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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

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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.

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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

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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.

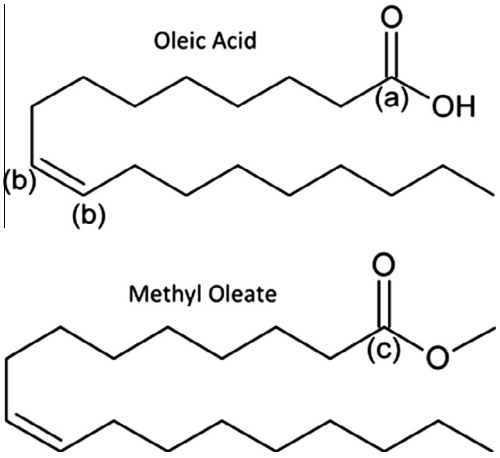

Fig. 1. Structure and nomenclature of the fuels tested. Oleic acid was ^{13}C labelled at sites: (a) oleic acid-1-^{13}C, and (b) oleic acid-9,10-^{13}C. Methyl oleate was labelled in position (c), methyl oleate-1-^{13}C.