladommatos [a], Paul Hellier [a], Anne-Lise Jourdan [b]

[a] Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, UK
[b] Bloomsbury Environmental Isotope Facility, UCL Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK

HIGHLIGHTS

- The ^{13}C isotope has been used to trace specific carbon atoms during combustion.
- Two molecules were investigated, the biofuels oleic acid and methyl oleate.
- The double bonded C in oleic acid forms particulate at about the same rate as the average carbon atom.
- The carbonyl carbon in methyl oleate and oleic acid does not convert to particulate.

ARTICLE INFO

ABSTRACT

The paper is concerned with particulate formation from the fuels oleic acid and methyl oleate. In particular the paper reports, quantitatively, the propensity of individual carbon atoms in these two molecules in being converted to particulate. The conversion of individual carbon atoms to particulate was traced by 'labelling' individual carbon atoms in those two fuel molecules with isotopic carbon-13 (^{13}C) and then measuring how many of the labelled atoms was found in the particulate. This allowed the measuring of the conversion rates of individual fuel carbon atoms to particulate. In the case of oleic acid, three carbon atoms were selected as being particularly relevant to particulate formation, and ^{13}C labelled. One of the carbon atoms was double bonded to the oxygen atom on the carboxylic acid group; and the other two were part of the oleic acid molecule alkyl chain and double bonded to each other. In the case of the methyl oleate, one carbon atom was ^{13}C labelled. This was the carbon atom that was double bonded to one of the oxygen atoms of the ester group. Experimental results are presented for particulate matter (PM) formed in a laminar flow tube reactor, and also in a direct injection compression ignition engine. The tube reactor has been used for the pyrolysis of oleic acid and methyl oleate at 1300 °C, under oxygen-free conditions and at air–fuel equivalence ratios (λ) of 0.1, and 0.2. Samples of PM were also collected from the compression ignition engine at an intermediate engine load. Isotope ratio mass spectrometry (IRMS) has been used to determine the relative abundance of ^{13}C in the initial fuel and in the resulting PM. Significant differences in the relative conversion rates of individual carbon atoms are reported; a negligible contribution to PM from the carbon atom directly bonded to two oxygen atoms was found in both the engine and reactor. The labelling technique used in this paper requires low quantities of ^{13}C labelled molecules to enrich otherwise unlabelled oleic acid; enrichment is at volumetric concentrations typically less than 0.7% (v/v). In addition, emissions data from the engine and tube reactor, including unburned hydrocarbons, CO, CO_2, NO_x, and PM size and number distributions measured by differential mobility spectrometer, are also presented.

1. Introduction

The high energy density of triacylglycerols, relative to many other biomass sources, mean that they are a useful starting material for conversion to fuels that can be used as petroleum diesel fuel

* Corresponding author.
   E-mail address: aaron.eveleigh.10@ucl.ac.uk (A. Eveleigh).

alternatives. Thermal or chemical conversion processes can be used to process triacylglycerols to yield oxygenate and hydrocarbon molecules. Transesterification of triacylglycerols with methanol, for example, produces fatty acid methyl esters, and these can be blended with fossil diesel fuel, or completely substitute fossil diesel fuel in compression ignition engines. Methyl oleate is one such methyl ester, and a number of studies indicate that the combustion characteristics of methyl oleate make it suitable for use as a diesel surrogate or blending with fossil diesel fuel [1,2]. Oleic acid is a fatty acid and is found in ordinary sunflower oil at around 40% by composition, and up to 80% in a hybrid variety named 'high oleic sunflower oil' [3]. Fatty acids such as oleic acid can be combusted in a compression ignition engine without further processing, but reduce engine durability and performance with increased injector nozzle coking and piston ring sticking due to the high viscosity and poor volatility of the acids, which result in poor injection system pumping efficiency and formation of large droplets in the injected spray. To overcome these issues fatty acids can be processed, for example, by transesterification or pyrolysis [4]. In the study presented here the fatty acid oleic acid, and corresponding fatty acid methyl ester, methyl oleate, have been investigated in terms of conversion to PM of specific carbon atoms within these two fuel molecules. The difference in physical properties and combustion characteristics of these fuels is also of interest to assess whether these properties influence their conversion during combustion.

The presence of oxygen-bearing molecules in fuel reduces tailpipe particulate matter emissions, and can also improve or maintain other regulated emissions such as NO_x, CO, CO_2, and unburned hydrocarbons. Some studies show that particulate emissions decrease in a linear manner with increasing oxygen mass in the fuel, independent of the structure of the oxygenate functional group. A number of studies, however, report that the ability to reduce PM emissions is different for the various oxygenate functional groups, and the molecular structure of oxygenated groups is identified as being responsible for these differences [5–7]. Understanding the mechanism of how oxygen bound within a fuel reduces PM emissions is of interest for the design and processing of cleaner burning fuels; identifying how individual carbon atoms within a molecule convert to PM gives useful insights on the direct impact of the local molecular structure. This knowledge could be used to inform the production and processing of future fuels, which could be designed to produce lower levels of PM and other toxic combustion emissions.

In the field of combustion, isotope labelling is a relatively unexplored diagnostic technique. The majority of studies in the literature that track a labelled component in fuel or oil to combustion products, generally utilise the radioactive isotope carbon-14 (^{14}C) [5,8–17]. Ferguson in 1957, used ^{13}C labelled propane at high levels of enrichment to track the formation of soot from specific carbon atoms in propane [18]. A recently reported method uses ^{13}C as a label to identify the relative conversion rates of specific carbon atoms in a fuel to PM, using only low concentrations of labelled compounds [7]. This technique can provide information into how functional group chemistry can influence the relative probability of a carbon atom from a specific molecular locality being converted to particulate matter. The technique requires only low levels of ^{13}C enrichment, which means that previously prohibitively expensive isotope techniques can be performed in more cost-effective manner, this research required enrichment at levels less than 0.7%. Such low levels of enrichment are detectable due to the precision of IRMS analysis. This methodology, combined with the use of an ultra-low volume fuel system, for direct injection compression ignition engines, such as the type used for the research reported here, extends further the viability and practicality of such studies.

In this paper, particulates have been generated in a laminar flow reactor at 1300 °C, under oxygen-free conditions and at air–fuel equivalence ratios (λ) of 0.1, and 0.2, from the pyrolysis of isotope labelled oleic acid and methyl oleate. The conditions that have been employed in the reactor are, in a general sense, similar to the conditions in the core of a compression ignition engine spray, in that the conditions are oxygen-deficient and at high temperature. Concurrently, exhaust particulate matter was collected from a modern compression ignition engine during combustion of isotope tagged oleic acid and methyl oleate. The results from the reactor, where conditions were laminar, homogenous, steady, and well controlled are useful for interpreting the results from the engine where the conditions were more complex, highly turbulent, heterogeneous, unsteady, and less controllable. Both the chemical and physical properties of the fuel, for example, can impact the combustion characteristics in a compression ignition engine; in the reactor, chemical effects dominate the conversion of carbon in the fuel to pyrolysis products.

2. Experimental systems and methods

2.1. ^{13}C labelled fuels

As it was mentioned in the introduction, fuels with only very low levels of ^{13}C enrichment were used to carry out the experiments. Methyl oleate and oleic acid, which had the natural abundance of ^{13}C (referred to as the *unenriched* fuel) were enriched with small amounts of fuel that was ^{13}C labelled at specific molecular locations (the *labelled* fuel). The resulting blended fuel, which was composed of mainly unenriched fuel and a much smaller labelled component is referred to in this paper as the *enriched fuel*. Fig. 1 shows the molecular locations of the ^{13}C atom(s) in the labelled oleic acid and methyl oleate fuels.

Unenriched oleic acid with a certified purity >99% was acquired (Alfa Aesar, 31997), and small amounts of labelled oleic acid-1-^{13}C, labelled at location 'a' (Aldrich, 490423), or oleic acid-9,10-^{13}C (locations 'b-b')(Aldrich, 646466) was added. Likewise, unenriched methyl oleate was obtained with certified purity >96% (Alfa Aesar, H31358), and labelled methyl oleate-1-^{13}C, with a purity of 99% (Aldrich 605867) was added. GC–MS analysis of the unenriched methyl oleate showed that the balance of the molecules (<4%) were structurally similar to methyl oleate, such as methyl stearate.
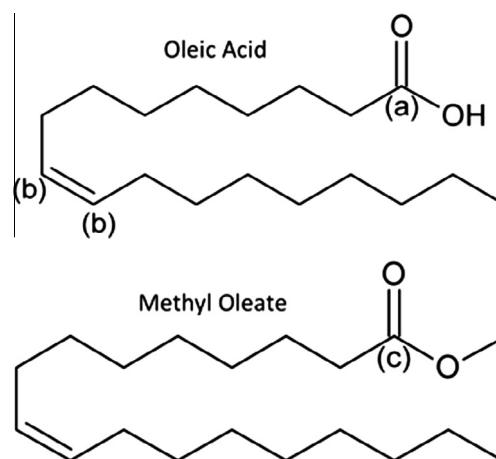

Fig. 1. Structure and nomenclature of the fuels tested. Oleic acid was ^{13}C labelled at sites: (a) oleic acid-1-^{13}C, and (b) oleic acid-9,10-^{13}C. Methyl oleate was labelled in position (c), methyl oleate-1-^{13}C.

Molar calculations were used to find the volumetric quantities needed to enrich the unenriched fuel by the desired amount. For example, 110 ml of oleic acid was labelled with approximately 0.73 ml of oleic acid-1-^{13}C (labelled at position 'a'); 110 ml was a sufficient quantity for both reactor and engine tests. The small volumes of ^{13}C labelled fuel were measured using a capillary piston pipette (Gilson, CP100).

The experiments were designed in order to assess the following molecular features in terms of their conversion to PM (see Fig. 1):

- The relative conversion rate of the carbon atom labelled in oleic acid-1-^{13}C, labelled 'a' in Fig. 1, to PM.
- The extent to which the tagged carbon atom in methyl oleate-1-^{13}C, 'c', is converted to PM, and identify whether this is different to the conversion of 'a' in oleic acid.
- Assess whether the double bonded carbon atoms within oleic acid, 'b', convert to PM to a greater extent than the average carbon atom in oleic acid.

2.2. Engine experiments

All engine experiments in which exhaust gas PM was collected were conducted on a commercially available modern direct injection compression ignition engine, converted and instrumented to run as a single cylinder research engine. As the ^{13}C isotope tagging technique utilised in this study necessarily required high assay fuels, available in only small quantities due to their high cost, use was made of a novel low volume fuel system. This system, based on the concept first developed by Schönborn et al. [19], utilises fossil diesel as a hydraulic fluid, pressurised to fuel injection pressures by a conventional common rail fuel circuit, to pressurise test fuels for high pressure direct injection. The low volume fuel system (and engine test facility) utilised in this current work has been described in detail by the authors previously [1]. The low volume engine fuel system can operate with sample fuel volumes of between 100 and 250 mL and can be heated in the case of high melting point or high viscosity fuels. The low volume fuel system was held at a constant temperature of 40 ± 2.5 °C, and the engine was normally aspirated with air at atmospheric temperature and pressure for all experiments. For all engine experiments a 6-hole solenoid valve injector (DELPHI) of orifice diameter 154 µm and spray angle of 77° was used. Table 1 shows further details of the research engine employed.

The engine exhaust gas composition was determined by continuous gas sampling at approximately 180 mm downstream of the engine exhaust valves and analysed by an automotive gas analyser system (Horiba MEXA9100 HEGR), which measured CO, CO_2, NO_x, unburned hydrocarbons, and O_2 in the exhaust gasses. In addition, sub-micron size particles in the exhaust gas were

characterised using a particle size spectrometer (Cambustion DMS 500), which gives outputs of particle size, number and mass in real-time. Sampling of exhaust gas for particulate measurements were made via a heated line and performed at the sampling conditions described previously [1].

All engine tests were conducted at 1200 rpm, fuel injection pressure of 450 bar and a constant start-of-fuel-injection of 5 crank angle degrees (CAD) before top-dead-centre (BTDC). For all tests, the injection duration was varied between 648 µs and 770 µs to maintain a constant engine IMEP of 4 bar at the constant speed of 1200 rpm.

2.2.1. Particulate sample collection

Samples of particulate matter from the engine exhaust gases for ^{13}C isotope analysis were collected onto glass fibre filters (Fisherbrand, Microfiber filter MF300) of 0.22 µm pore size. The engine exhaust gas flow was split and diverted through the glass fibre filter approximately 700 mm downstream of the engine exhaust valves, with the main exhaust path partially restricted to ensure sufficient exhaust gas flow through the filter. Fig. 2 shows the exhaust sampling arrangement in schematic form.

Following collection, the filters were cut in half with stainless steel scissors. One half of the filter paper was then placed into a borosilicate glass petri dish and immediately frozen, until required for analysis; the material deposited onto the filter consisted of a non-volatile organic fraction (NVOF) and some semi-volatile material, or volatile organic fraction (VOF). The other half of the filter was baked at 300 °C for 4 h in a nitrogen atmosphere, in order to remove the VOF, leaving on the filter mostly carbonaceous particulates. This baked material is hereafter referred to as the non-volatile organic fraction (NVOF). The samples of PM (NVOF + VOF), and the samples containing only the NVOF were both measured in order to compare the conversion rates of the labelled carbon atoms to both fractions.

2.3. Laminar flow tube reactor

Fig. 3 shows a schematic representation of the laminar tube reactor facility used in this research, which has been described in previous work [7]. This setup consisted of a feed system for metering the introduction of fuel, air and nitrogen (components 1–7), a
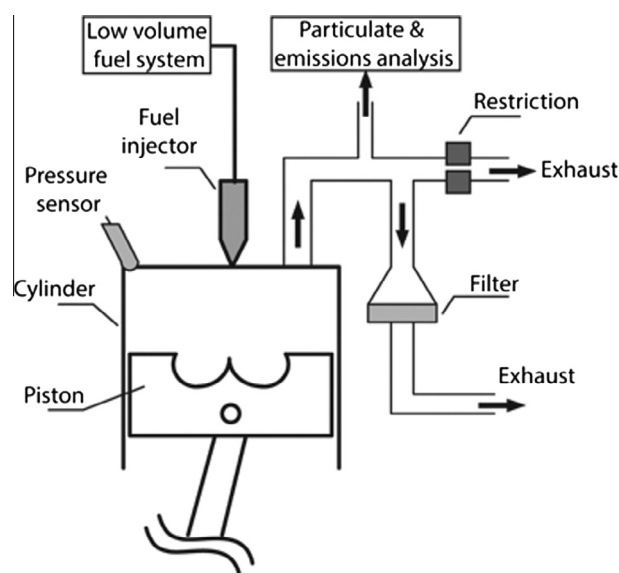
Fig. 2. Schematic representation of the arrangement for particulate sample collection from the compression ignition engine.

Table 1
Test engine specification.

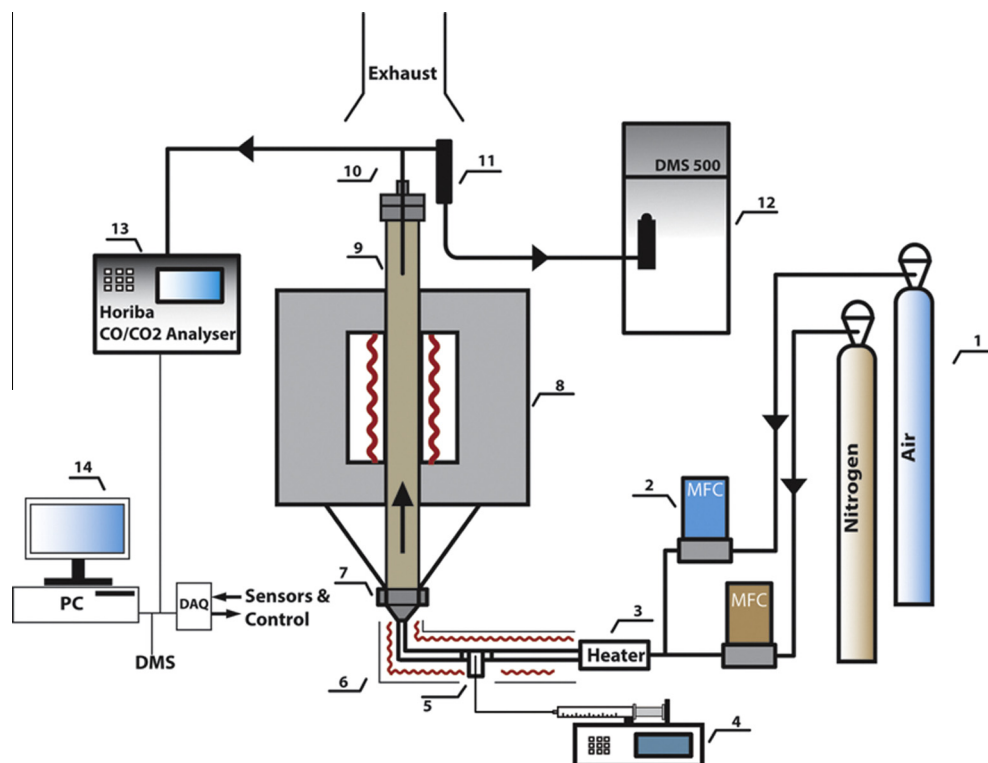|	
Engine head model	Ford Duratorq
Engine bottom end model	Ricardo Hydra
Injectors	6-hole solenoid controlled (DELPHI DFI 1.3)
Number of cylinders	1
Cylinder bore	86 mm
Crankshaft stroke	86 mm
Swept volume	499.46 cc
Compression ratio	18:1
Maximum cylinder pressure	150 Bar
Peak motoring pressure at test conditions	43 bar
Piston design	Central ω-bowl in piston
Oil temperature	80 ± 2.5 °C
Water temperature	80 ± 2.5 °C

Fig. 3. Laminar flow reactor rig. (1) Compressed air and nitrogen cylinders. (2) Mass flow controllers. (3) Process heater. (4) Syringe pump. (5) Vaporiser. (6) Heated and insulated stainless steel tube. (7) Mixer. (8) Electric oven. (9) Reactor tube. (10) Stainless steel sample tube. (11) Remote dilution cyclone. (12) Fast particulate spectrometer (13) CO and CO_2 analyser. (14) PC and data acquisition.

high temperature reactor (components 8,9), and a means of collecting and analysing effluent gasses (components 10–14).

Liquid fuels were fed into the tube reactor system at a controlled rate by means of a mechanical syringe pump, passing the fuel through a stainless steel capillary into a heated vaporiser. The flow rate of fuel into the reactor was fixed to a constant carbon flow rate, 21,500 ppm total hydrocarbon content on a C_1 basis. The vaporiser consisted of a stainless steel tee, packed with 3 mm borosilicate glass beads. The vaporiser and the stainless steel pipework to the reactor were heated by a tape heater, which was controlled by a PID controller. Vaporised fuels were entrained in a preheated carrier gas, consisting of nitrogen and varying concentrations of O_2; gas flow rates were controlled by mass flow controllers (Bronkhorst, EL-flow). A total flow rate of 20 L/min carrier gas was used, with a resultant gas residence time in the reactor of ~1 s. A fast flame ionisation detector (Cambustion, HFR400) was used to profile fuel concentration across the diameter of the reactor inlet, following the static mixer, in order to verify inlet radial homogeneity. The FID response is dependent on the molecular structure of the sample, response factors were applied to the measurements and were obtained from reference [20].

The reactor tube was constructed of alumina and had an internal diameter of 104 mm, with an overall reactor length 1440 mm, and a heated zone of 600 mm at the centre. The reactor was heated by an electric oven (Nabertherm, RHTV 120–600), and all reactor experiments reported herein were conducted at 1300 °C.

Samples of particulates were collected for isotopic analysis by thermophoretic deposition onto a borosilicate glass plate. After collection, the samples were transferred to borosilicate glass vials, and immediately frozen until they were required for analysis. A 6 mm stainless steel sample tube was positioned inside the reactor 200 mm from the outlet, along the centreline of the reactor, and used to withdraw effluent gasses for analysis. Particulate size and number measurements were made using a Cambustion DMS500

differential mobility instrument. A non-dispersive infrared gas analyser (Horiba AIA-120) was used to monitor CO and CO_2 species in the effluent from the reactor.

2.4. Analysis by IRMS

Elemental analysis isotope ratio mass spectroscopy (EA-IRMS) was used to analyse the isotopic composition of the PM samples. The experimental methodology involved IRMS analysis of both the PM and the fuel from which the PM was derived. These measurements allowed the calculation of the conversion rate of specific carbon atoms in the fuel molecules to PM.

Prior to IRMS analysis, solid PM samples were weighed into tin capsules, which were loaded with the equivalent of 70 µg ± 5 of carbon in the form of PM samples or standard reference material (weighed using Mettler Toledo, XP6 micro-balance); the capsules were then sealed and compacted to exclude atmospheric air. For samples that were generated in the diesel engine, particulate matter was removed from the surface of the filter using a stainless steel spatula. A separate EA-IRMS analysis of the glass fibre filter showed that it did not contain carbon; therefore, inclusion of glass fibres in the tin capsule did not influence the outcome of the analysis.

Liquid samples of fuel were collected by capillary action, using short sections of Pyrex capillary tube (~0.5 mm internal diameter, and ~3 mm length), these were transferred to smooth wall tin capsules, which were then sealed using a capsule sealing press.

Samples were introduced to an elemental analyser (Thermo Finnigan, Flash EA, 1112 series) using an automated sample carousel. Within the elemental analyser, samples were first combusted to CO_2 at 1020 °C. The resulting CO_2 then passed to an online IRMS (Thermo Finnigan, Delta V), where the relative $^{13}C/^{12}C$ ratios were measured for the PM, fuel, and standard reference materials.

Measurements by IRMS are relative to an international standard. For carbon analysis the most commonly referred to standard is PDB (Pee Dee Belemnite), a marine fossil. Measurements are reported in terms of $\delta^{13}C$ permil, as defined in Eq. (1), and PDB is assigned zero on the δ-scale. The environmental source of PDB has depleted and therefore secondary standards that have been calibrated against PDB are used. In this work, the standards IAEA-CH7 ($\delta^{13}C$ −32.15), USGS 24 ($\delta^{13}C$ −16.05), IAEA-C6 ($\delta^{13}C$ −10.80) and USGS 40 ($\delta^{13}C$ −26.39) were measured in duplicate at the beginning and end of each batch of samples analysed. The standard reference materials were used for the purpose of calibration and correction for instrument drift.

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{Sample} - \left(\frac{^{13}C}{^{12}C}\right)_{Standard}}{\left(\frac{^{13}C}{^{12}C}\right)_{Standard}} \right) \times 1000 \qquad (1)$$

2.5. Interpretation of isotopic measurements

This section summarises the methodology to provide an estimate for the percentage composition of the PM derived from a particular carbon atom [7]. This methodology relies on the isotope abundance ($\delta^{13}C$) data measured as described above, in Section 2.4. The isotopic composition of all native (unenriched) and enriched fuels ($\delta^{13}C_F$), and the PM derived from these ($\delta^{13}C_{PM}$) were measured. The difference in relative isotopic abundance between native and enriched versions of fuel (ΔF) and particulate matter (ΔPM) was calculated first, as described in Eqs. (2) and (3), below:

$$\Delta(F) = \delta^{13}C_F^* - \delta^{13}C_F^n \qquad (2)$$

$$\Delta(PM) = \delta^{13}C_{PM}^* - \delta^{13}C_{PM}^n \qquad (3)$$

The suffix F refers to a fuel sample, while the suffix PM refers to a sample of particulate derived from the fuel. The symbol ($*$) indicated that the sample had an enriched ^{13}C concentration, while the symbol (n) refers to the unenriched ('native') fuel or PM derived from the native fuel, which contained the natural abundance of ^{13}C only. The parameter Δ_{max} was then calculated, as in Eq. (4), and represents the maximum enrichment that would be expected if each of the carbon atoms in the labelled molecules added had been ^{13}C labelled.

$$\Delta_{max} = \frac{\Delta(F)}{n_{labelled}} \times n_{total} \qquad (4)$$

$n_{labelled}$ represents the number of labelled carbon atoms in the molecule under investigation, and n_{total} is the total number of carbon atoms in the molecule. For example, in the case of oleic acid-1-^{13}C, $n_{labelled}$ is 1, and n_{total} is 18.

Δ_{max} is then used to calculate the fraction of PM originating from the labelled atoms ($F_{labelled}$), from Eq. (5):

$$F_{labelled} = \frac{\Delta(PM)}{\Delta_{max}} \qquad (5)$$

The product of $F_{labelled} \times 100$ gives the % of the PM which was derived from the labelled carbon atoms.

3. Results and discussion

3.1. Emissions analysis

For all fuels tested, particulates formed in the tube reactor were generally between 200 and 1000 nm in size; total mass and average particle diameter information is provided as Supplementary data. Concentrations of CO and CO_2 evolved from the reactor were monitored, and it was observed that pyrolysis of methyl oleate and oleic acid produced high concentrations of CO, and minor concentrations of CO_2. For example, pyrolysis of oleic acid produced 2110 ppm of CO and 89 ppm of CO_2. Comparatively low quantities of CO_2 were expected due to the conversion of carbon dioxide by a hydrogen atom to carbon monoxide and a hydroxyl radical ($CO_2 + H \rightarrow CO + OH$) [21]; where the hydroxyl radical becomes available to oxidise soot or unburned hydrocarbons.

Fig. 4 shows the size and number distribution of particulates measured in the exhaust and also the total mass of particulates emitted in the engine tests of methyl oleate, oleic acid and the reference diesel. A typical bi-modal distribution of particulates is observed for each of the fuels, with oleic acid producing significantly greater peaks in the number of particles produced in the size range of 10–200 nm (Fig. 4). This can probably be attributed to the higher viscosity of the oleic acid relative to the methyl oleate and reference fossil diesel, which results in reduced efficiency of fuel and air mixing prior to the start of combustion, resulting in a greater degree of diffusion combustion in which the majority of soot formation occurs during diesel combustion.

Engine emissions measurements (including CO, CO_2, NO_x, O_2, and THC) is provided as Supplementary data.

3.2. Results of the isotope tracer investigation

Fig. 5 shows the percentage of carbon in the PM that was derived from the ^{13}C labelled carbon atoms for each of the following fuels tested in the laminar flow reactor at 1300 °C: oleic acid-1-^{13}C (labelled at the carboxylic acid carbon), oleic acid-9,10-^{13}C (double bonded carbons), and methyl oleate-1-^{13}C (methyl ester carbon).
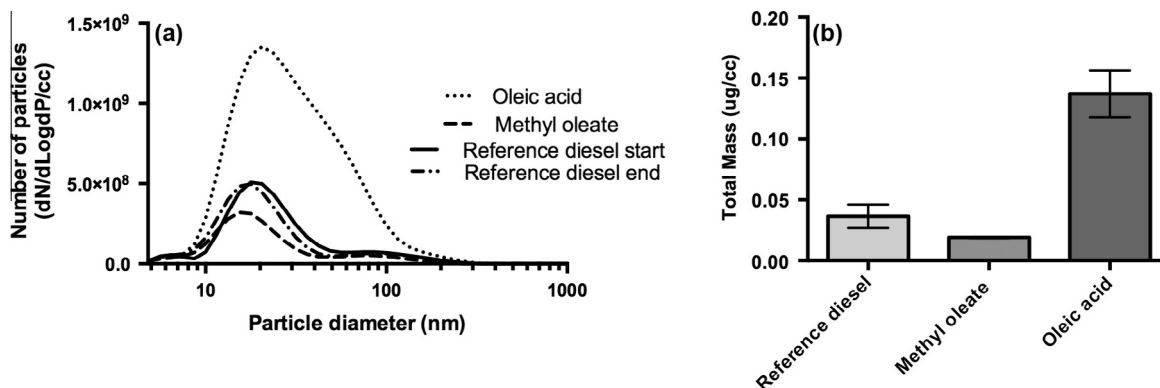

Fig. 4. Diesel engine particulate matter emissions as measured by the Cambustion DMS500 instrument; (a) particulate number and size distributions, and (b) calculated total mass concentration of PM.
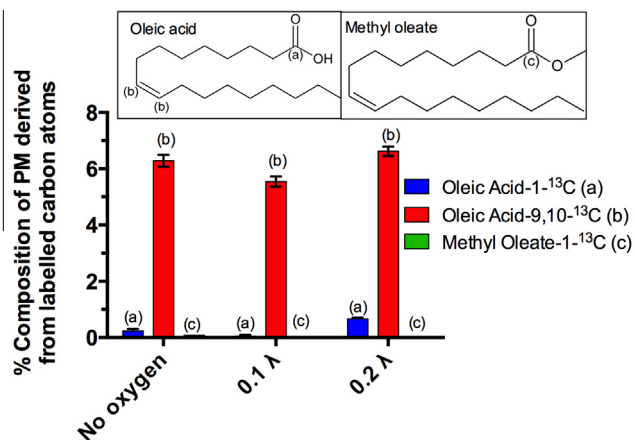
Fig. 5. Percentage composition of PM derived from the labelled carbon atoms in oleic acid-1-^{13}C ('a'), oleic acid-9,10-^{13}C ('b'), and methyl oleate-1-^{13}C ('c'), formed in a laminar flow reactor with varying air–fuel ratios. The result for the conversion of the labelled atoms oleic acid-9,10-^{13}C ('b') is shown on a per carbon atom basis. Error bars show the standard deviation of 3–6 measurements.

Fig. 6. Composition of PM derived from ^{13}C labelled carbon atoms, sampled from a diesel engine exhaust gas. The result for the conversion of the labelled atoms oleic acid-9,10-^{13}C ('b') is shown on a per carbon atom basis. Error bars show the standard deviation of 3–6 measurements.

The carboxyl carbon ('a') in oleic acid-1-^{13}C, which is attached to two oxygen atoms, was not found to contribute a significant amount of carbon (determined to be 0.24%) to the PM formed during pyrolysis; this result was the same under oxygen-free conditions and with small amounts of air (λ = 0.1, and 0.2). If each of the 18 carbon atoms in oleic acid converted to particulate matter at an equal rate to PM, one would expect that each carbon atom position in the molecule would contribute 5.55% to the total PM mass. Similarly, the carbon atom in the ester group ('c') of methyl oleate was also not found to any extent in the PM; only 0.07% of the carbon in the PM was determined to have come from this carbon atom. The result that the carbon atom directly bonded to two oxygen atoms in methyl oleate did not form PM in the reactor is consistent with previous work, where the equivalent carbon atom in ethyl acetate was not converted to PM formed under similar pyrolytic conditions [7].

The composition of particulate matter formed from the two double bonded carbon atoms labelled in oleic acid-9,10-^{13}C (b–b), is shown Fig. 5. Knowing that the oxygenated carbon atom does not convert to PM, if each of the remaining carbon atoms converted at an equal rate to PM, each carbon atom would contribute 5.88%. It can be seen that the conversion of the double bonded carbon atoms is not much greater than what might be expected from that of the average carbon atom in oleic acid. The calculated composition of PM formed from a carbon atom in the double bond remains relatively unchanged (between 5.5% and 6.6%, per carbon atom) by the quantity of oxygen available in the reactor.

Fig. 6 shows the results of the isotope tracing experiment obtained from the diesel engine. For each molecule, results are shown for two types of PM samples. One of them (labelled **, Fig. 6) is the PM as collected, containing both volatile and non-volatile organic fractions (VOF + NVOF); and the other (labelled *, Fig. 6) is for diesel PM, where volatile organic compounds were baked off by means of the oven, leaving the NVOF remaining (Section 2.2.1).

The results of the tracer experiments carried out in the diesel engine yielded similar results to those obtained in the reactor, as is apparent in Fig. 6. The carbon atoms (a) and (c) directly bonded to the two oxygen atoms, in the cases of both oleic acid and methyl oleate, were not detected in the non-volatile fraction (NVOF) of the PM formed in the engine. Small amounts (about 1 to 2% levels) of the tracer were observed in the unbaked filters (NVOF + VOF). This may have arisen from unburned fuel in the exhaust gas depositing
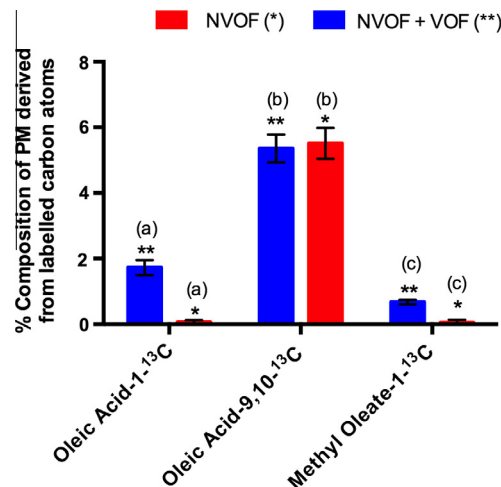
on the filter. It should be noted that in the case of the particulate generated in the diesel engine, which was collected on a glass fibre filter, the particulate had absorbed on it organic species which could originate from the parent fuel and the lubricating oil or which were intermediate compounds formed during the combustion of the fuel and lubricating oil. For example, a ^{14}C labelling investigation by Buchholz et al. studied the conversion of engine oil to PM in a diesel engine ran with biodiesel; they found that less than 5% of the NVOF in PM arose from the engine oil [13]. As a result, it is expected that engine oil had only a small influence on the calculated conversion rates of carbon atoms from the fuel to PM.

Fig. 6 also shows that the double bonded carbon atoms (b)-(b) in oleic acid (oleic acid-9,10-^{13}C) were each found to constitute about 5.5% of the PM formed in the engine; indicating that they form soot at about the same rate as the average carbon atom of this 18 carbon atom molecule. It is interesting to note from Fig. 6 that the conversion rate of the labelled carbon atoms to PM was unchanged by baking the filters. This indicates that there is no preferential incorporation of the double bonded carbon atoms into the NVOF or VOF of the PM.

Table 2
Summary of physical conditions prevailing in the laminar tube reactor and compression ignition engine.

| Tube reactor	Compression ignition engine
Homogenous mixture of fuel and air	Stratified
Fuel concentration of 21,500 ppm (C1 basis)	Overall fuel concentration of ~ 25,000 ppm
Conducted under pyrolytic conditions, and λ = 0.1 and 0.2	Globally lean, stoichiometric in combustion regions, rich spray core
Temperature 1300 °C	Calculated maximum global in-cylinder temperature 1000 °C; flame temperature ~2000 °C [22]
Laminar	Turbulent
Residence time ~1 s	Duration of combustion ~ 0.008 s Residence time (fuel injection to end of exhaust stroke) ~ 0.05 s
Atmospheric pressure	Variable pressure, with peak pressure of ~ 60 bar
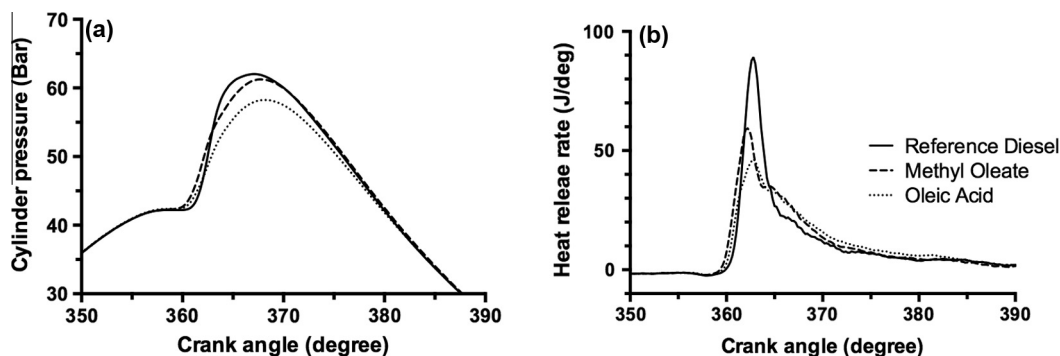
Fig. 7. (a) In-cylinder pressure and (b) apparent heat release rates of methyl oleate, oleic acid, and reference diesel at constant injection timing.
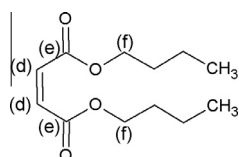

Fig. 8. Molecular structure of dibutyl maleate (DBM), labelled at sites (d), (e), and (f).

All of the measured $\delta^{13}C$ values and calculated parameters for the results discussed in this section are supplied in Supplementary data.

3.3. Influence of the formation conditions on the conversion of atoms to PM

So far the results have shown the conversion rate to PM of ^{13}C labelled carbon atoms in a tube reactor and a diesel engine. It was observed that the conversion rate of the labelled atoms in both systems was very similar despite the differing physical conditions experienced by the fuel molecules in the tube reactor and diesel engine. For example, the two carbon atoms in the double bond of oleic acid (b)–(b) were found to constitute around 11% of PM from both the reactor and the diesel engine. Table 2 lists some of the major differences in the formation conditions of the PM between the two different systems. This is a significant result as it shows that the relative conversion rate of individual carbon atoms to PM is conserved over a range of conditions including pressure, temperature, availability of oxygen, carbon concentration, etc.

Similarly, comparable levels of the isotope tagged carbon bonded to two oxygen atoms were found in the PM formed from both methyl oleate and oleic acid collected from the diesel engine (Fig. 6). This suggests soot formation from these carbon atoms to have been insensitive to the different in-cylinder conditions present during combustion. Fig. 7 shows the in-cylinder pressure and apparent net heat release rate of methyl oleate, oleic acid and the reference fossil diesel fuel. Apparent from Fig. 7b is the higher peak heat release rate and premixed burn fraction of methyl oleate relative to oleic acid. The dissimilar particulate profiles observed in the cases of oleic acid and methyl oleate, shown in Fig. 4a, further supports the suggestion that the in-cylinder conditions and degree of overall fuel conversion to PM (NVOF) does not impact on the fate of COO and C≡C groups within a fuel molecule.

3.4. Conversion of carbon in the ester and carboxylic group to PM

The results of this study that the carbon atom directly bonded to the two oxygen atoms in methyl oleate and oleic acid are significant, and useful for determining the optimal distribution of oxygen

within in a molecule. The results presented in this paper are in agreement with the results of Buchholz et al. who investigated the conversion to PM of specific carbon atoms labelled with ^{14}C in a somewhat different molecule, dibutyl maleate (DBM), shown in Fig. 8 [5]. DBM contains a carbon–carbon double bond (d), two ester groups (e), and two '1-butyl' carbon atoms (f) and each of these groups was specifically labelled with ^{14}C in turn and combusted in a diesel engine. The carbon atom directly bonded to two oxygen atoms (e) was not found in either the exhaust PM or in-cylinder deposits. The double bonded (d), and 1-butyl carbon atoms (f) in DBM was found to form PM in the exhaust at about the same rate as the average carbon atom in the molecule.

Mueller et al. studied the combustion of DBM and tri-propylene glycol methyl ester (TPGME), $C_{10}H_{22}O_4$ [6]. They concluded that the distribution of oxygen in TPGME, which is mainly present as ether groups, was more effective at reducing PM formation than the ester group in DBM. Buchholz and Mueller suggested that the ester structure is an inefficient means of reducing PM formation, since it could produce CO_2 directly, effectively 'wasting' an oxygen atom, which could otherwise be available to prevent another non-ester carbon atom from becoming PM. Numerical simulation of the combustion of DBM indicated that 30% of the oxygen, contained in the ester group, is unavailable for PM precursor reduction, and therefore the distribution of oxygen is not optimal. It was also suggested that the carbon–carbon double bond in DBM could form the PM precursor acetylene directly, and therefore one might expect that the contribution of the double bonded group might have been greater than that of the average carbon atom. The experimental results presented in this paper for oleic acid, and the results of Buchholz et al. on DBM show that there is not a significantly greater contribution to PM from the doubly bonded carbon atoms.

4. Conclusions

Selective labelling of carbon atoms in oleic acid and methyl oleate with ^{13}C has allowed the determination of the relative conversion rates of those atoms to particulate. The high-sensitivity of IRMS measurements make it suitable for determination of carbon atom conversion rates, even with low concentrations of ^{13}C enrichment, and it has been shown that ^{13}C isotope labelling can be applied to both reactor and engine studies. The following conclusions can be drawn from this study:

1. The oxygenated carbon atom in oleic acid and methyl oleate is not found in the engine exhaust PM (despite dissimilar combustion phasing), or in PM formed in the tube reactor; this indicates that the carbon–oxygen double bond does not break during combustion or pyrolysis, thereby preventing its conversion to PM or its precursors.

2. The carbon atoms involved in the double bond in oleic acid, are found to convert to PM at approximately the same rate as would be expected from the average carbon atom in oleic acid; that is a result that was found in both engine and reactor tests.

3. The results from both the engine and reactor are consistent, in that the outcome of the tracer study is the same regardless of the source of the PM.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2015.03.037.

References

[1] Hellier P, Ladommatos N, Allan R, Rogerson J. Influence of fatty acid ester alcohol moiety molecular structure on diesel combustion and emission. Energ Fuel 2011.

[2] Soloiu V, Weaver J, Ochieng H, Duggan M, Davoud S, Vlcek B. Experimental study of combustion and emissions characteristics of methyl oleate, as a surrogate for biodiesel in a direct injection diesel engine. SAE technical paper; 2013.

[3] Purdy R. High oleic sunflower: physical and chemical characteristics. J Am Oil Chem Soc 1986;63:1062–6.

[4] Dhar A, Kevin R, Agarwal AK. Production of biodiesel from high-FFA neem oil and its performance, emission and combustion characterization in a single cylinder DICI engine. Fuel Process Technol 2012;97:118–29.

[5] Buchholz BA, Mueller CJ, Upatnieks A, Martin GC, Pitz WJ, Westbrook CK. Using Carbon-14 Isotope tracing to investigate molecular structure effects of the oxygenate dibutyl maleate on soot emissions from a DI diesel engine. SAE Trans: J Fuels Lubricants 2004;113.

[6] Mueller CJ, Pitz WJ, Pickett LM, Martin GC, Siebers DL, Westbrook CK. Effects of oxygenates on soot processes in DI diesel engines: experiments and numerical simulations. New York, (NY, ETATS-UNIS): Society of Automotive Engineers; 2003.

[7] Eveleigh A, Ladommatos N, Balachandran R, Marca A. Conversion of oxygenated and hydrocarbon molecules to particulate matter using stable isotopes as tracers. Combust Flame 2014;161:2966–74.

[8] Homan HS, Robbins WK. A carbon-14 tracer study of the relative fractions of various fuel carbons in soot. Combust Flame 1986;63:177–90.

[9] Schmieder RW. Radiotracer studies of soot formation in diffusion flames. In: Symposium (International) on Combustion. vol. 20, 1985, p. 1025–33.

[10] Mack JH, Flowers DL, Buchholz BA, Dibble RW. Investigation of HCCI combustion of diethyl ether and ethanol mixtures using carbon 14 tracing and numerical simulations. 2004.

[11] Mack JH, Flowers DL, Buchholz BA, Dibble RW. Using biofuel tracers to study alternative combustion regimes. Nucl Instrum Method Phys Res Section B: Beam Interact Mater Atoms 2007;259:414–20.

[12] Buchholz BA, Cheng A, Dibble R. Isotopic tracing of bio-derived carbon from ethanol-in-diesel blends in the emissions of a diesel engine. SAE SP; 2002. p. 37-46.

[13] Buchholz BA, Dibble RW, Rich D, Cheng A. Quantifying the contribution of lubrication oil carbon to particulate emissions from a diesel engine. SAE technical paper; 2003.

[14] Mayer WJ, Lechman DC, Hilden DL. The contribution of engine oil to diesel exhaust particulate emissions. SAE technical paper; 1980.

[15] Hilden DL, Mayer WJ. The contribution of engine oil to particulate exhaust emissions from light-duty, diesel-powered vehicles. SAE technical paper; 1984.

[16] Buchholz BA, Mueller CJ, Martin GC, Cheng AS, Dibble RW, Frantz BR. Tracing fuel component carbon in the emissions from diesel engines. Nucl Instr Method Phys Res Section B: Beam Interact Mater Atoms 2004;223–224:837–41.

[17] Cheng AS, Buchholz BA, Dibble RW. Isotopic tracing of fuel carbon in the emissions of a compression-ignition engine fueled with biodiesel blends. SAE Trans 2003;112:2015–20.

[18] Ferguson RE. An isotopic tracer study of carbon formation in hydrocarbon flames. Combust Flame 1957;1:431–7.

[19] Schönborn A, Ladommatos N, Williams J, Allan R, Rogerson J. Effects on diesel combustion of the molecular structure of potential synthetic bio-fuel molecules. SAE paper 24-0125; 2007

[20] Ulberth F, Gabernig R, Schrammel F. Flame-ionization detector response to methyl, ethyl, propyl, and butyl esters of fatty acids. J Amer Oil Chem Soc 1999;76:263–6.

[21] Liu F, Guo H, Smallwood GJ, Gülder ÖL. The chemical effects of carbon dioxide as an additive in an ethylene diffusion flame: implications for soot and NO_x formation. Combust Flame 2001;125:778–87.

[22] Sison K, Ladommatos N, Song H, Zhao H. Soot generation of diesel fuels with substantial amounts of oxygen-bearing compounds added. Fuel 2007;86:345–52.