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Quantification of the Fraction of Particulate Matter Derived from a Range of ^{13}C-Labeled Fuels Blended into Heptane, Studied in a Diesel Engine and Tube Reactor

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Supporting Information

ABSTRACT: This paper presents the results of an experimental study that was carried out to determine the conversion rates to particulate matter (PM) of several liquid fuel hydrocarbon molecules and specific carbon atoms within those molecules. The fuels investigated (ethanol, *n*-propanol, *i*-propanol, acetone, and toluene) were blended in binary mixtures with *n*-heptane to a level of 10 mol percent. The contribution of the additive molecules to PM was quantified using a carbon-13 (^{13}C) labeling experiment, in which the fuel of interest was enriched with ^{13}C to serve as an atomic tracer. Measurement of the ^{13}C/^{12}C in the fuel and in the resulting PM was carried out using isotope ratio mass spectrometry. The fuel binary mixtures were tested under pyrolysis conditions in a tube reactor and also combusted in a direct injection compression ignition engine. In the tube reactor, samples were generated under oxygen-free pyrolysis conditions and at a temperature of 1300 °C, while the engine experiments were carried out at an intermediate load. Both in the tube reactor and in the engine it was found that, dependent on the fuel molecular structure, there were significant differences in the overall conversion rates to PM of the fuel molecules and of the "submolecular" carbon atoms. A separate experiment was also carried out in the compression ignition engine, with *n*-heptane as fuel, in order to determine the contribution of the engine lubrication oil to exhaust PM; the results showed that a significant portion (~60%) of the total particulate was derived from the lubrication oil.

1. INTRODUCTION

The combustion of alternative transport fuels, particularly those from renewable sources, has become increasingly important in moving away from the use of fossil fuels. In the EU, for example, The European Parliament Renewable Energy Directive has stipulated that by 2020 a minimum of 10% of gasoline and diesel fuels for road transport must be derived from renewable resources.[1] Bioethanol has long been used as an additive or substitute for gasoline.[2] While biodiesel is currently the most widely used alternative to fossil diesel for compression ignition combustion, short-chained alcohols, such as ethanol, have also been considered for blending into conventional diesel fuel.[3] While bioethanol is produced on the largest industrial scale, a number of other bioalcohols, some with even more than five carbon atoms in their molecular structure, may also be produced from biomass.[4] For example, the acetone−butanol−ethanol (ABE) production by *Clostridium acetobutylicum* is an alternative industrial microbial fermentation process that naturally yields acetone, butanol, and ethanol in the ratio of 3:6:1.[5] Similarly, the continuous fermentation of glucose by *C. beijerinckii*, producing *i*-propanol, butanol, and ethanol (IBE) has also been demonstrated.[6] Clearly, future fuels could be produced to contain a range of oxygen-containing molecules, with oxygen bound in functional groups including alcohols, ketones, aldehydes, ethers, esters, and carboxylic acids.

Because of the low cetane number of short-chained alcohols such as ethanol and propanol, they are not suitable as single-component fuels in compression ignition engines and have not been considered as such. However, a number of studies have been carried out where such molecules have been blended into heptane or diesel fuels and combusted in compression ignition engines,[7,8] shock tubes,[9,10] and flow reactors[11] to investigate how the additive molecule influences the combustion characteristics and exhaust emissions. Surrogate fuels are typically composed of a small number of pure compounds, and have certain properties that match those of the target fuel; *n*-heptane is often used as a diesel fuel surrogate.[12] *n*-Heptane is a primary reference fuel for octane rating in combustion engines and has a cetane number of 56, which is similar to that of conventional diesel fuel, which is around 52 in the EU. In this paper *n*-heptane has been used as a surrogate for diesel fuel; in part this was to simplify the isotope labeling experiment, the interpretation of which is greatly simplified by using well-defined fuel mixtures.

Fuel molecular structure is an important parameter that influences soot formation during compression ignition combustion,[13] and there are many examples of experimental studies that show that oxygenated fuel additives reduce soot formation and emissions in diesel engines.[14−20] In these studies it has consistently been shown across a wide range of test engines and engine operating conditions that the extent of the reduction of soot emissions is largely controlled by the amount

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of oxygen in the fuel. For example, Miyamoto et al. blended four oxygenates (di-*n*-butyl ether, ethylhexyl acetate, ethylene glycol mono-*n*-butyl ether, and diethylene glycol dimethyl ether) in turn into diesel fuel and made measurements of the exhaust particulate mass emissions from a direct injection compression ignition engine.[14] As the oxygen content of each blend was gradually increased, the exhaust soot emissions steadily decreased, and when the oxygen content of the fuel reached about 25−35% by mass, the particulate emissions were reduced to near-zero levels. While some earlier studies concluded that the reduction of particulate in diesel engine exhaust was dependent mainly on the percentage mass of oxygen in the fuel rather than the type of oxygenate,[21,22] there is now consensus that there are differences that are dependent on the oxygenate molecular structure.[15,18,23−26] For instance, Liotta and Motalova found that some oxygen-containing functional groups appeared to be more efficient at reducing exhaust particulate matter than others; with ether groups apparently more effective at lowering particulate emissions compared to alcohols.[15] Mueller and colleagues compared dibutyl maleate (DBM) and tripropylene glycol methyl ether (TPGME) combustion in a compression ignition engine and a constant volume vessel.[24] They reported that in both systems TPGME was more effective than DBM at reducing soot formation. Numerical modeling simulations of compression ignition conditions have also predicted differences between the effectiveness of different oxygenates to reduce soot precursor formation; Westbrook et al. concluded that the distribution of oxygen in structures where two oxygen atoms are bonded to one carbon atom, such as in esters, are particularly inefficient.[23]

Part of the difficulty of evaluating the effects of the fuel molecular structure on the particulate emissions of practical systems such as compression ignition engines is that the chemical effects are often obscured due to indirect changes such as fuel volatility, ignition timing, local stoichiometry, etc. To this end, many experiments have been carried out using simplified systems, such as diffusion flames or flow reactors, to isolate the fuel chemical effects. For example, diffusion flame tests have been widely used to evaluate the *sooting tendencies* of different fuels.[27−34] The order of sooting tendencies, as determined by the smoke point, for hydrocarbon fuel molecules of a given carbon number is known to increase in the following order: alkanes < *iso*-alkanes < alkenes < cycloalkanes < alkynes < aromatics.[34] While for mono-oxygenated fuel molecules the order is aldehydes < alcohols < ketones < ethers.[32] For dioxygenated compounds, the order is acids < esters < diethers.[32] It is clear that structural group chemistry can have an appreciable influence on the conversion of fuel molecules to soot and PM emissions. Recent works by Pepiot-Desjardins et al. and by Barrientos et al. have developed a structural group contribution approach for interpreting the observed effects of oxygenated fuels on reducing soot emissions from diffusion flames.[32,33] Because this paper is concerned with the probability of the conversion of individual carbon atoms from various molecules and functional groups to particulate matter (PM) emissions, it is very much related to the question of individual group contributions. This is discussed in greater detail in Discussion.

Isotopically labeled molecules may be used as tracers to determine the extent of conversion of the labeled molecule(s) or atoms(s) to various combustion emissions, including PM, unburned hydrocarbons, and CO_2. A number of isotope techniques have been used over the years for combustion and pyrolysis research, particularly those involving ^{14}C radiotracer techniques.[35−43] Overall, there have been fewer studies reported in the literature that have used ^{13}C tracer techniques, which have been utilized in some recent publications.[44−47] A major benefit of using ^{13}C rather than ^{14}C labeling is that ^{13}C is a stable isotope and does not carry the same health and environmental risks of using radioactive isotopes. In addition, commercially produced ^{13}C-containing molecules can be obtained relatively inexpensively, especially when used at only low levels of enrichment. Previous work by the authors made use of molecules selectively labeled with^{13}C, dosed into fuels at low levels of enrichment, with detection by high-resolution isotope ratio mass spectrometry (IRMS). Measurement of the $^{13}C/^{12}C$ ratio in the particulate matter and that of the fuel from which it was derived allowed the calculation of the fraction of the PM which was derived from the selectively ^{13}C-labeled molecules or atoms. The isotope technique was used to assess some individual atom contributions to exhaust particulate emissions from molecules including a fatty acid methyl ester (methyl oleate) and of a free fatty acid (oleic acid) combusted as single-component fuels in a diesel engine and tube reactor.[45] In this work the methodology has evolved for use with binary or multicomponent fuel mixtures and allows whole molecules within a mixture, or of individual carbon atoms within a molecule, to be assessed in terms of their contribution to PM emissions.

PM in engine exhaust contains carbon that may be derived from either the fuel being burned or from the engine lubrication oil. Therefore, in the process of assessing the extent of the conversion of labeled fuel mixtures to PM, it is also helpful to determine the extent of the engine oil contribution to the exhaust PM. In the literature different types of tracers have been employed to measure oil consumption, including the use of noncarbon elemental tracers such as sulfur;[48] trace metals;[49] hydrocarbons present in the fuel or oil;[50,51] and using isotopically labeled lubrication oils or fuels. The most direct way to measure the contribution of oil to PM is by carrying out an isotope labeling tracer experiment, where either the fuel or the oil is isotopically enriched. A method along these lines was first introduced by the work of Mayer and colleagues in 1980, which relied on using lubrication oil artificially enriched with ^{14}C.[38,39] More recently, researchers have exploited natural variations in the ^{14}C abundance of fuel and oil for the purpose of PM source apportionment.[41,52] In addition to the main results of this paper, concerning the conversion of various fuel molecules to PM, this paper also introduces an alternative methodology for establishing the portion of the PM derived from the lubrication oil, using heptane fuel enriched with only low levels of the stable ^{13}C isotope.

In the present study, measurements were made using PM collected from a compression ignition engine as well as a laboratory flow reactor. In the flow reactor, oxygen-free pyrolysis conditions at 1300 °C were employed. These conditions are broadly consistent with those in the soot-forming regions within the spray core of a direct-injection compression ignition, where there are high-temperature, oxygen-deficient air/fuel regions.

2. METHODS

2.1. Fuels. A number of oxygenated and hydrocarbon molecules were blended with heptane to a level of 10 mol percent; these were ethanol, *i*-propanol, *n*-propanol, acetone, and toluene. Table 1 shows how the 10% molar concentration of the various molecules in heptane

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Table 1. Mixture of Various Compounds in Heptane at a Level of 10 mol %

	mole % of fuel	volume % of the fuel	% of fuel carbon	% wt. oxygen in the fuel blend
ethanol	10	4.24	3.08	1.69
1-propanol	10	5.37	4.55	1.66
2-propanol	10	5.49	4.55	1.66
acetone	10	5.27	4.55	1.67
toluene	10	7.47	10.00	0

corresponds to the overall percent of fuel carbon, volume fraction of the fuel, and the percentage weight oxygen in the fuel blend. Because the molecules were blended with heptane, it was of interest to identify the conversion rate to PM of carbon in the added compound relative to that for the heptane, i.e., to determine whether, overall, the added component tends to form PM to a greater or lesser extent than the heptane molecule itself. To make this determination, a ^{13}C tracer experiment was carried out where the additive component (ethanol, 1-propanol, etc.) was enriched with small amounts of the fuel where all of the carbon atoms were ^{13}C-labeled. Furthermore, selected "submolecular" locations within the molecule of the added fuel were also labeled with ^{13}C in order to identify the relative contribution to PM of the selected carbon atom(s). The molecular structures and nomenclature of the ^{13}C-labeled fuels are shown in Figure 1.

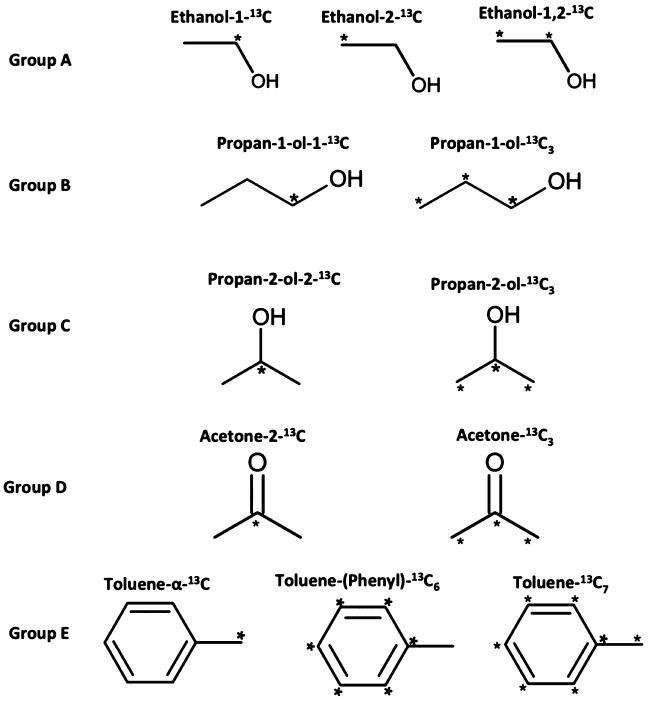

Figure 1. Structure and nomenclature of ^{13}C-labeled molecules investigated, which were blended into *n*-heptane. * indicates the location of the ^{13}C label.

The selection of molecules that were blended into heptane and tested in both a flow reactor and compression ignition engine, allowed the following to be determined:

- The overall contribution of the ethanol fuel (shown in group A) component to PM when blended into heptane; identify the separate conversion rates of the two individual carbon atoms within ethanol; assess the influence of the presence of the hydroxyl group in the ethanol molecule on the conversion to PM of the carbon atom adjacent to the hydroxyl group.
- Comparison of the overall conversion rates to PM of 1- and 2-propanol (group B and C) molecules when blended into heptane, in order to determine whether there is an effect of moving the hydroxyl group from the end on a carbon chain to the central carbon atom.
- Whether the carbon atom directly bonded to the hydroxyl group is converted to PM at a different rate for 1- and 2-propanol than the other carbon atoms of these molecules.
- Testing labeled acetone-in-heptane (group D) to identify the overall conversion rate to PM of the acetone in the blend.
- By comparison of the result of acetone to that of 2-propanol, assess whether by going from 2-propanol (in which oxygen is single bonded to the central carbon) to acetone (which contains a double-bonded oxygen) there is an appreciable difference in (a) the overall conversion to particulate of the molecule as a whole in the heptane blend and (b) in the conversion rate to particulate of the carbon atom to which oxygen is bound directly.
- The extent of toluene (group E) conversion to PM relative to heptane and whether there is a difference in the conversion rate to PM of the carbon in the methyl group (labeled in toluene-α-^{13}C) and the carbon atoms in the phenyl group (labeled in toluene-*phenyl*-$^{13}C_6$).
- To identify whether differences in the PM formation conditions, in the diesel engine and the tube reactor, influence the conversion rates of the labeled molecules by comparing the results of the reactor and the diesel engine.

Small quantities of isotopically labeled fuels were procured from Sigma-Aldrich, each at a grade greater than 98% purity. The names and corresponding catalogue numbers follow: ethanol-$^{13}C_3$, 427039; ethanol-1-^{13}C, 324523; ethanol-2-^{13}C, 427047; propan-1-ol-$^{13}C_3$, 640689; propan-1-ol-1-^{13}C, 493341; propan-2-ol-2-^{13}C, 486744; propan-2-ol-$^{13}C_3$, 572055; toluene-$^{13}C_7$, 606626; toluene-p-$^{13}C_6$, 590835; toluene-α-^{13}C, 487082. The isotopically labeled fuels were each dosed into the fuel mixture, which was composed of the corresponding unlabeled compound at a level of 10 mol percent, and *n*-heptane (90%). The resulting fuel mixture, therefore, had only a very low level of enrichment; typically the level of enrichment was by 30 $\delta^{13}C$ (see Appendix A for a definition of the delta notation), which was still within the natural range of ^{13}C abundance found on earth. Molar calculations were used to predict the volume of labeled fuel required to provide the desired level of enrichment, and the actual enrichment achieved in each blend was confirmed using IRMS measurement of the resulting fuel.

2.2. Flow Reactor. The design and operating parameters of the flow reactor used for the pyrolysis of the various fuel blends are summarized here and have been described in greater detail previously.[44,53] The experimental facility consisted of a fuel feed system, which introduced vaporized liquid fuels into a high-temperature tube reactor and allowed for PM to be sampled at the reactor outlet.

The binary fuel mixtures were introduced to a vaporizer system by means of a syringe pump at a controlled flow rate. For all of the fuels tested in the reactor, the flow rate was fixed to a constant carbon concentration of 6000 ppm on a C_1 basis. The syringe pump was connected to the vaporizer by a stainless steel capillary tube, which issued into the center of a heated stainless steel pipe "tee" fitting that was packed with 3 mm borosilicate glass beads to ensure a large heat transfer area. The vaporizer section and stainless steel tube connected to the reactor was heated by a tape heater, which was controlled by a PID controller that was set to 150 °C for all experiments. The vaporized fuels were entrained into a preheated nitrogen carrier gas, at 150 °C, that flowed through the tee fitting. The flow rate of nitrogen was maintained constant at 20 L/min (STP) by a mass flow controller (Bronkhorst, EL-flow).

The reactor tube was constructed from alumina and was positioned vertically inside an electric oven (Nabertherm, RHTV 120−600). The experiments conducted in this paper were carried out at a temperature of 1300 °C, as measured at the reactor centerline in the zone of

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uniform heating. The reactor tube had an internal diameter of 104 mm and a total length of 1440 mm, with a zone of uniform heating of 600 mm at the center of the reactor. The gas residence time (t_r) in the constant volume of the 600 mm reaction zone of the reactor (V_r), was dependent on the volumetric flow rate of the gas (Q) at the reaction temperature (1300 °C) and pressure (1 atm) and was calculated as follows:

$$t_r(\mathrm{s}) = V_r(\mathrm{L})/Q(\mathrm{L/s}) \quad (1)$$

The conditions employed therefore resulted in a gas residence time of approximately 2.8 s.

2.3. Compression Ignition Engine. The engine experiments in which samples of particulate were collected was carried out on a naturally aspirated direct injection compression ignition engine, converted to run as a single-cylinder research engine. The engine parameters are provided in Table 2.

Table 2. Compression Ignition Engine Specification

engine head model	Ford Duratorq
engine bottom end model	Ricardo Hydra
injectors	6-hole (Delphi DFI 1.3)
injector control	1 μs steps (Emtronix EC-GEN 500)
number of cylinders	1
cylinder bore (mm)	86
crankshaft stroke (mm)	86
displacement (cc)	499.56
compression ratio	18:1
maximum cylinder pressure	150 bar
piston design	ω-bowl
oil temperature (°C)	80 ± 2.5
water temperature (°C)	80 ± 2.5

The engine was equipped with an ultralow volume fuel system, which made it possible to run the engine on volumes of fuel between 100 and 250 mL. The ability to operate the engine using only low volumes of fuel was beneficial due to the relatively high cost of the ^{13}C-labeled fuels. The fuel system used a conventional diesel engine common rail fuel circuit. However, the fossil diesel fuel in the common rail system was used only as a hydraulic fluid, to pressurize the low volumes of test fuel. The fossil diesel "hydraulic" circuit was separated from the test fuel by two free-moving pistons, which pressurized the test fuel and supplied the test fuel directly to the injector. Further details of the design and operation of the low volume fuel system have been provided in previous work.[54] The low volume fuel system was held at a constant temperature of 30 ± 5 °C for all tests reported in this paper.

The engine tests were conducted at a constant speed of 1200 rpm, fuel injection pressure of 450 bar, and a constant start-of-fuel-injection of 5 crank angle degrees (CAD) before top-dead-center (BTDC). In order to maintain a constant engine indicated mean effective pressure (IMEP) of 4 bar, the injection duration was varied between 639 and 755 μs for each fuel tested.

2.3.1. Exhaust Sampling. The composition analysis of the exhaust gases was carried out by the continuous sampling of the exhaust gas, at approximately 180 mm downstream of the exhaust valves, using a Horiba MEXA9100 HEGR exhaust gas analysis system, which measured concentrations of CO, CO_2, NO_x, UHC, and O_2. Real-time exhaust gas PM particle number and size distributions were also measured using a particle size spectrometer (Cambustion DMS 500), with sampling being carried out via a heated sampling line that withdraws exhaust gases at ∼180 mm from the exhaust valves and using the same instrument parameters employed in previous work.[54]

2.3.2. Collection of PM. Samples of particulate matter from the engine exhaust gases were collected onto glass fiber filters (Fisherbrand, Microfiber filter MF300). The engine exhaust was split into two paths at a "tee" fitting, and a portion of the engine exhaust gas was diverted through the glass fiber filter, while the main exhaust path was partially restricted to ensure a sufficient flow through the filter. The particulate filter was located approximately 700 mm downstream of the engine exhaust valves.

The PM collected onto the filter consisted of a solid carbonaceous substrate, or nonvolatile organic fraction (NVOF), with some semivolatile species adsorbed onto the PM, referred to as the volatile organic fraction (VOF). It was of interest to determine the contribution of the labeled fuels to the PM as a whole (comprising NVOF and VOF) and separately to the NVOF fraction of the PM (from which the VOF had been baked off). For this reason, following the collection of the PM samples, the loaded filters were cut in half using stainless steel scissors. One half of the filter (containing NVOF and VOF) was stored in a glass dish and frozen at −20 °C. The other half of the filter was heated to 300 °C in a nitrogen atmosphere for 4 h in order to drive off the VOF, leaving behind the NVOF. The samples containing the PM and the baked samples containing only the NVOF were analyzed individually by IRMS.

2.4. Isotopic Analysis. Measurements of isotopic abundance were made by elemental analysis−isotope ratio mass spectrometry (EA-IRMS). The system comprised two subsystems, the EA and the IRMS systems, and for all of the isotopic measurements the elemental analyzer (Thermo Finnigan, Flash EA, 1112 series) was interfaced to an online IRMS instrument (Thermo Finnigan, Delta V). The temperature of the combustion furnace of the EA was set at 1020 °C, where the sample was oxidized to CO_2, before being passed to the IRMS.

In order to determine the conversion rate to PM of a ^{13}C-labeled component of the fuel, measurements were required of the PM and fuel from which it was derived. For analysis, the solid PM samples were loaded into tin capsules with the equivalent of approximately 70 ± 5 μg of carbon. The tin capsules were then sealed and compacted before being loaded into the sample carousel of the EA instrument. The PM samples that were collected from the engine were removed from the surface of the glass fiber filter with a stainless steel spatula. A separate isotopic analysis of the unused filter showed that it did not contain carbon; therefore, inclusion of the glass fibers in the sample did not influence the outcome of the isotopic analysis.

In previous work, it was found that single-component liquid hydrocarbons could be introduced to the EA system by collecting liquid samples in short lengths of glass capillary and then sealing the capillary into smooth-wall tin capsules, in a way similar to that used for solid samples.[45] In this work, where binary mixtures of fuels were measured, it was found that this method of liquid sample introduction produced highly variable measurements. It is suggested that this was due to the difference in the volatility of the two binary fuels; for example, in the ethanol and heptane mixture, the more volatile component (ethanol) would preferentially evaporate while being transferred to the tin capsule, or prior to measurement. To overcome this, the liquid samples were injected directly into the EA system . A manual injection port was fabricated and installed at the EA inlet, in place of the automated sample carousel. The liquid samples were introduced using a micro syringe to directly inject 2 μL of sample through a silicone septum on the injection port into the combustion furnace of the EA system. Better reproducibility was obtained using this method (deviation typically <0.1 δ^{13}C).

Previous implementations of this type of ^{13}C tracer experiment were carried out by burning only single-component fuels.[44,45] In this paper, binary mixtures of fuels were tested; the calculation to determine the percentage conversion to PM of a ^{13}C-labeled component in a multicomponent mixture is supplied in Appendix A.

3. RESULTS AND DISCUSSION

3.1. Combustion and Emissions Analysis. Before considering the results of the isotopic analysis, this section presents the results of engine heat release data and the emissions analysis of the engine exhaust gas stream. Figure 2 shows the apparent net heat release rates of the reference fossil diesel, pure *n*-heptane and binary heptane blends. The engine experiments were undertaken in two batches that were

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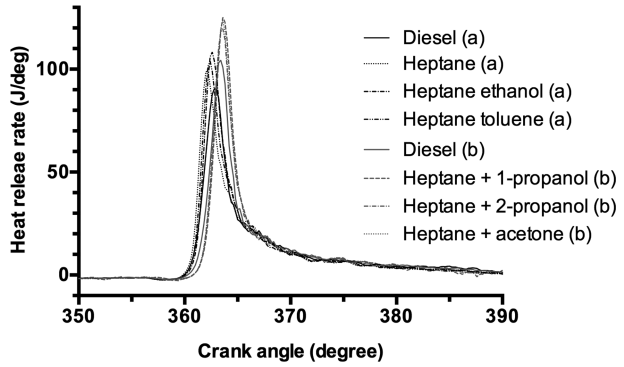

Figure 2. Apparent in-cylinder heat release rates at constant injection timing.

conducted several months apart; Figure 2 shows an increase in the duration of reference fossil diesel ignition delay at the later time of testing (batch "b"). It can be seen that pure *n*-heptane, heptane−ethanol, and heptane−toluene blends exhibited higher peak heat release rates relative to the reference fossil diesel tested at the same time (batch "a"), despite an approximately equal duration of ignition delay (Figure 2). However, the binary blends of heptane and 1-propanol, heptane and 2-propanol, and heptane and acetone exhibited both an increase in peak heat release rates and of the duration of ignition delay (of between 0.2 and 0.6 CAD) relative to the reference fossil diesel tested at the same time (Figure 2).

Figure 3 shows the total mass concentration of particulates in the diesel engine exhaust measured with the DMS500

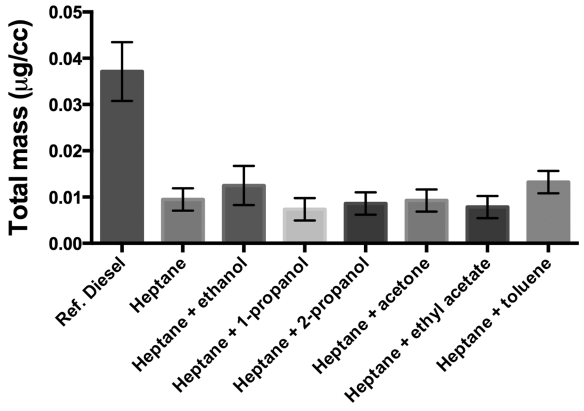

Figure 3. Total particulate mass emission measured in the exhaust gas of the compression ignition engine, fuelled with *n*-heptane binary mixtures. Measurements were made by the DMS500 instrument.

instrument. It is apparent that the reference fossil diesel fuel produced a higher total particulate mass, compared to each of the binary heptane blends, which produced only about a quarter of that of the reference diesel. Considering the range of experimental error bars applicable, it is not possible to draw any firm conclusions as to the influence of the addition of oxygenated molecules or toluene to heptane. The reader is reminded that only low levels of oxygenated molecules were added to heptane (see Table 1), for example the ethanol−heptane blend contained only 1.69% wt. of oxygen. In the literature, the addition of low levels of oxygenated molecules to diesel fuel can result in significant reductions in particle emissions. For example, Liotta and Montalvo investigated the influence of addition of oxygenated additives to diesel fuel on the particulate emissions from a heavy-duty diesel engine. They reported that per 2% (wt.) oxygen to diesel resulted in a 12−18% reduction in particulate emissions, which was dependent on the oxygenate structure.[15] Conventional diesel fuel is composed of hundreds of hydrocarbon molecules, of which about 20% are aromatic molecules, which are known to produce high levels of soot. Thus, replacing part of the aromatic diesel fuel with straight-chain hydrocarbons would decrease soot emissions, independently of the oxygen content. In this paper, heptane was used as a surrogate for diesel fuel; heptane is a paraffinic fuel that produces low levels of soot emissions compared to diesel fuel (see Figure 3). Thus, only a very small difference in the emissions would be expected, which was not detectable using the particle spectrometer (DMS500) employed in this work.

The particle size distribution (PSD) spectra of the PM in the engine exhaust and data concerning the gaseous engine emissions, including CO, CO_2, THC, and NO_x, are supplied as Supporting Information.

3.2. Lubrication Oil Contribution to PM. Particulate matter in the engine exhaust contained carbon that was derived from both the fuel and the lubrication oil. In order to determine the contribution of the engine lubrication oil to the particulate matter in the exhaust, a separate ^{13}C isotope tracer experiment was carried out. In this experiment the compression ignition engine was fuelled with *n*-heptane fuel, which was enriched with heptane-1-^{13}C, and using nonenriched lubrication oil that had only a natural isotopic composition. Further details of the technique and calculation to derive the oil contribution to diesel PM are given in Appendix B.

Figure 4 shows the percentage of the PM derived from the engine oil, and the fuel. The results are shown for samples of

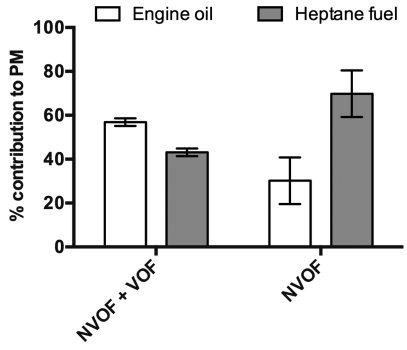

Figure 4. Percent contribution of the lubrication oil and *n*-heptane fuel to the exhaust PM (NVOF + VOF) and the NVOF fraction of the PM. All bars were calculated based on the experiment in which heptane-1-^{13}C was labeled and measurements were carried out by EA-IRMS.

PM as collected, which contained volatile and nonvolatile organic fractions (VOF and NVOF), and for samples where the VOF had been removed, leaving only the NVOF. The majority of the carbon in the PM (NVOF and VOF), approximately 57%, was derived from the lubrication oil, and the remaining 43% was from the heptane fuel. The NVOF fraction of the PM, however, was mainly composed of carbon derived from the heptane fuel (~70%), with 30% from the lubrication oil. The finding that the fuel contributed more to the NVOF was expected, because the carbon in the NVOF is mostly in the form of solid soot particles; and the formation of soot particles from fuel occurs in oxygen-deficient air/fuel regions in the core of the injector fuel spray.[55] A source apportionment of the VOF

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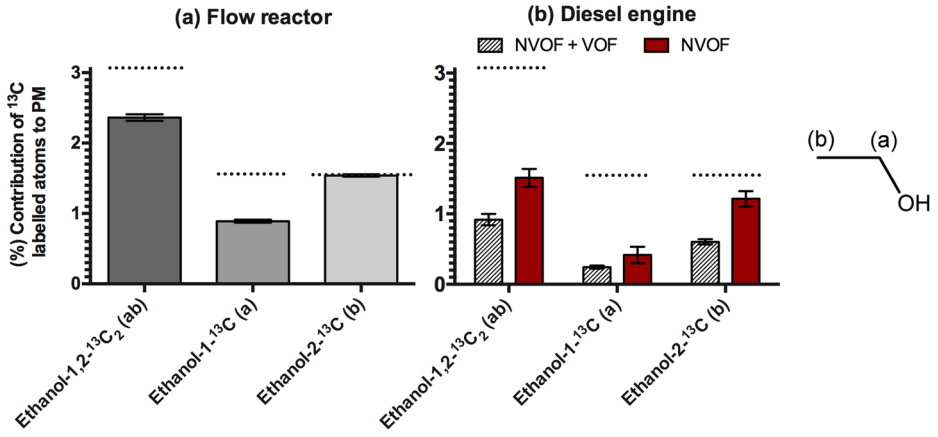

Figure 5. Percentage composition of the PM derived from labeled ethanol carbon atoms, labeled in ethanol-1-^{13}C, ethanol-1-^{13}C, ethanol-1,2-^{13}C, and blended into *n*-heptane in (a) the flow reactor and (b) diesel engine. The dotted lines indicate the mass percent of the fuel carbon at the labeled position.

as a separate fraction could not be carried out because the mass of carbon in the VOF was not known; however, it would appear from Figure 4 that much of the VOF was derived from the lubrication oil. A study by Sakurai et al. also indicated that the majority of the volatile fraction of diesel particles was composed of unburned lubricating oil.[56] Sampling of the exhaust particles from a diesel engine exhaust, operated with a Fischer−Tropsch fuel and a low-sulfur diesel fuel, indicated that the volatile component of the diesel particles was almost entirely (95%) from the lubrication oil (15W40).

The result that the fuel contributed more greatly to the NVOF is also consistent with work carried out by Buchholz and colleagues, who found that about 4% of the NVOF was derived from the lubrication oil, when the diesel engine was fuelled with biodiesel.[52] In this paper, the engine was fuelled using heptane, which overall produced far less particulate mass than fossil diesel (see Figure 2); hence, compared to operation of the engine on diesel fuel, it is the expected result that the lubrication oil would account for a greater proportion of both the VOF and NVOF.

The isotopic composition of the lubrication oil taken from the engine sump, which had been used for several months, was measured and found to be −27.8 δ^{13}C ± 0.1. The isotopic signature of the fresh lubrication oil was −27.7 δ^{13}C ± 0.1, indicating that the age of the oil did not have a significant influence on its isotopic composition. The lubrication oil had an isotopic signature similar to that of the unenriched heptane fuel (−25.4 δ^{13}C); therefore, in experiments where the conversion of labeled fuels to PM was being assessed, the presence of lubrication oil in the PM would tend to "dilute" the influence of the isotopic labeling. In other words, the presence of engine oil in the exhaust PM, would naturally suppress the apparent contribution of the labeled compound, compared to the reactor where there was no lubrication oil, but the overall calculated percentage contribution of the fuel component to PM would still be reliable.

The results presented in the following section must therefore be interpreted considering the contribution of the lubrication oil to the exhaust PM.

3.3. Conversion of ^{13}C-Labeled Fuels to PM. *3.3.1. Ethanol-in-Heptane.* Figure 5 shows the result of the isotope tracer experiment for the 10% ethanol-in-heptane fuel, which was tested in the flow reactor and the diesel engine. Figure 5a shows the results of the PM generated in the flow reactor. Three results bars are shown. The first bar, for ethanol-1,2-^{13}C (ab), shows the combined contribution to PM of the two ethanol carbon atoms in the binary mixture. The two carbon atoms in ethanol overall contributed 2.4% of all the carbon in the PM; the reader is reminded that the total ethanol carbon content in the fuel was 3.08%. This means that the ethanol converted to PM at a lower rate than the heptane component of the binary mixture; the ethanol molecule as a whole contributed to PM at a rate of only ∼75%, relative to its composition in the fuel (2.40/3.08). Considering now each of the two carbon atoms separately, it is shown that the hydroxyl carbon (a) is considerably less likely to convert to PM in comparison to the methyl carbon (b). The hydroxyl carbon atom (a) was found to constitute 0.89% of the PM, whereas in the fuel the hydroxyl carbon constituted 1.54% of the total carbon. An interesting result is that of the methyl carbon atom (b); it constituted 1.54% of the PM carbon, which was the same percentage of carbon that it accounted for in the fuel at the methyl position. This is a significant result because it indicated that, under these conditions, the presence of the oxygen in the ethanol molecule appears to influence only the hydroxyl carbon atom to which it is attached, and it did not affect the carbon atom to which it is not directly attached.

The results from the diesel engine are shown in Figure 5b. Separate bars are shown for the overall PM collected (NVOF and VOF) and the baked sample containing just the NVOF. It is seen that despite the two carbon atoms of ethanol together making up 3.08% of the carbon in the fuel, the carbon that came from the ethanol (a + b) was found to constitute only ∼0.91% of the carbon in the PM and ∼1.51% of the NVOF. The hydroxyl carbon (a) was found to contribute ∼0.24% of the PM and ∼0.41% of the NVOF alone; these contributions were significantly lower than those of the methyl carbon (b), which contributed ∼0.60% and ∼1.21%, respectively. Of course, considering that carbon derived from the engine oil accounted for about 57% and 30% of the PM and NVOF, respectively, the results of the engine and reactor are broadly consistent. The relative rates at which the hydroxyl and methyl carbon atoms of ethanol contributed to PM in the engine were ∼0.4:1 for the hydroxyl carbon-to-methyl carbon; in the case of the reactor, the rate was 0.58:1. Therefore, in the engine, the relative contribution of the hydroxyl carbon atom to PM appeared a little lower compared to that in the reactor.

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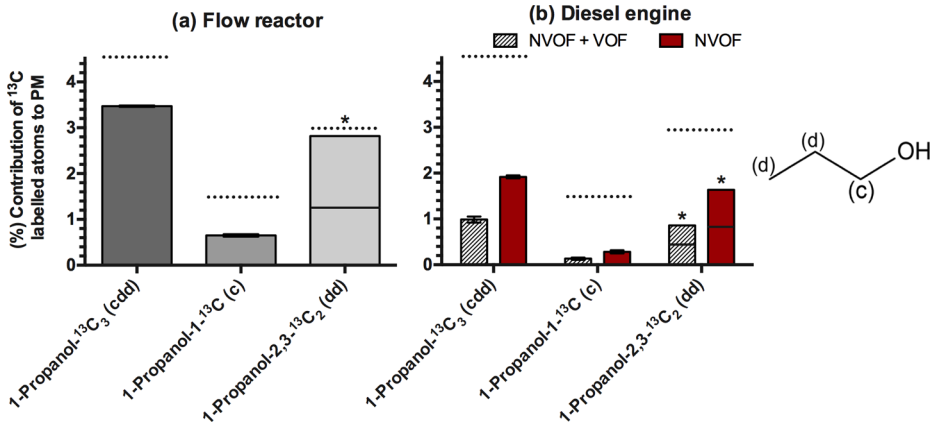

Figure 6. Percentage PM carbon derived from labeled carbon atoms in 1-propanol-1-^{13}C (c), 1-propanol-$^{13}C_3$ (cdd), and 1-propanol-2,3-^{13}C* (dd) blended into *n*-heptane and formed in (a) tube reactor and (b) diesel engine. * indicates that the value was calculated by subtraction and not measured individually. The dotted lines indicate the mass percent of the fuel carbon at the labeled position.

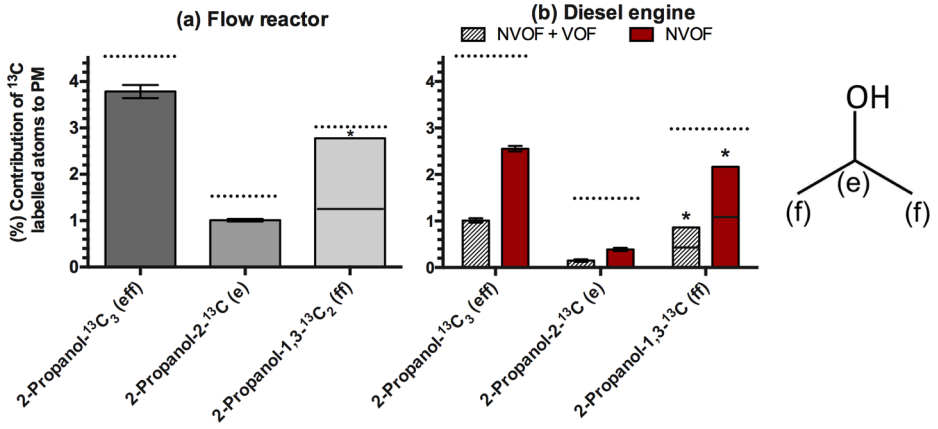

Figure 7. Percentage PM carbon derived from labeled carbon atoms in 2-propanol-$^{13}C_3$ (eff), 2-propanol-2-^{13}C (e), and 2-propanol-1,3-^{13}C* (dd) blended into *n*-heptane and formed in (a) tube reactor and (b) diesel engine. * indicates that the value was calculated by subtraction and not measured individually. The dotted lines indicate the mass percent of the fuel carbon at the labeled position.

It is pleasing to note that the result of the experiments is the same regardless of how the labeling experiment is carried out, that is, whether the carbon atoms are ^{13}C labeled in turn or if both of the carbon atoms are labeled together. For example, the results from the reactor (Figure 5a) show that the methyl carbon (in ethanol-2-^{13}C) contributed 1.53% of the carbon in the PM, while the hydroxyl carbon (ethanol-1-^{13}C) contributed 0.87%, which makes the sum of the two atoms 2.4%. In the version of the experiment where both carbon atoms were labeled simultaneously (ethanol-1,2-^{13}C), it was found that the total contribution to PM was 2.36%. Considering experimental errors, this is in agreement with the sum of the results for the two atoms obtained from two individual experiments. There is also agreement in the results from the diesel engine (Figure 5b) where, for example, with both atoms labeled simultaneously the contribution to the NVOF of the labeled ethanol carbon atoms was 1.63%, while the sum of the individual carbon atom contributions to PM was 0.42% + 1.21% = 1.63%. This is further evidence for the effectiveness of the isotope tracer technique used in this work.

In the literature, Buchholz and colleagues used ^{14}C tracing to determine the overall contribution to PM emissions of the ethanol component of ethanol-in-diesel blends from a medium-duty direct-injection compression-ignition engine.[37] Various amounts of ethanol were blended into fossil diesel fuel, at levels from 9% to 37% volume. It was found for all tests that the carbon from the ethanol component was present to a lesser degree in the PM compared to that for the diesel fuel. For example, in the blend of 9% (v/v) ethanol-in-diesel, carbon from the ethanol was found to comprise 2.4% of the overall PM, whereas it accounted for 5.7% of the carbon mass in the fuel; that is, the mass fraction of carbon derived from ethanol in the PM was 42% of the carbon mass fraction that ethanol accounted for in the fuel. Notwithstanding differences in the experimental system and fuel composition, the result of Buchholz is consistent with this work; by comparison, this paper reports a mass fraction for the PM derived from the ethanol that is only 30% of its mass fraction in the fuel. It should be noted, however, from Figure 2, that the overall PM mass emissions were much lower for heptane than for the reference diesel.

3.3.2. 1-Propanol-in-Heptane. Figure 6 shows the result of the labeling experiment for the 1-propanol-in-heptane blend. For the flow reactor, Figure 6a, it is apparent that while 1-propanol accounted for 4.55% of the fuel carbon, only 3.47% of the PM carbon was derived from the propanol component. The hydroxyl carbon atom (c) converted to PM at a lower rate than the other two carbon atoms in 1-propanol; overall it contributed 0.65% of the PM. It is seen that the other two alkyl carbon atoms (dd) were present in the PM at about the

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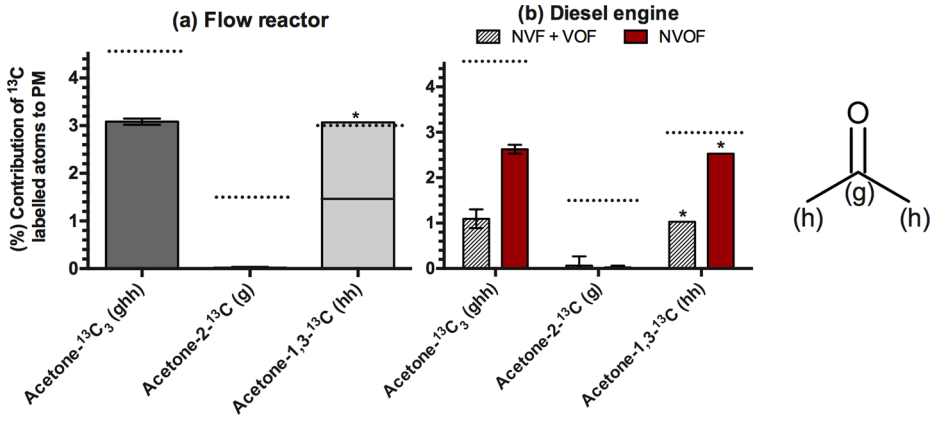

Figure 8. Percentage PM carbon derived from labeled carbon atoms in acetone-2-^{13}C (g) and acetone-$^{13}C_3$ blended into *n*-heptane and formed in (a) tube reactor and (b) diesel engine. * indicates that the value was calculated by subtraction and not measured individually. The dotted lines indicate the mass percent of the fuel carbon at the labeled position.

same rate as they were present in the initial fuel; meaning that they converted to PM at approximately the same rate as the heptane component. Therefore, the lower rate of conversion of the 1-propanol molecule overall, compared to heptane, was attributable solely to the effect of the hydroxyl group acting on the attached carbon atom.

The result from the diesel engine, Figure 6b, shows that ∼0.9% of the overall PM (NVOF and VOF) was derived from the 1-propanol component of the binary mixture, whereas ∼1.9% of the NVOF originated from the 1-propanol. This shows that, similar to the above result for ethanol, carbon derived from the 1-propanol was found mainly in the NVOF, rather than in the volatile fraction of the PM. The hydroxyl carbon atom was found in the NVOF at a rate of ∼0.28%. Similar to the result for 1-propanol in the tube reactor, in the engine the hydroxyl carbon atom contributed significantly less to PM than the alkyl carbon atoms, which each contributed ∼0.82% of the NVOF.

3.3.3. 2-Propanol-in-Heptane. Shown in Figure 7 are the results for the 2-propanol-in-heptane fuel tested in both the flow reactor rig and the compression ignition engine. Considering first the result of the flow reactor, Figure 7a, 3.79% of the PM carbon was derived from the 2-propanol (eff), where it accounted for 4.55% of the fuel carbon. The hydroxyl carbon atom (e) in 2-propanol contributed 1% of the carbon PM, which was proportionally less than that of the other methyl carbons (ff), which each contributed 1.38%. The reader is reminded that the equivalent *hydroxyl* carbon atom in 1-propanol, above, converted to PM at a lower rate of 0.65%. This result is consistent with previous work carried out on single-component alcohols, which found that the hydroxyl carbon in secondary alcohols converted to PM at a lower rate than in primary alcohols.[44] The relative rate of conversion for the 2-propanol hydroxyl carbon atom was 66% relative to its mass fraction in the fuel (i.e., 1/1.54). It is apparent that the carbon atom (e) attached to the secondary alcohol group in 2-propanol tends to convert to PM at a higher rate (66%) than the equivalent carbon in 1-propanol (42%).

Figure 7b shows the result of the 2-propanol-in-heptane binary mixture blends tested in the compression ignition engine. The overall contribution of the 2-propanol component to the overall PM (NVOF and VOF) was ∼1%, and ∼2.6% to the NVOF alone, compared to the level of 4.55% in the fuel. While 2-propanol contributed to the overall PM at about the same rate as 1-propanol (∼1%), in comparison, a greater portion of the NVOF was derived from 2-propanol (2.6% compared to 1.9%). The hydroxyl carbon atom (e) constituted 0.15% of the PM and 0.39% NVOF. Because of experimental errors, it is not clear whether in the engine there was a difference in the conversion rate between the hydroxyl carbon atoms of 1- or 2-propanol, as was observed in the results of the reactor.

3.3.4. Acetone-in-Heptane. Consider first the result from the flow reactor, shown in Figure 8a. Overall, the acetone component of the fuel accounted for 4.55% of the carbon, while in the resulting PM, from that fuel, only 3% of the carbon was derived from acetone (labeled in acetone-$^{13}C_3$ (ghh)). It is apparent that the carbonyl carbon atom (g) does not convert to particulate matter. Despite the lack of contribution from the carbonyl atom (C═O), there was a significant contribution to PM from the remaining two carbon atoms (hh) in the acetone molecule. The two methyl carbon atoms in acetone (hh) comprised 3.08% of the carbon in the fuel, and it was calculated that the PM derived from these carbon atoms contained about the same level (∼3.07%); this indicates that the two methyl carbon atoms in acetone convert to particulate at about the same rate as the average carbon atom in heptane. It appears that the presence of oxygen in the form of a carbonyl group influences only the carbonyl carbon atom but does not appear to have any effect on the likelihood of the methyl carbon atoms (hh) becoming available for soot formation.

Consider now the result from the diesel engine, shown in Figure 8b. The conversion of the acetone component of the binary fuel mixture was found to be about 1% of the overall PM (NVOF + VOF). Approximately 2.6% of the NVOF was derived from the acetone component of the fuel, which was the same rate as that of 2-propanol, discussed above. Consistent with the result obtained in the reactor, the carbonyl carbon (g) did not contribute to the exhaust PM, while the methyl carbon atoms (hh) of acetone contributed significantly to the PM, particularly to the NVOF.

The present experimental results, which show that oxygen-bound carbon atoms are less likely to be incorporated into PM, is consistent with results of other researchers in the literature.[44,57] When going from the hydroxyl moiety in 2-propanol to the ketone functional group of acetone, the carbon double-bonded to oxygen in the ketone makes the attached carbon even less likely to participate in the formation of PM. It

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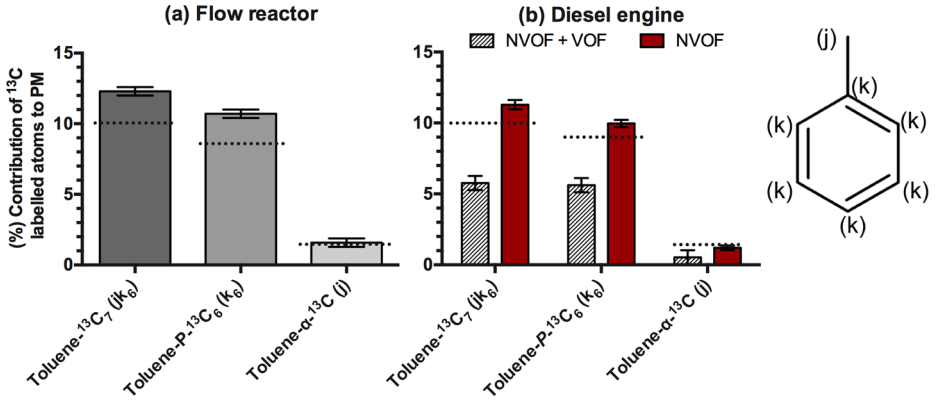

Figure 9. Percentage PM carbon derived from labeled carbon atoms in toluene-$^{13}C_7$ (jk_6), toluene-α-^{13}C (j), and toluene-*P*-$^{13}C_6$ (k_6) blended into *n*-heptane and formed in (a) tube reactor and (b) diesel engine. The dotted lines indicate the mass percent of the fuel carbon at the labeled position.

is suggested that in the case of the carbonyl functional group that oxygen stays attached to the neighboring carbon atom during pyrolysis, making it unavailable for participation in reactions that result in PM formation. Overall, in the reactor this meant that the acetone molecule overall contributed to PM at a lower rate than 2-propanol.

3.3.5. Toluene-in-Heptane. Figure 9a shows the result of the tracer study of the toluene-in-heptane blends carried out in the flow reactor. The toluene component comprised 10% of the carbon in the fuel, and it can be seen that carbon atoms derived from the toluene composed 12.5% of the PM; this means that the toluene was about 25% more likely to become PM than the heptane component. The result that toluene had a higher propensity to form PM was expected, due to the higher *sooting tendency* of aromatics relative to aliphatic molecules, which has been widely reported in the literature.[28] In Figure 9a it appears that the methyl carbon in toluene (j) contributed to PM formation at a slightly lower rate than the phenyl ring (k) but at about the same rate compared to the average heptane atom and at about the same rate as it was present in the fuel, indicated in Figure 9a by a dotted line above the bar of the methyl carbon. The result suggests that during pyrolysis demethylation of toluene occurs at least to some extent; otherwise the same rate of contribution to the PM could be expected for the methyl and phenyl ring. The methyl carbon (j) of toluene converts to PM at about the same rate as the alkane chain of heptane, but at a reduced rate compared to the phenyl ring (k). It is tentatively suggested that the heptane and the methyl carbon of toluene contribute to soot by a similar mechanism involving C_1, C_2, and C_3 carbon fragments. The phenyl ring, however, may polymerize directly to form PAHs retaining its aromatic structure; indeed, the literature shows that a range of C_2, C_3, as well as aromatic and polycyclic aromatic molecules are produced during shock tube pyrolysis of toluene.[58] The overall result for the pyrolysis of the heptane−toluene mixture, in the reactor, is that the toluene component contributed more than the heptane component to soot formation. This is in alignment with the literature, which shows that under well-controlled conditions increasing the toluene percentage in a binary mixtures of toluene−heptane results in an increased soot yield over a wide range of temperature conditions.[9] In addition, Homan and Robbins measured atom-specific yields using a ^{14}C technique and reported that carbon atoms contained within aromatic rings were converted to soot by a factor of about 1.5 compared to nonaromatic carbons.[42]

In Figure 9b it is seen that toluene (labeled in toluene-$^{13}C_7$ (jk_6)) overall accounted for ∼5.78% of the PM (NVOF + VOF) from the diesel engine, whereas toluene accounted for 10% of the carbon in the fuel. The baked sample, which contained just the NVOF, was composed of ∼11.3% of carbon derived from toluene. It is clear that the toluene component of the fuel had a greater tendency to form PM than the heptane, particularly considering the contribution of the engine lubrication oil to PM. This is in agreement with the results from the reactor.

Figure 9b shows that the phenyl ring (k) in toluene had an increased propensity to form the NVOF, compared to the methyl carbon atom (j); similar to the result obtained in the reactor experiments. The aromatic ring contributes ∼10% of the NVOF, meaning that each of the six carbon atoms in the ring contributed ∼1.67%. The methyl group, however, contributed about ∼1.2% of the carbon in the NVOF.

4. DISCUSSION

The above results have shown some interesting differences between the various oxygen-containing functional groups in limiting the carbon atoms that they are attached to in becoming PM. For example, the ketone carbon atom in acetone was not found in the PM in either the reactor or the engine, while carbon atoms of the alcohol group in ethanol, 1-propanol, and 2-propanol all contributed to differing extents to PM. Chemical kinetic modeling studies have been employed in order to predict and explain variations between the efficiencies of different oxygen containing functional groups in suppressing soot formation.[23,24,59] One such study by Westbrook et al. involved the modeling of the fuel-rich diesel-ignition of binary mixtures of various oxygenates (including alcohols, ethers, esters, and carbonates) in heptane and used the kinetic model to examine how oxygenated additives suppress soot formation.[23] They explained that C−O moieties in oxygenated molecules survive fuel-rich ignition intact, preventing the carbon from forming soot precursor molecules. Their analysis showed that many of the oxygen atoms contained in the oxygenates react to directly produce carbon monoxide (CO), the strong CO bond does not break during the ignition process, and ultimately the carbon atom never becomes available for soot formation. The results of this paper are consistent with the explanation that oxygenate CO bonds remain intact, but suggest that the extent to which CO bond cleavage occurs varies significantly between different oxygenates.

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It was mentioned in the Introduction that Pepiot-Desjardins et al.[33] and Barrientos et al.[32] developed a group additivity-based approach in order to interpret the sooting tendency differences between different types of oxygenated additives. Group additivity theory predictions involve the division of molecules into smaller groups where each group has a numerical contribution to the property being estimated. The group theory predictions of sooting tendency were found to correlate well with the observed sooting tendencies of molecules recorded in several experimental databases, including data for both premixed and nonpremixed flames. The group theory analysis indicated that replacing a terminal methyl (CH_3) group of a molecule with an alcohol or aldehyde group resulted in an improvement in the sooting tendency, and the aldehyde group was more efficient than the alcohol group at reducing sooting. Similarly, midchain groups, such as secondary alcohols, ketones, and esters, had a beneficial effect on sooting tendency; esters had the largest reduction on sooting tendency, but on a per carbon atom basis, the ketone was the most efficient. These results also appear to be consistent with the findings of this paper, where there is overlap, which shows that the ketone (acetone) was significantly more efficient than secondary alcohol (2-propanol) at preventing the carbon atom in that group form becoming PM. In future work, screening a wider range of molecules and groups using isotope tracing will address whether other individually measured group contributions are consistent with the group theory predictions and could be used to account for more complex molecular interactions.

It should be noted that in experimental studies carried out on diffusion flames, in some cases the addition of oxygenated additives increased the overall rate of soot formation.[29,60,61] McEnally and Pfefferle added oxygenated molecules at 1000 ppm concentrations into nonpremixed methane flames.[29] They found that the sooting tendencies of primary alcohols were similar to that of *n*-alkanes of the same carbon number, and secondary alcohols produced higher levels of soot than equivalent *n*-alkanes. Aldehydes and ketones formed the same amount of soot as an equivalent *n*-alkane with one fewer carbon atom. The levels of soot formation from the primary and secondary alcohols were explained as being due to four-center reactions involving the removal of the alcohol group and a neighboring hydrogen atom, a process that resulted in the formation of water, which is relatively inert, and an alkene, which is known to promote soot formation. Because secondary alcohols contain more neighboring hydrogen atoms available to form the four-center intermediate, the rate is faster for secondary than for primary alcohols.

In this paper, the carbon involved in the ketone group of acetone does not convert to soot, while the remaining methyl carbon atoms in acetone appeared to contribute to soot formation at the same rate as the heptane component. This result appears to agree with the work of McEnally and Pfefferle, discussed above, that found that ketones behaved like alkanes with one fewer carbon atom.[29] This suggests that the strong C═O bond does not break during pyrolysis or diffusion flame combustion and prevents the carbon from becoming soot. The isotopic results for each of the alcohols showed that the carbon atom attached to the hydroxyl group converted to soot, but at a reduced extent compared to other carbon atoms that were not attached to oxygen. It was also evident that the carbon attached to the hydroxyl group (OH) in 1-propanol (a primary alcohol) converted to soot at a considerably lower rate than the equivalent atom in 2-propanol (a secondary alcohol). The result of the reactor appeared to indicate that the OH group in 1-propanol and 2-propanol was separated from the carbon atom about 42% and 66% of the time, respectively. This appears to provide support for the greater prominence of the four-center reaction in secondary alcohols, described by McEnally and Pfefferle; however, it should be noted that in the current work the overall sooting tendency of fuels was not established in the tube reactor.

Table 3 highlights some of the differences in the physical conditions experienced by the fuels in the flow reactor and diesel engine used in this work. Considering these major differences in the formation conditions, the results for the two systems are broadly consistent. For example, the reduced rate of PM formation from the *hydroxyl* carbon atoms (in ethanol, 1-propanol, and 2-propanol) was observed in both systems; so too was a negligible contribution to PM of the *carbonyl* group in the acetone molecule. This result shows that the influence of the local molecular structure of the fuel on the conversion of carbon to PM is conserved over a range of conditions including pressure, temperature, availability of oxygen, carbon concentration, etc. This is supported by previous work in which the oxygen-free pyrolysis of ethanol resulted in PM that was derived from the methyl carbon preferentially, at a methyl-to-hydroxyl carbon ratio of 2:1 and was insensitive to temperature over the range of 1200−1450 °C.[44,53] Similarly, Lieb and Roblee combusted ethanol in a diffusion flame and using a radiotracer technique also found a conversion ratio of 2:1.[43] The apparent conservation of the relative conversion rates of carbon atoms involved in different functional groups to PM under a range of conditions is promising for the development and application of the group additivity-based approaches for estimating sooting tendency for more complex practical systems.

Table 3. Summary of Physical Conditions Present in the Tube Reactor and Compression Ignition Engine

tube reactor	compression ignition engine
homogenous mixture of fuel and air	stratified
fuel concentration of 6000 ppm (C1 basis)	overall fuel concentration of ∼25 000 ppm
oxygen-free pyrolysis conditions	globally lean, stoichiometric in combustion regions, rich spray core
temperature 1300 °C	calculated maximum global in-cylinder temperature 1000 °C; flame temperature ∼2000 °C[20]
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

5. CONCLUSIONS

^{13}C isotopic labeling experiments were successfully undertaken to determine the extent of the conversion of labeled fuels to PM in a flow reactor and in a diesel engine. Furthermore, an isotope tracer experiment was also applied to determine the content of PM that was derived from the lubrication oil. The most significant findings reported in this paper follow:

- When the diesel engine was fuelled with heptane, carbon derived from the lubrication oil accounted for 57% of the carbon to the PM (NVOF and VOF) and only ∼30% of the NVOF. Therefore, the engine oil contributed a

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significant portion of the PM, and most strongly to the VOF.

- In the flow reactor and diesel engine, the *hydroxyl* carbon atom in the alcohol-containing fuels (ethanol, 1-propanol, and 2-propanol) contributed to PM formation at a reduced rate compared to alkyl carbon atoms.
- In the reactor, the hydroxyl carbon atom in the secondary alcohol, 2-propanol, converted to PM at a higher rate than the equivalent atom in the primary alcohol 1-propanol. This indicated that when going from a primary alcohol to a secondary alcohol, the hydroxyl group becomes less likely to stay attached to the neighboring carbon.
- The ketone functional group, in acetone, was found to prevent the formation of PM from the carbon atom it was directly bound to. This result was found to be consistent for the PM formed in both the reactor and the diesel engine. The *methyl* carbon atoms of acetone formed PM in the reactor at about the same rate as heptane alkyl carbon atoms.
- In the reactor, for the toluene-in-heptane binary mixture, the toluene component formed PM at a rate about 25% higher than the heptane component. In addition, it was found that the carbon atoms contained in the phenyl ring of toluene formed PM at a rate higher than the *methyl* carbon.
- In the diesel engine, it was found that the toluene component of the fuel formed NVOF at a much higher rate than the heptane component.

APPENDIX A: CALCULATION TO DETERMINE THE COMPOSITION OF PM

This section sets out the methodology used for interpreting the measured ($\delta^{13}C$) isotopic data. First, the isotope ratio data, as measured by the IRMS instrument, is initially reported as delta values (in permil units, ‰), eq 2. It is defined as the difference between the $^{13}C/^{12}C$ rates in the sample, compared to that of an international standard reference material.

$$\delta^{13}C_{VPDB} = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{Sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{Standard}} - 1 \right) \times 1000 \tag{2}$$

For the binary mixtures and multicomponent fuels, the enrichment process and measurements that are required to determine the percentage conversion of a molecule or carbon atom to PM are the same as for the single-component fuels.[45] Four $\delta^{13}C$ measurements were required: first the unenriched (native) and the corresponding enriched fuel ($\delta^{13}C_F$), and for the particulate matter, derived from both of the unenriched and enriched fuels ($\delta^{13}C_{PM}$). For each fuel and derived PM, the difference in isotopic composition between the unenriched and the enriched versions called Δ_F and Δ_{PM} were calculated as follows:

$$\Delta_F = \delta^{13}C_F^* - \delta^{13}C_F^n \tag{3}$$

$$\Delta_{PM} = \delta^{13}C_{PM}^* - \delta^{13}C_{PM}^n \tag{4}$$

where the * refers to the enriched fuel or the PM derived from it and the n refers to the unenriched (native) fuel or PM derived from it.

Δ_{max} is a parameter that represents the maximum possible Δ_{PM} value obtainable (i.e., if the PM contained carbon derived only from the labeled carbon atoms), and is defined as follows:

$$\Delta_{max} = \frac{\Delta_F}{R_f \cdot n_{labeled}} \cdot \sum_{f=1}^{t} (R_f \cdot n_{f_{total}}) \tag{5}$$

where $n_{labeled}$ represents the number of carbon atoms which were labeled in the tagged molecule; R_f is the molar ratio of a given component f, t the total number of components in the multicomponent mixture, and $n_{f_{total}}$ the total number of carbon atoms in component f.

The final step to calculate the fraction of the PM that was derived from labeled carbon atoms ($f_{labeled}$) is as follows:

$$F_{labeled} = \frac{\Delta_{PM}}{\Delta_{max}} \tag{6}$$

The product $F_{labeled} \times 100$ gives the percent contribution overall of the labeled C atom(s) to PM, taking into account all of the carbon atoms in the added compound and that of the heptane. The fraction contribution to PM of the carbon atoms that were not ^{13}C labeled could be calculated as simply $1 - F_{labeled}$.

APPENDIX B: METHODOLOGY TO DETERMINE THE LUBRICATION OIL CONTRIBUTION TO THE PM

A source apportionment was carried out of the PM collected from the exhaust of the compression ignition engine in order to determine the fraction of carbon that had been derived from the lubrication oil and the fuel. The experiment was carried out by fueling the engine with heptane (99% HPLC-grade, Sigma-Aldrich 650536), which had been enriched with a small amount of heptane-1-^{13}C (Sigma-Aldrich, 492728). The natural heptane had an isotopic signature of −25.4 $\delta^{13}C \pm 0.1$, and the enriched version was 21.0 $\delta^{13}C \pm 0.1$. The engine oil used was Castrol Magnatec 10W40 and had been used in the engine for several months before carrying out the tests detailed in this paper. The used lubrication oil was measured by IRMS and found to have an isotopic signature of −27.8 $\delta^{13}C \pm 0.1$, and the fresh oil was −27.7 $\delta^{13}C \pm 0.1$; therefore, there was a negligible change in the isotopic composition over time due to contamination of the oil by PM.

The sampling and running conditions employed in the engine for the purpose of this experiment were identical to those used for the engine experiments where the fuel binary mixture tracer experiments, which were described in the paper. The isotopic $^{13}C/^{12}C$ measurements of the PM samples were also made using the same analytical techniques. The samples of lubrication oil were prepared for EA-IRMS analysis by sealing the weighed samples into smooth-wall tin capsules and submitting the samples in the same way as for solid PM samples.

The exhaust PM contained carbon derived from both the fuel and the lubrication oil; therefore, the isotopic composition is determined by the weighted sum of the oil and fuel $\delta^{13}C$ values, as follows:

$$\delta^{13}C_{PM} = (\delta^{13}C_{fuel} \times a) + (\delta^{13}C_{oil} \times b)$$

where $\delta^{13}C_{PM}$, $\delta^{13}C_{fuel}$, and $\delta^{13}C_{oil}$ are the isotopic compositions of the exhaust particulate matter, fuel, and lubrication oil,

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respectively. a and b are the mass fractions of PM carbon derived from the fuel and oil, respectively, where $a + b = 1$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.6b00322.

Compression ignition engine particle size distributions (page S2); compression ignition engine exhaust gas emissions (page S3); fuel and particulate isotopic measurements and calculated parameters (pages S4–S8) (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

IRMS = isotope ratio mass spectrometry
EA = elemental analysis
THC = total hydrocarbon content
PM = particulate matter
VOF = volatile organic fraction
NVOF = nonvolatile organic fraction
CAD = crank angle degrees
BTDC = before top-dead-center
IMEP = indicated mean effective pressure
PSD = particle size distribution
STP = standard temperature and pressure

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