



Conversion of oxygenated and hydrocarbon molecules to particulate matter using stable isotopes as tracers



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ABSTRACT

Fuels are continuing to be derived from fossil sources, but as production technology improves, biofuels and synthetic fuels are expected to emerge as scalable long-term sources of liquid fuels. Efforts are being made to ensure that this next-generation of fuels is cleaner burning than the last. In order to inform the production and processing of cleaner burning fuels, more needs to be known about how molecular structure influences the formation of pollutant emissions. Reducing airborne quantities of particulate matter (PM) is of particular interest for human health and the environment. This publication presents a ¹³C labelling technique, which has been developed and applied to identify the influence of local molecular structure on the formation of PM. The paper applied the technique based on the ¹³C stable isotope to trace the conversion of individual carbon atoms to PM in the case of several oxygenated and hydrocarbon molecules. A laminar tube reactor facility has been used for generating and collecting samples of PM under pyrolysis conditions. A number of single-component oxygenated and hydrocarbons (ethanol, propanol, pentanol, cyclopentanol, ethyl acetate, and toluene) have been enriched with ¹³C at specific carbon atom locations and the ¹³C/¹²C isotope ratios of PM were measured. The contribution to PM of particular carbon atoms within a molecule was evaluated, and the results shed new light of how individual carbon atoms in a molecule convert to PM. It was found that the conversion to PM of different atoms within a molecule varies widely, depending on the identity of their neighbouring moiety. Furthermore, it was shown that oxygen-containing functional groups have a significant influence on the formation of particulates, partly through a reduction in the conversion to PM of carbon atoms, which are adjacent to oxygen atoms.

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1. Introduction

Combustion generated emissions, such as NO_x, and particulate matter (PM), have long been identified as being detrimental to human health. In urban areas, high concentrations of PM have been linked to respiratory and cardiac diseases [1]. Following a recent review by the World Health Organisation, PM has been identified as a *group 1* carcinogenic agent, satisfying *sufficient evidence of carcinogenicity in humans* [2]. Recently, the importance of reducing airborne quantities of PM has come to the forefront for its prospect of reaping immediate climatic benefits. There has been suggestion that, unlike CO₂, the precipitation of PM over a timescale of weeks means that the average PM concentration in the atmosphere can be reduced more rapidly than that of CO₂, by taking measures that lower the emission of PM in the atmosphere [3,4]. Increasingly stringent legislation over the past 20 years restricts the emission

of PM from various combustion sources, including vehicles [5]. This has given increasing momentum to efforts that focus on improving the combustion characteristics of fuels, which could reduce regulated emissions. This paper introduces a comprehensive application of stable ¹³C isotope labelling as a means of assessing quantitatively to what extent specific individual carbon atoms in a molecule convert to PM. Understanding how molecular structure influences the conversion of individual carbon atoms to toxic emissions can be used to modify fuels in order to mitigate PM and other emissions.

In direct injection diesel engines, PM is formed following ignition in oxygen-deficient regions of vaporised fuel; fuel/air equivalence ratios (ϕ) in these regions is approximately 2–4 [6]. Temperatures prevailing in the spray core during soot formation can range from 1500 to 2000 K, with highest levels of formation occurring in the range of 1600–1800 K [7]. These temperatures do not appear to be greatly affected by whether the diesel fuel is oxygenated or non-oxygenated; for example, a blend of 70% diesel mixed with 30% esterified rape-seed oil is found to have an average

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flame temperature, at 40% heat release, which is only 60 K less than that for the petroleum-derived diesel fuel alone [8]. The conditions in the tube reactor used to obtain the results presented in this paper resemble, in a broad sense, those of the spray core in a diesel engine, in that they were oxygen deficient with soot produced at temperatures ranging from 1475 to 1725 K.

There have been a number of investigations into how the molecular structure of hydrocarbons influences the formation of PM [9–11], often performed in atmospheric flames or flow reactors under well-controlled conditions [12]. For example, Ruiz et al., compare the tendency of acetylene (C_2H_2) and ethylene (C_2H_4) to form PM in a flow reactor at concentrations of 15,000 ppm. Acetylene was found to convert to PM in greater proportions at all temperatures in the range of 1000–1200 °C [13]. Such studies, on individual molecules, can provide useful insights on how the tendency of a molecule to form PM is affected by various molecular functional groups.

Isotope tracking methods have not been used to a significant extent for monitoring emissions from combustion processes. A ^{13}C labelling method by Ferguson (1957) used propane enriched with ^{13}C at specific carbon atoms at levels of ^{13}C enrichment exceeding 20% (mole per cent), in order to identify whether a two-carbon fragment of propane was responsible for soot generation in a flame [14]. Attempts during the 1970s and 1980s used a radiocarbon tracer, ^{14}C , to track the contribution of individual hydrocarbon components in a mixture, and the contribution of individual carbons to PM, using a decay-counting method [15–18]. More recently, a more efficient method using ^{14}C has been used to track the formation of emissions from dibutyl maleate (DBM) using accelerator mass spectrometry (AMS) [19]. On the whole, only a small number of molecules have been studied so far using isotope tracking, and to the best of our knowledge, the stable ^{13}C nuclide has not previously been used as a tracer at low concentrations during the formation of PM.

Organic molecules can be synthesised to contain a ^{13}C nuclide as a label, at a known position within a molecule. The compounds selected for this study are a homologous series of molecules, with systematic variations. Particular attention has been given to oxygenated molecules; being able to predict a favourable distribution of oxygen within a molecule allows fuels to be designed or post-processed to yield cleaner burning properties. This work contributes to a number of experimental studies which focus on identifying what changes could be made to individual fuels in order to make informed changes to produce cleaner burning fuels [20,21].

2. Methods

2.1. Fuel molecules investigated

A series of seven single-component C2–C7 oxygenated and hydrocarbon molecules were investigated, having a total of twelve ^{13}C labelled molecular structures, as shown in Fig. 1; where an asterisk denotes which carbon atoms in the molecules have been ^{13}C labelled. Pure labelled compounds were manufactured by Isotec, and sourced from Sigma–Aldrich, all of the compounds acquired had a certified abundance of at least 98% ^{13}C for the enriched carbon position. The pure labelled molecules were used to enrich unlabelled but otherwise identical molecules. The labelled compounds were added using a capillary piston pipette (Gilson, MICROMAN, CP100). Dilutions were specific to the hydrocarbon used, for example 45 μ L ethanol-1- ^{13}C was used to enrich 100 mL of standard ethanol, but as the number of carbon atoms in the molecules increases greater volumetric quantities were generally required to maintain the desired level of ^{13}C enrichment. The desired level of enrichment could be predicted using molar calculations.

Using the selection of molecules mentioned above, the influence of the following molecular features on PM formation was assessed:

- Whether the presence of the alcohol moiety ($-OH$) lessens the contribution to PM of the carbon atom to which it is attached (groups 1,2,3).
- The influence on PM formation of increasing chain length of a primary alcohol (by comparing groups 1,2,3).
- The influence on PM of moving an alcohol group from the end of a hydrocarbon chain to a mid-chain position (group 2).
- Composition of the PM formed from straight-chained primary alcohols, secondary aliphatic alcohols, and an alicyclic secondary alcohol (groups 1,2,3).
- Whether the carbon atom in the ester functional group ($R-CO_2-R'$) of ethyl acetate forms PM to different extent to its neighbouring carbon (group 4).
- Whether the carbon atoms in the phenyl group of toluene contribute to PM in the same quantities as the methyl group, and whether the ' α '-position (toluene- α - ^{13}C) contributes to PM differently than other phenyl carbon atoms (group 5).

2.2. Generation of particulate matter

PM has been generated under pyrolytic conditions in a tube reactor, in the temperature range 1200–1450 °C. Figure 2 shows a schematic of the experimental facility. This consisted of a nitrogen carrier gas feeding system (1,2,3), hydrocarbon vaporiser (5), static mixer (7), reactor tube (9) and PM collection and analysis system (10).

Nitrogen was used as a carrier gas with a flow rate of 20 L/min for all experiments, metered by a mass flow controller (2). The oxygenated compounds and hydrocarbon molecules used as fuels were injected into the nitrogen carrier stream at a fixed concentration of 10,000 ppmv, diluted in the nitrogen. Liquids were introduced into the nitrogen carrier stream through a vaporiser system (5,6), which was located approximately 200 mm upstream of the inlet to the tube reactor (9). A mechanically driven syringe (4) fed the fuel molecules at a known flow rate through a stainless steel capillary into the heated stainless steel vaporiser tube (5,6) packed with borosilicate glass beads (3 mm diameter) so that the vapour could be entrained by the nitrogen carrier gas. The vaporiser was heated by a tape heater (6) surrounding the pipe packed with borosilicate beads. In order to avoid condensation of the vapour, the nitrogen gas was heated by a PID controlled heater (3) to 200 °C; the vaporiser (5,6) was maintained at 200 °C by a separate PID. After the introduction of the fuel into the nitrogen stream, the combined stream passed through a static mixer (7), packed with 8 mm stainless steel ball bearings, positioned at the inlet of the reactor; the mixer ensured a homogenous mixture at the reactor inlet. The temperature of the static mixer was monitored by a type K thermocouple to ensure that the temperature was maintained above 180 °C.

The 1440 mm long, 104 mm diameter tube reactor (9) was positioned vertically in an electric furnace. A length of about 600 mm of the reactor tube had a heated zone, which was assumed to have longitudinally uniform temperature. The furnace was heated electrically with a PID control system monitoring the 600 mm heated section to the desired temperature in the range (1200–1450 °C). The longitudinal temperature profile of the reactor tube heated section was measured using a type B thermocouple. The gas residence time in the reactor, defined as the reaction zone volume divided by the gas flow rate, varied with temperature (e.g. 1.2 s at 1200 °C) but was always within the laminar flow regime.

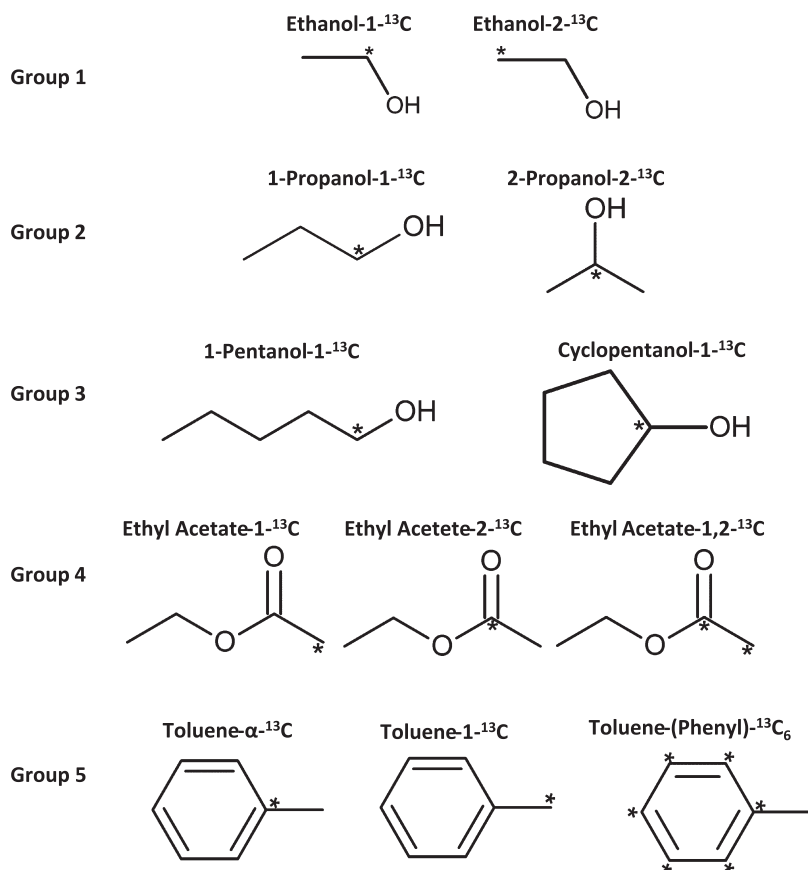


Fig. 1. Nomenclature and structure of ^{13}C labelled molecules. * Indicates the position of the ^{13}C label.

Samples of PM were collected at the exit of the reactor tube by means of thermophoresis onto a borosilicate glass plate. The PM was removed from the glass with a stainless steel spatula, and transferred into borosilicate glass vials and immediately frozen to $-20\text{ }^{\circ}\text{C}$, until it was required for analysis.

2.3. Sample analysis by EA-IRMS

The levels of ^{13}C enrichment in the prepared compounds used in this study are very low, still within the natural abundance variability range for ^{13}C in the natural environment on Earth (which is around 1%). Because of this elemental analyser isotope ratio mass spectrometry (EA-IRMS) methods were used to follow the ^{13}C tracer from the chosen fuel compounds to the particulate matter produced by a pyrolysis process described above.

When ready for isotope ratio mass spectrometric analysis, the samples of PM were transferred to small tin capsules, which are a standard mean of introducing solid samples to an elemental analyser. Tin capsules were loaded with the equivalent of $70 \pm 5\ \mu\text{g}$ of carbon (weighed using Mettler Toledo, XP6 micro-balance) in the case of all solid samples tested. The capsules were folded and compacted to seal in the sample so as to exclude atmospheric air. A similar method was also used for the measurement of the isotopic composition of the parent fuel from which the PM was formed. Samples of liquid fuels required more sensitive handling than samples of PM, due to their volatility. For that reason, a procedure to minimise liquid sample evaporation in the preparation process was used. Short lengths ($\sim 3\text{ mm}$) of Pyrex glass capillary tubes were used to collect liquid hydrocarbon samples by capillarity. The capillaries were then immediately transferred to a smooth-walled tin capsule and enclosed using a capsule sealing press.

All of the PM samples and associated standards were loaded into the carousel of an autosampler and analysed by means of EA-IRMS. At regular intervals the tin capsules were dropped into the combustion furnace of the elemental analyser (Thermo Finnigan, Flash EA, 1112 series) where samples are combusted at $1000\text{ }^{\circ}\text{C}$ in the presence of oxygen, and CO_2 is produced. Using a helium carrier gas, this CO_2 is then introduced to an online isotope ratio mass spectrometer (DELTA XP, Thermo Fisher Corporation).

Isotopic ratio data measured by IRMS instrumentation is reported as delta values (in permil units, ‰), defined as the relative difference between the $^{13}\text{C}/^{12}\text{C}$ ratio in the sample with respect to an international reference material (Eq. (1)). The international reference material for carbon isotope analysis is the Pee Dee Belemnite (PDB). For the purpose of calibration and correction for instrument artefacts three isotopically certified standards IAEA-CH7, USGS24, and IAEA-C6 ($\delta^{13}\text{C}$ -32.15 , -16.05 , and -10.80 respectively) were measured together with liquid and solid samples. A duplicate of each was run at the beginning and end of each batch of samples (typically 100 capsules). Following every 10 samples, two USGS24 (graphite) standards were run, and used to identify and correct for any drift in the instrument. The standards are also used to evaluate errors associated with measurement, an error analysis can be found in Appendix B. Batches of liquid samples were measured separately; these batches were generally smaller and USGS24 was run more regularly (every 5 samples). An automated sampler was not used for liquid samples, each sample was prepared immediately before analysis and manually submitted for analysis, in order to avoid loss of sample through evaporation.

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

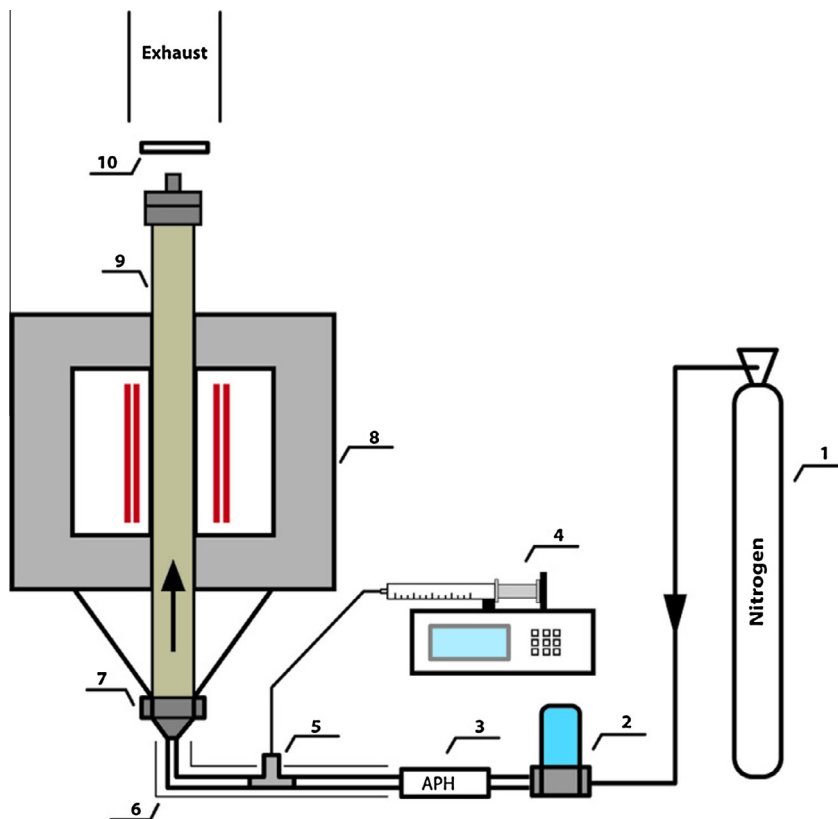


Fig. 2. Experimental rig for liquid hydrocarbon pyrolysis and sample collection. (1) Nitrogen cylinder. (2) Mass Flow Controller. (3) Air process heater. (4) Syringe pump. (5) Vaporiser. (6) Insulated and heated section of pipe. (7) Static mixer. (8) Tube Furnace. (9) Alumina reactor tube. (10) Borosilicate glass collecting disc.

2.4. Interpretation of isotope abundance data

As described in the sections above, we measured the isotopic composition for all of native and labelled compounds used as fuels ($\delta^{13}C_F$) and the particulate matter derived from them ($\delta^{13}C_{PM}$) at a range of temperatures. For each labelled compound and derived PM we calculated the difference in isotopic composition between the labelled and the native versions called $\Delta(F)$ and $\Delta(PM)$ as follows:

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

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

where the (*) refers to the labelled fuel or the PM derived from it, and the (n) refers to the 'native', unlabelled fuel or PM derived from it.

We also calculate the parameters Δ_{max} and $F_{labelled}$ according to Eq. (4) and (5) as follows:

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

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

where $n_{labelled}$ represent the number of carbon atoms labelled and n_{total} represents the total number of carbon atoms within the chemical compound used as fuel. The origin and significance of these two parameters is described in detail in Appendix A. The parameter Δ_{max} represents the maximum enrichment that could be reached by the chemical compound used as fuel if all its carbon atoms would be equally enriched by the addition of a quantity of a tracer 100%

^{13}C at all its carbon atoms. The parameter $F_{labelled}$ represents the contribution fraction of the labelled C atom in the fuel to PM formation. The product $F_{labelled} \times 100$ gives the % contribution of the labelled C atom to PM. A table containing the measured delta values, and calculations applied to these is also supplied in Appendix A.

3. Results

Figure 3, shows the contribution of the labelled carbon in the fuel to PM. For the series of fuels tested ^{13}C labelled carbon atoms in the molecules have been assigned letters in order to aid the following explanation. In the case of ethanol, it is clearly seen that the OH carbon, shown as "a" in Fig. 3, contributes much less to the overall mass of PM compared to the methyl-carbon (b), calculated to be approximately 27% and 68% respectively. Since the measurements of the individual contributions from the OH and the methyl carbon atoms to the overall PM were made independently, including experimental error, the results are found to corroborate by totalling close to 100%. Ethanol-1- ^{13}C was tested at various levels of ^{13}C enrichment and it was found that the result is consistent regardless of enrichment. Figure 3 also shows, for of all of the alcohols tested, the carbon adjacent to the OH group contributed, on average, less to the PM than the other carbon atoms in the molecule.

Additionally, Fig. 3 also shows that carbon "c" in 1-propanol-1- ^{13}C contributes less than the carbon atom "d" in 2-propanol-2- ^{13}C . That is, when the OH group is moved from the end of the propanol chain to the central carbon atom, then the contribution of the OH carbon atom increases somewhat; even so, the contribution of the OH carbon atom in both propanol structures remains low (16% compared to 22%). Turning now to pentanol and cyclopentanol, Fig. 3 shows that when the -C-OH

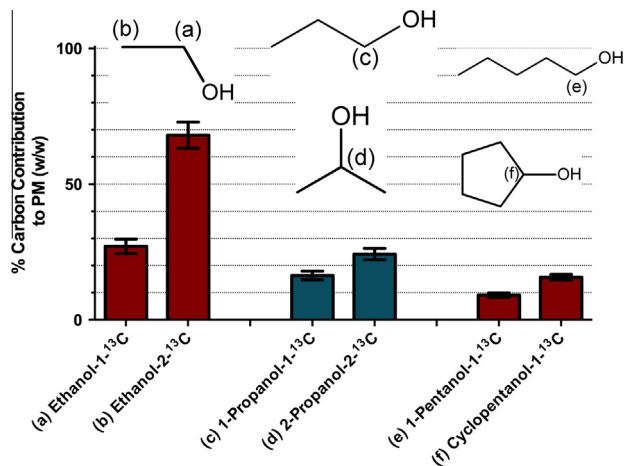


Fig. 3. Percentage contribution by mass to PM from labelled positions in a series of alcohol containing hydrocarbons. Samples were generated by pyrolysis at 1300 °C. Error bars represent the standard deviation of 3–6 measurements.

functional group is incorporated into cyclopentanol, rather than pentanol, the conversion rate of the carbon atom increases somewhat, but, again, the contribution of the –OH carbon atom in PM remains low at roughly 16%.

Considering now ethyl acetate in Fig. 4, it can be seen that the ester bond in the ethyl acetate has a strong influence over the carbon atom “g”, which is bonded to two oxygen atoms. The carbonyl position (g) was found to contribute a negligible amount of carbon to PM. The figure also shows that the carbon atom at the end of the chain (h) contributes 32% of the PM carbon mass. Figure 4 also shows the result for the combined contribution of two ¹³C tagged carbon atoms (both labelled “i” in the figure) for ethyl acetate-1,2-¹³C. Note that this combined contribution of the two tagged carbon atoms at positions “i” is equal to the PM arising from the carbon atom at position “h” alone (the reader is reminded that the carbon atom “g” did not show any significant conversion to PM). This is a significant observation and it confirms the result

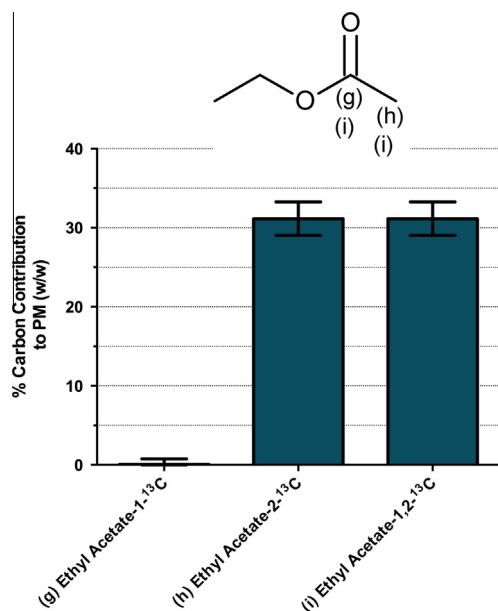


Fig. 4. The percentage contribution by mass to PM from tagged positions is shown for ethyl acetate. Samples were generated by pyrolysis at 1300 °C. Error bars show error based on the standard deviation of 3 measurements.

obtained for position “g”; reinforcing the finding that contribution of carbon “g” is negligible, regardless how the ¹³C isotope labelling test is carried out. Buchholtz et al. [19] also observed that the ester group contributes negligibly to PM.

Figure 5 shows that all three investigated permutations of tagging toluene (j,k,l) result in similar contributions to PM (~12% each carbon atom). From the contributions measured, it can be seen that PM is not formed preferentially from either *phenyl* or *methyl* carbon atoms.

Finally, Fig. 6 shows results from a set of tests, which were carried out in order to evaluate whether the results above are affected by pyrolysis temperature. The results shown in this figure suggest that, in the case of ethanol labelled, at either the OH or the methyl carbon, the percentage conversion from either position remains almost insensitive to temperature from 1200 to 1450 °C. This was also found to be true for all of the other molecules tested including toluene.

Isotope measurements of PM formed from the unenriched ‘base-line’ fuels at various temperatures show negligible changes in ¹³C conversion rates. This indicates that at the high temperatures used,

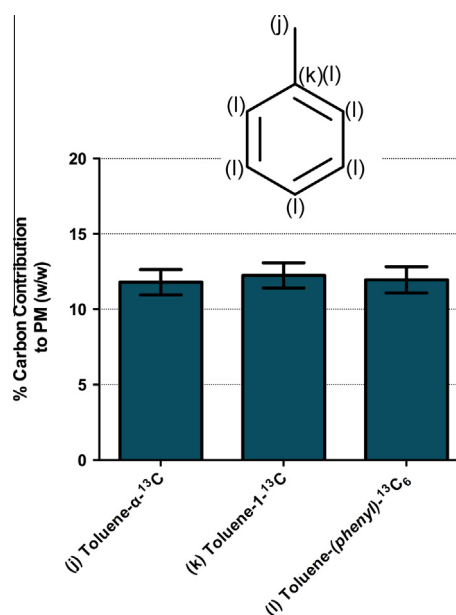


Fig. 5. Percentage contribution by mass to PM from labelled positions within toluene. Result of toluene-(phenyl)-¹³C (l) is given on a per-carbon atom basis. Samples were generated by pyrolysis at 1300 °C.

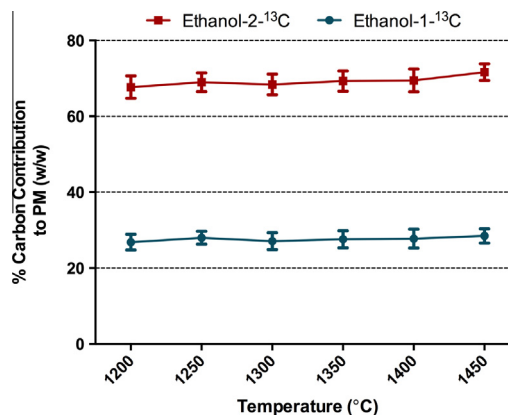


Fig. 6. Percentage contribution by mass to PM is shown in the temperature range 1200–1450 °C, from the measurements of both tagged positions in ethanol.

kinetic isotope effects specific to the ^{13}C –C bond are negligible, and that chemical effects of the carbon bond dominate ^{13}C conversion. If ^{12}C formed PM preferentially compared to ^{13}C , for example, at lower temperatures, then as temperature rises one might expect a drift towards ^{13}C ‘heavier’ PM, caused by gradually increasing reactivity of ^{13}C .

4. Discussion

If carbon atoms within an organic molecule were equally likely to contribute to PM, then the isotopic composition of the PM would be identical to the measurement of isotope ratio in the parent fuel. It has been shown that this is not the case, for a range of oxygenated molecules, where carbon atoms contribute differently depending on the identity of the neighbouring moiety. Carbon atoms which neighbour oxygen atoms convert considerably less to PM.

The result from ethanol showed that 68% of PM from ethanol arose from the methyl-position, and a similar result was also found by an earlier study of PM formed from ethanol in a Bunsen flame, using a ^{14}C radiotracer technique, where a carbon conversion ratio of 2:1, methyl-to-hydroxyl carbon, was reported [18]. We also show that the ester group (R–CO₂–R') from ethyl acetate has a negligible contribution to the overall mass of PM produced, indicating that the carbon atom is converted to CO₂ directly rather than to PM, which has been predicted by the modelling studies conducted by Mueller et al. [22]. Significantly, in practical terms, this indicates that ester group carbon atoms are not available for oxidation and energy release during a combustion process.

The temperature (in the range 1200–1450 °C) at which PM was generated did not greatly affect the isotopic composition measured for the PM. Changes in the isotopic signature might have been expected at different pyrolysis temperatures, as the temperature could shift the molecular fragmentation patterns. Experimental and modelling investigations into the pyrolysis of toluene [23] suggest that there is minimal decomposition of toluene into phenyl and methyl fragments over this temperature range; instead, precursors of particulates and polycyclic aromatic hydrocarbons (PAHs) are predicted to form directly, incorporating the phenyl and the methyl group. However, our measurements concern the overall conversion of carbon atoms to PM, and inevitably conversion from different carbon containing fragments may occur at different stages of PM formation.

In part, ^{13}C labelling techniques have not been used previously in pyrolysis or combustion research due to high cost of single-component ^{13}C labelled compounds. Ferguson's implementation of ^{13}C labelling, previously mentioned, used levels of ^{13}C enrichment which are well outside the natural abundance of isotopes for which IRMS spectrometers are generally used [14]. Laboratories that normally carry out research within the natural abundance of isotopes are reluctant to use highly enriched isotopic compounds because this poses a risk of contamination of the IRMS instrumentation from exposure to levels greatly in excess of natural abundance. Furthermore, if high levels of ^{13}C enrichment are used for studies such as this, it could make the fuel for flame or engine tests prohibitively expensive, as a substantial amount of fuel is normally required for the necessary quantity of PM to be collected for analysis. Therefore, the use of the high precision isotope ratio mass spectroscopy methods could become an additional experimental tool in combustion research because of the very small amounts of ^{13}C labelled compounds that are required, which could mean that ^{13}C labelling of fuels for research purposes could become more widely used.

An alternative to ^{13}C labelling is using ^{14}C , a long-lived radioisotope. The natural abundance of ^{14}C is 1.2 parts to 10¹² in atmospheric CO₂, and in petroleum the abundance is 1 part in

10¹⁵ due to the thousands or millions of years that ^{14}C had decayed underground. Small quantities of ^{14}C labelled molecules can be used to enrich the isotope abundance of crude oil derived fuels to that of present day ^{14}C natural abundances [19]. Accelerator mass spectrometry (AMS) is a highly sensitive method that can be used to accurately measure ^{14}C abundance. Although ^{14}C synthesised compounds tend to be much more expensive than their ^{13}C analogues, even smaller quantities of ^{14}C are required for enrichment.

By comparison to ^{14}C measurements, which have a negligible $^{14}\text{C}/^{12}\text{C}$ background, ^{13}C has a considerably greater $^{13}\text{C}/^{12}\text{C}$ background. But despite the high background quantities of ^{13}C in nature (~1%), the precision of the isotope ratio measurements, and the technique itself (measurements represent only relative differences between the isotopic composition of the compound of interest relative to a standard) make it suitable for tracer studies. Some benefits of ^{13}C labelling techniques include:

- (1) ^{13}C measurements using IRMS are nowadays routine and have been used widely for geochemical applications.
- (2) There is a fairly wide availability of commercially produced ^{13}C labelled compounds, reducing the need for custom synthesis.
- (3) Increased practicality, by avoiding procedural precautions necessary for working with radioactive carbon-14.
- (4) ^{13}C measurements by IRMS are less expensive than ^{14}C measurements by AMS; IRMS is generally about 50–100 times cheaper.

5. Conclusions

To conclude, this study details a ^{13}C labelling technique that has been successfully applied to tracking carbon atoms from individual oxygenated and hydrocarbon molecules to PM formation in a reactor at pyrolysis temperatures of 1200–1450 °C. This provides direct experimental evidence of the behaviour of different chemical groups in a molecule, during pyrolysis, and could also be applied to combustion research in an oxidising environment. It is a promising avenue for aiding interpretation and validating results of modelling studies and can also help the interpretation of experimental results from combustion studies. Using this labelling technique it is shown that carbon atoms within molecules contribute differently to PM formation, depending on the identity of their neighbouring moiety. It was found that oxygen-containing functional groups have a significant influence on the formation of particulates, partly through a reduction in the contribution of adjacent carbon atoms to PM.

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Appendix A. Example of calculation to derive the contribution of the labelled carbon atom to the formation of particulate matter, based on stable isotope measurements

For simplicity we are describing the calculation protocol for the case of ethanol used as a fuel. For all other molecules the protocol is identical, and the molecules are treated as being made of two

components: the labelled carbon atom being one component and all the other carbon atoms being the second component.

Ethanol is a molecule containing two carbon atoms. In this molecule C_1 is the carbon atom bonded to the functional group (OH) and C_2 is the methyl carbon. When adding a ^{13}C labelled ethanol tracer 100% labelled at one carbon atom, only one carbon atom in the resulting fuel ethanol will be isotopically enriched in ^{13}C , and the enriched site is appropriately named.

When calculating the contribution of a carbon atom from the fuel (in this example the fuel is ethanol) to the production of particulate matter, we will always compare the behaviour of a labelled fuel with the 'native' (unlabelled) counterpart.

For the 'native' ethanol (before the addition of a labelled compound) we measured an overall $\delta^{13}\text{C}_{E_n}$ of -27.8 permil, and we will assume that the isotopic composition (delta values) of the individual carbon atoms in this fuel is identical to the overall composition of this fuel (i.e. $\delta^{13}\text{C}_{E_n} = \delta^{13}\text{C}_{C_1} = \delta^{13}\text{C}_{C_2} = -27.8$ permil). In reality the two carbon atoms in the ethanol molecule probably have slightly different isotopic compositions, but these cannot be measured individually. Thus assuming that both carbon atoms have the same isotopic composition and equal to the overall composition of this compound is the best assumption one can make.

For the case of the ethanol enriched (labelled) to an overall delta value of $\delta^{13}\text{C}_{E_l} = -6.1$ permil and labelled at C_2 , the delta value of C_2 can be calculated using Eq. (A1), knowing that each carbon atom contributes equally to the bulk (overall) isotopic composition of this labelled fuel and assuming that C_1 has an isotopic signature equal to -27.8 permil (this carbon atom is unaffected by the labelling):

$$\delta^{13}\text{C}_{E_l} = [(\delta^{13}\text{C}_{C_1}) * (0.5)] + [(\delta^{13}\text{C}_{C_2}) * (0.5)] \quad (\text{A1})$$

We can then calculate the isotopic composition of the C_2 position, knowing that this labelled ethanol has a bulk isotopic composition of $\delta^{13}\text{C}_{E_l} = -6.1$ permil and that each carbon atom contributes equally to its bulk isotopic composition. For simplicity, we will call the unenriched ethanol E_n and the labelled ethanol we mentioned above as E_l . Following this calculation we retrieve a delta value for the C_2 position in this labelled ethanol to be $\delta^{13}\text{C}_{C_2} = +15.6$ permil.

Using the isotopic delta values for the individual carbon atoms in E_n and E_l , and knowing the isotopic compositions of the particulate matter derived from these two ethanol sources, we can calculate the contributions of each carbon atom (C_1 and C_2)

from the ethanol molecule to the PM formation. We do not expect the isotopic signatures of the carbon atoms in the fuels to transfer to the particulate matter without being altered by potential fractionation paths, therefore we need to take into account the fractionation factors when calculating the isotopic signatures of C_1 and C_2 that gets incorporated into the PM (this means that the isotopic signatures of C_1 and C_2 that form PM might not be identical to their original signatures while in the ethanol, but they will be proportional with the signatures from the starting fuel).

The fractionation factors (describing the partitioning of an isotopic species between the starting and the end material, in our case ethanol and PM derived from it) for C_1 and C_2 are:

$$\alpha_{C_1} = \frac{1000 + (\delta^{13}\text{C}_{C_1})_{E_n}}{1000 + (\delta^{13}\text{C}_{C_1})_{PM_n}} \quad (\text{A2})$$

and

$$\alpha_{C_2} = \frac{1000 + (\delta^{13}\text{C}_{C_2})_{E_n}}{1000 + (\delta^{13}\text{C}_{C_2})_{PM_n}} \quad (\text{A3})$$

From Eqs. (A2) and (A3) we can calculate the $(\delta^{13}\text{C}_{C_1})_{PM_n}$ and $(\delta^{13}\text{C}_{C_2})_{PM_n}$ as a function of the fractionation factor and use these isotopic signatures in the mass balance equation that can be written for the PM derived from the E_n , Eq. (A4). The same fractionation factors can be written for the case of the ^{13}C labelled ethanol and derived PM, from which we can calculate $(\delta^{13}\text{C}_{C_1})_{PM_l}$ and $(\delta^{13}\text{C}_{C_2})_{PM_l}$ and use them in the mass balance equation that can be written for the PM derived from the E_l , Eq. (A5).

For the PM derived from E_n we can write:

$$\delta^{13}\text{C}_{PM_n} = a * \left(\frac{1000 + (\delta^{13}\text{C}_{C_1})_{E_n}}{\alpha_{C_1}} - 1000 \right) + b * \left(\frac{1000 + (\delta^{13}\text{C}_{C_2})_{E_n}}{\alpha_{C_2}} - 1000 \right) \quad (\text{A4})$$

For the PM derived from E_l we can write:

$$\delta^{13}\text{C}_{PM_l} = a * \left(\frac{1000 + (\delta^{13}\text{C}_{C_1})_{E_l}}{\alpha_{C_1}} - 1000 \right) + b * \left(\frac{1000 + (\delta^{13}\text{C}_{C_2})_{E_l}}{\alpha_{C_2}} - 1000 \right) \quad (\text{A5})$$

Table A1

Experimental results and calculated parameters, from samples generated at 1300 °C.

Fuel ID	Molecule name	$\delta^{13}\text{C}$ Fuel	$\delta^{13}\text{C}$ PM	$\Delta(F)$	$\Delta(\text{PM})$	Δ_{max}	F
1	Native Ethanol	-27.83	-31.19	-	-	-	-
2	Ethanol-2- ^{13}C	-6.14	-1.53	21.69	29.66	43.38	0.68
3	Ethanol-1- ^{13}C	-17.16	-25.75	10.67	5.44	21.34	0.25
4	Ethanol-1- ^{13}C	-6.06	-19.40	21.77	11.79	43.54	0.27
5	Ethanol-1- ^{13}C	3.10	-14.15	30.93	17.04	61.86	0.28
6	Native 1-Propanol	-30.80	-33.13	-	-	-	-
7	1-Propanol-1- ^{13}C	-7.20	-21.54	23.60	11.59	70.80	0.16
8	Native 2-Propanol	-28.06	-29.70	-	-	-	-
9	2-Propanol-2- ^{13}C	-4.50	-13.83	23.56	15.87	70.68	0.22
10	Native Ethyl Acetate	-30.25	-33.45	-	-	-	-
11	Ethyl Acetate-1- ^{13}C	-8.21	-33.25	22.04	0.20	88.16	0.00
12	Ethyl Acetate-2- ^{13}C	-7.86	-5.18	22.39	28.27	89.56	0.32
13	Ethyl Acetate-1,2- $^{13}\text{C}_2$	-6.73	-18.69	23.52	14.76	47.04	0.31
14	Native 1-Pentanol	-28.45	-31.29	-	-	-	-
15	1-Pentanol-1- ^{13}C	-3.53	-20.85	24.92	10.44	124.60	0.08
16	Native Cyclopentanol	-24.31	-24.75	-	-	-	-
17	Cyclopentanol-1- ^{13}C	4.30	-2.26	28.61	22.49	143.05	0.16
18	Native Toluene	-24.46	-24.35	-	-	-	-
19	Toluene-1- ^{13}C	0.94	-2.58	25.40	21.77	177.80	0.12
20	Toluene-(phenyl)- $^{13}\text{C}_6$	-0.23	-4.08	24.23	20.27	28.27	0.12 ^a
21	Toluene-a- ^{13}C	0.32	-3.89	24.78	20.46	173.46	0.12

^a Per carbon atom.

In Eqs. (A2), (A3), (A4), (A5) we used the following notations:

$\delta^{13}C_{PM_n}$ and $\delta^{13}C_{PM_l}$ = the measured delta values for the PM derived from E_n and E_l respectively (for the examples we are working on these values are –31 permil and –1.5 permil respectively) – see Table A-1.

$(\delta^{13}C_{E_n})$ and $(\delta^{13}C_{E_l})$ = the measured delta values for the ‘native’ and labelled ethanol (for the examples we are working on these values are –27.8 permil and –6.1 permil respectively) – see Table A-1.

a and b = contributions of C_1 and C_2 to the PM formation. Note that regardless from which ethanol fuel PM is derived, the proportions in which C_1 and C_2 contribute to PM are the same. Also $a + b = 1$, i.e. the total mass of the PM formed from any ethanol fuel is made up of contributions from C_1 and C_2 .

α_{C_1} = the fractionation factor describing the distribution of ^{13}C for C_1 between the starting and the ethanol and PM derived from it. α_{C_2} = same as above but for C_2 .

$(\delta^{13}C_{C_1})_{E_n}$ and $(\delta^{13}C_{C_1})_{E_l}$ = the delta value of C_1 in the E_n and E_l respectively (both equal to –27.8 permil, as the tracer was added to C_2 in E_l).

$(\delta^{13}C_{C_2})_{E_n}$ and $(\delta^{13}C_{C_2})_{E_l}$ = same as above for C_2 (equal to –27.8 permil and +15.6 permil respectively, as mentioned above).

$(\delta^{13}C_{C_1})_{PM_l}$ and $(\delta^{13}C_{C_1})_{PM_n}$ = the delta value of C_1 in the PM derived from E_l and E_n respectively.

$(\delta^{13}C_{C_2})_{PM_l}$ and $(\delta^{13}C_{C_2})_{PM_n}$ = the delta value of C_2 in the PM derived from E_l and E_n respectively.

Using Eqs. (A4) and (A5) we can then calculate

$$\Delta(PM) = \delta^{13}C_{PM_l} - \delta^{13}C_{PM_n} \quad (A6)$$

from which we can calculate a and b . This is possible because we know (i) $a + b = 1$, (ii) the fractionation factors α_{C_1} and are the same for the formation of PM from E_n and from E_l , (iii) $(\delta^{13}C_{C_1})_{E_n} = (\delta^{13}C_{C_1})_{E_l} = -27.8$ permil (C_1 isotopic composition is unaffected by the addition of the ^{13}C label at C_2 in E_l , (iv) the term containing α_{C_1} cancels out while solving this equation, (v) α_{C_2} can be assumed as equal to 1, at temperatures above 1000 °C and (vi) $(\delta^{13}C_{C_2})_{E_l} = +15.6$ permil and $(\delta^{13}C_{C_2})_{E_n} = -27.8$ permil as mentioned above.

From solving Eq. (A6) we find

$$b = \frac{\Delta(PM)}{(\delta^{13}C_{C_2})_{E_l} - (\delta^{13}C_{C_2})_{E_n}}$$

For the example we discussed so far, the value for $b = 0.68$. This means that C_2 (the labelled carbon atom in this example) has a 68% contribution to the formation of PM when ethanol is used as a fuel.

The same approach can be applied for any of the molecules considered in this study and in doing so we noticed that the denominator in the calculation of b is equal to the maximum enrichment one could expect if all the carbon positions in the fuel molecule are enriched to the same amount. This also means that one does not have to calculate the isotopic composition of the enriched position in any given molecule used as fuel; thus for simplicity, we have then calculated the term Δ_{max} as:

$$\Delta_{max} = \frac{\Delta(F)}{n_{labelled}} * n_{total} \quad (A7)$$

where $n_{labelled}$ represents the number of labelled carbon atoms of the organic compound used as fuel, n_{total} represents the total number of carbon atoms in the molecule of the compound used as fuel and $\Delta(F)$ represents the difference in the isotopic composition of the labelled compound ($\delta^{13}C_{F_l}$) used as fuel and the same compound prior to the addition of the ^{13}C tracer ($\delta^{13}C_{F_n}$), thus

$$\Delta(F) = \delta^{13}C_{F_l} - \delta^{13}C_{F_n} \quad (A8)$$

Generalising from the example considered for the case of ethanol, we define a term, which we call F , representing the fractional contribution to the formation of PM of the labelled carbon atom(s) from the fuel molecule, as follows:

$$F = \frac{\Delta(PM)}{\Delta_{max}} \quad (A9)$$

The contribution to the formation of PM for the rest of the unlabelled carbons is equal to $1 - F$.

Table A-1 presents a summary of the isotopic compositions measured for all native and labelled fuels considered in this study as well as the parameter F , representing the contribution of the labelled carbon atom in the fuel to the formations of PM.

Appendix B. Error analysis

There are several sources of error to be considered. Generally, the systematic and random errors associated with measurements by IRMS of $\delta^{13}C$ were negligible, as repeat measurements of standard reference material showed precise repeatability ($\sigma \ll 0.1$, in all duplicate measurements of USGS24); this also indicates sample size effects to do with variability in the weighed samples was also negligible. Predictions of δ -values for samples were back calculated from values obtained from standard reference material using a linear fit ($R^2 \geq 0.994$, in all batches). For liquid samples, there was greater variability in the measurements if $\delta^{13}C$ ($\sigma = 0.3$, typically, but larger in more volatile liquids), this is likely due to $^{13}C/^{12}C$ fractionation, through evaporation, in some samples prior to measurement; isotopically ‘‘lighter’’ volatile compounds may evaporate more readily than ‘‘heavier’’ ^{13}C labelled ones; although this process is limited by capillary collection of liquids and immediate measurement, previously mentioned. There was less variability in the PM samples ($\sigma = 0.11$, average) than for the liquid samples, increased variability in PM samples in comparison to standard measurements may also be attributed to low levels of liquid fractionation prior to PM generation.

Error bars shown on graphs in this paper are based on the standard deviation of measurements; where calculations have been applied, the extreme values of the combined standard deviations have been used in calculation of the error bars.

Appendix C. Correction for background

The smooth-walled tin capsules used for liquid measurements were found to produce a very low intensity CO_2 peak while combusted in the elemental analyser, therefore corrections were applied to the results that were obtained using these capsules. For any given sample, the amplitude response from the sample can be calculated by subtracting the area of the peak recorded for the blank capsule from that of the measured sample and capsule together, Eq. (A10). Likewise, the isotopic ratio measured is influenced by the $\delta^{13}C$ of the blank capsule. Thus using the mass balance Eq (A11) we can calculate the $\delta^{13}C$ of the sample (Eq. (A12)):

$$Area_{sample} = Area_{measured} - Area_{blank} \quad (A10)$$

$$\delta_{measured} \times Area_{measured} = \delta_{sample} \times Area_{sample} + \delta_{blank} \times Area_{blank} \quad (A11)$$

$$\delta_{sample} = \frac{\delta_{measured} \times Area_{measured} - \delta_{blank} \times Area_{blank}}{Area_{sample}} \quad (A12)$$

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