

Spark combustion reactor for ^{13}C -carbon isotope enrichment analysis of gases

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A novel spark combustion reactor was designed, built, and utilized for quantitative ^{13}C -carbon isotope determination of highly enriched permanent gases. The analytical methodology developed is straightforward and begins by loading the reactor with hydrocarbon and oxygen using a steel gas manifold. High voltage is applied to the platinum electrode spark plug incorporated into the reactor, which rapidly converts hydrocarbon to carbon dioxide (and other products). Carbon dioxide species are then quantitated by quadrupole mass spectrometry. The primary reactor consists of a three-way stainless steel tee, plus the following components connected to threaded ports: (1) a platinum electrode spark plug sealed with a Viton O ring, (2) a steel gas storage cylinder, and (3) a manual bellows valve terminated with a VCO type connector. Making use of the spark combustion reactor, the ^{13}C -carbon fraction of highly enriched $^{13}\text{CH}_4$ was measured to be ≥ 99.5 at. % ^{13}C . This portable, static reactor permits determination of the $^{13}\text{C}/^{12}\text{C}$ isotope fraction for permanent gases utilizing mass spectrometric detection. The analytical system presented is relatively rapid (due to spark ignition), straightforward, and flexible (applicable to hydrocarbon gases using various gas detectors). Its limitation in performance for ^{13}C isotope work is probably due to carbon embedded in the reactor interior. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544089]

I. INTRODUCTION

A wide array of analytical instrumentation and methodology has been applied to quantitative ^{13}C -carbon isotope measurements. For the case of solid and liquid materials, various carbon–hydrogen analyzers have been developed based upon thermal combustion of hydrocarbon with oxygen in quartz cells. The coupling of such CH analyzers with gas chromatography/mass spectrometry (GCMS) permits ^{13}C -carbon isotope enrichment determination of the material.¹ Such experimental systems are relatively complex, inflexible, and expensive.

One significant challenge to measuring ^{13}C -carbon isotope enrichment in gas-phase materials is that of gas transfer and manipulation while avoiding contamination. Often, specialized pressure-vacuum manifolds are designed to handle gas reactants and products while also maintaining system integrity. Thus one possible approach to isotope analysis is to utilize a pressure-vacuum manifold to introduce analyte gas into a mass spectrometer and directly quantitate the ^{12}C -carbon and ^{13}C -carbon molecular ions. For gas-phase hydrocarbons, the latter approach can be complicated by ion fragmentation and proton transfer reactions.²

The present approach to measuring the ^{13}C -carbon isotope fraction of permanent gas started with the design of a robust, portable, electric spark combustion reactor to (partially) convert hydrocarbon to carbon dioxide. Since carbon dioxide contains no hydrogen, the complication of proton transfer reactions within a mass spectrometer is avoided. Previous methane–oxygen flow reactors have been fabricated,

for example, to investigate spark discharge characteristics³ and silent discharge oxidation.⁴ Special shock tube reactors have also been constructed to investigate methane–oxygen kinetics.⁵ Our experimental system incorporates a steel gas manifold, the spark reactor, and a process-gas, quadrupole mass spectrometer. The analytical methodology is straightforward and applicable to labeled ^{13}C gas-phase hydrocarbons.

II. EXPERIMENT

A. Spark combustion reactor

An isometric drawing of the device is presented in Fig. 1. Stainless steel fittings and valves were obtained from Cincinnati Valve and Fitting. Swagelok bellows valves with a working pressure limit of 1000 psi were used. Pressure gauges were equipped with steel Bourdon tubes (McDaniel Controls). Platinum electrode spark plugs were obtained from NGK (type 6120, gap of 1 mm). Two ceramic–metal joints in the spark plug were manually sealed with epoxy (Hardman general purpose, Harcros Chemicals). An electric spark [approximately 10 000 V (ac), 0.5 MHz] was applied to the plug by momentarily contacting the center plug post with a Tesla coil generator (Electro-Technic products, model BD-50E). A 0.5 in. FNPT tee (Cajon Inc.) was modified by tapping 14 mm threads to accept the plug. A spark plug was sealed to its reactor port by compression with either a Viton O ring [10.7 mm inner diameter (i.d.) \times 3.5 mm] or a flat copper gasket (14.5 mm i.d. \times 2 mm). The reactor internal volume was 0.05 l.

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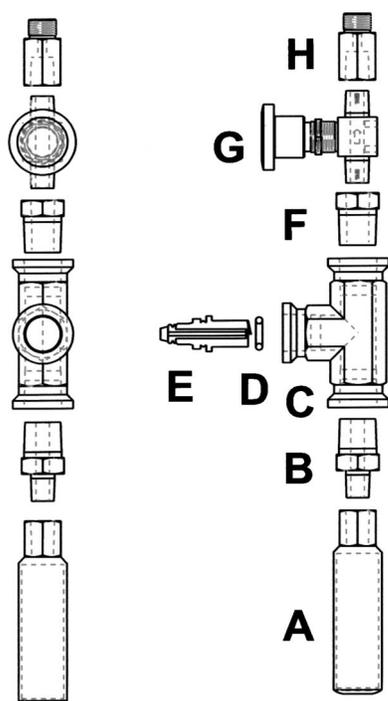


FIG. 1. Exploded drawing of the spark combustion reactor showing top and side perspectives. The reactor components are (A) 25 ml reactor cylinder with NPT port; (B) adapter 0.25–0.5 in. NPT port; (C) 0.5 in. NPT tee; (D) Viton O ring; (E) platinum electrode spark plug with M14-1.25 thread; (F) bushing 0.5–0.25 in. NPT port; (G) steel bellows valve with 0.25 in. NPT ports; (H) adapter 0.25 in. NPT to VCO port. Each NPT port connection is sealed with PTFE tape.

B. Gas manifold

A stainless steel gas manifold was designed and built at Isotec to handle vacuum and moderate pressures. The primary components of the gas manifold system are shown in Fig. 2 with the reactor attached. Construction of the system involved making threaded connections of several fitting types: NPT (National Pipe Taper) (wrapped with PTFE tape), VCO O ring compression, spark plug O-ring compression, and Swagelok tube compression. The assembled reactor/manifold was systematically checked to be gas tight by monitoring helium leak or dynamic vacuum measurements. Other major components not shown in Fig. 2 include the thermal conductivity vacuum gauge connected through “component Q” (Teledyne–Hastings model VT-6) and the 0.25 in. steel tube connected to “component S.” The latter steel tube is ultimately connected to the manifold vacuum pump (Leybold–Trivac model D4B). Functionally the manifold system enables dynamic vacuum, loading of reactants, spark ignition of reactants, and containment of pressurized products while avoiding contamination by air. Typically the manifold system (including the reactor) was dynamically evacuated to 15 mTorr using a mechanical pump.

C. Materials

Methane- ^{13}C was prepared at Isotec from a precursor that was 99.9 at. % ^{13}C . Ethylene- $^{13}\text{C}_2$ was prepared from a starting material with enrichment >99 at. % ^{13}C . Gas chromatography of the reactants was carried out using pulsed

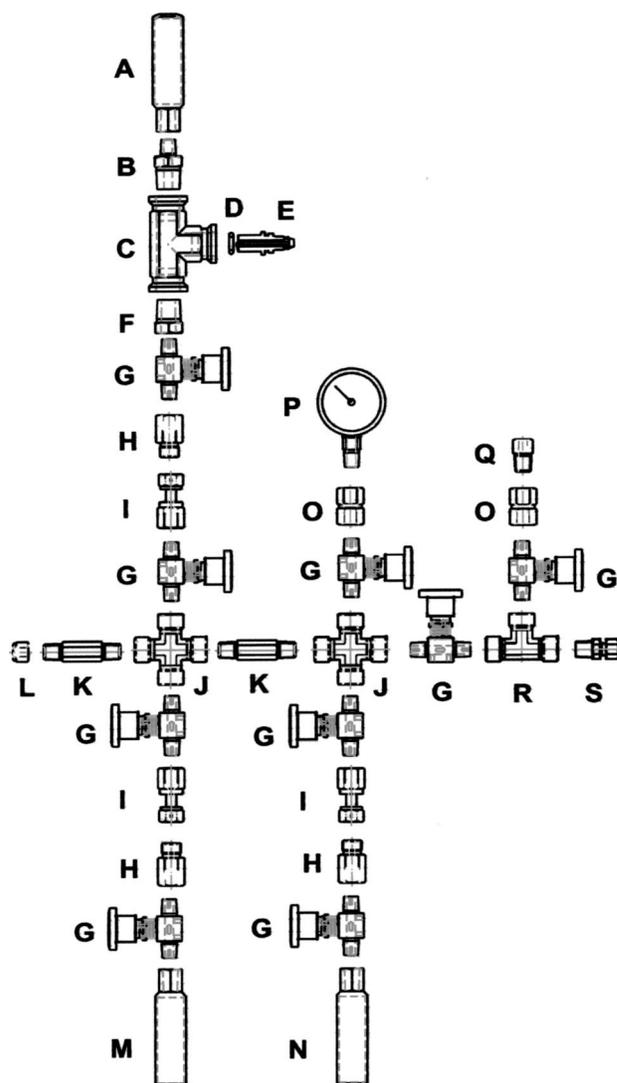


FIG. 2. Exploded drawing of the gas reactor-manifold system. The system components are (A) 25 ml reactor cylinder with NPT port; (B) adapter 0.25–0.5 in. NPT port; (C) 0.5 in. NPT tee; (D) Viton O ring; (E) platinum electrode spark plug with M14-1.25 thread; (F) bushing 0.5–0.25 in. NPT port; (G) steel bellows valve with 0.25 in. NPT ports; (H) adapter 0.25 in. NPT to VCO port; (I) adapter 0.25 in. VCO to NPT port; (J) 0.25 in. NPT cross; (K) 0.25 in. NPT hexagonal coupler; (L) 0.25 in. NPT cap; (M) methane- ^{13}C cylinder with NPT thread; (N) oxygen cylinder with NPT thread; (O) 0.25 in. NPT hexagonal coupler; (P) vacuum-pressure gauge with steel Bourdon tube; (Q) bushing 0.25–0.125 in. NPT for connection to the thermal conductivity vacuum gauge; (R) 0.25 in. NPT tee; (S) adapter 0.25 in. NPT to 0.25 in. Swagelok tube fitting for connection to the vacuum pump.

discharge helium ionization detection (GC-PDHID, Agilent model 6890A). The hydrocarbons were found to contain 50–100 ppm vol carbon dioxide (presumably >99 at. % ^{13}C). Oxygen gas (purity 99.998%) was obtained from Matheson Trigas and measured as containing less than 1 ppm vol natural abundance carbon dioxide.

D. Mass spectrometer

An Extrel Questor-III quadrupole mass spectrometer was used to determine isotope ratios. A gas-metering inlet system built in-house at Isotec was interfaced to the Questor-III source. This process-gas mass spectrometer was equipped

with open-source electron ionization at 100 eV, quadrupole mass filter (unit mass resolution), and electron multiplier detection. Vacuum background and product mass scans were obtained at 10 amu/s. Typically about 10^{-7} Torr combustion product was metered into the analyzer region for measurement.

E. Procedure

An outline of the experimental protocol follows. First, assemble the spark combustion reactor including the spark plug and gas seal (O ring). Sometimes the reactor was “conditioned” by loading it to 30 psia oxygen and applying voltage for about 15 min. Next the reactant cylinders and reactor were attached to the gas manifold system. The manifold system was evacuated to 15 mTorr back to the valve-isolated reactants. The manifold system was closed to dynamic vacuum, and then quickly filled with 15 psia methane- ^{13}C and 30 psia oxygen. At this stage, residual gas in the manifold was pumped out. It is important to confirm that the outer electrode of the spark plug is electrically grounded (**warning:** take appropriate action to shield the analyst from the reactor prior to ignition). Next momentarily apply the Tesla coil to the center spark plug electrode, and confirm the faint “ping” that indicates successful combustion. Detach the reactor from the manifold, and transfer it to the gas inlet system of the quadrupole mass spectrometer. Evacuate the mass spectrometer inlet system to its base pressure (for example, monitor the background signal at m/z 28), and measure the background signal from m/z 44 to 49. Carefully throttle the combusted product gas into the mass spectrometer, and again collect the sample signal from m/z 44 to 49.

F. Calculation of 13-carbon isotope enrichment

Computation of the $^{13}\text{C}/^{12}\text{C}$ isotope fraction was carried out by two techniques. First the ^{13}C fraction was estimated simply by calculating the (background corrected) ratio of the m/z 45 signal to the m/z (44+45) signal. Next the ^{13}C isotope fraction was computed by fitting the (background corrected) mass spectrometric signals from m/z 44 through 49. The fitting algorithm was a Simplex least squares search⁶ written in Visual Basic (version 6.0, Microsoft Inc). For our case of highly enriched hydrocarbon gases (>98 at. % ^{13}C) the two techniques gave similar results to 0.1 at. % ^{13}C . Minor amounts of ^{14}C isotope were estimated to be insignificant for the present calculations.

III. RESULTS AND DISCUSSION

The application of spark electric ignition to hydrocarbon combustion can be traced to Barsanti and Matteucci, who patented internal combustion engines that reacted coal–gas and air in a cylinder.⁷ Later, Bosch and Honold developed high voltage arc igniters that had stationary electrodes.⁸ Essentially, the spark combustion reactor is a static combustion bomb that utilizes spark plug ignition. Figure 1 gives an isometric view of the reactor that outlines its design. Reactor components were selected for high reliability and functionality. The spark plug itself incorporates platinum electrodes

to minimize fouling (which can occur since the reaction system starts at ambient temperature). It was discovered that the ceramic–metal joints in the plug require additional sealing in order to maintain useful vacuum. The spark plug gas seal to the reactor tee was also crucial to achieve vacuum, and this issue was addressed by compressing a fluorocarbon O ring between the plug and tee. Using only a rotary oil pump, the spark combustion reactor could be dynamically evacuated to about 10^{-2} Torr. An alternate spark plug gas seal consisting of a copper gasket gave similar ultimate vacuum.

The reactor unit was leak tested by directly attaching it to a gas chromatograph (GC-PDHID). Under dynamic vacuum, the reactor leak was <2 ppmv total air. Next the reactor itself was isolated to create internal static vacuum for 10 min, and the resultant air leak was measured to be ~50 ppm vol (this corresponds to <1 ppm vol carbon dioxide). When the reactor was utilized for hydrocarbon combustion, it typically required less than 1 min between isolating the reactor from vacuum and loading it to positive pressure with gas reactants. Thus the leakage of atmospheric carbon dioxide into the reactor during experimentation is estimated at <1 ppm vol.

The moderate size of this reactor (mass of 0.7 kg) allows portability, so it was easily interfaced to the multipurpose gas manifold shown in Fig. 2. With this design, the combustion process is decoupled from any specific detector. For the purpose of ^{13}C isotope fraction measurement, mass spectrometric detection was utilized to obtain the required data. However, one significant advantage of the spark reactor is the flexibility to carry out combustion (on the manifold) and later transfer it to the appropriate gas analyzer of interest. In addition, the reactor itself is compact, mechanically rugged, and designed for vacuum-pressure service.

The reactor was used to obtain ^{13}C – ^{12}C isotope measurements for various lots of methane- ^{13}C . Reactant pressures were loaded to favor combustion to carbon dioxide (methane) or carbon monoxide (ethylene). For methane, the quantitative isotope fraction was determined to be 99.6 at. % ^{13}C (precursor material 99.9 at. % ^{13}C). It was empirically found that the reactor required several combustion cycles to reach 99.6 at. % ^{13}C . This is probably the main limitation in performance of the present analytical approach. Since multiple sources of $^{12}\text{CO}_2$ exist, it is interesting to itemize them:

- (1) oxygen: measured to contain <1 ppm vol carbon dioxide;
- (2) methane- ^{13}C : measured to contain <100 ppm vol CO_2 ; it was synthesized from precursor material with isotope enrichment of 99.9 at. % ^{13}C ;
- (3) reactor leakage: measured steady-state air leakage under dynamic vacuum <2 ppm vol; measured leakage after 10 min static vacuum of 47 ppm vol air;
- (4) reactor body composition: steel 316L contains ≤ 0.03 mass % carbon;⁹
- (5) spark plug composition: platinum electrodes; epoxy filled ceramic–metal joints; stainless steel; ceramic; other materials.

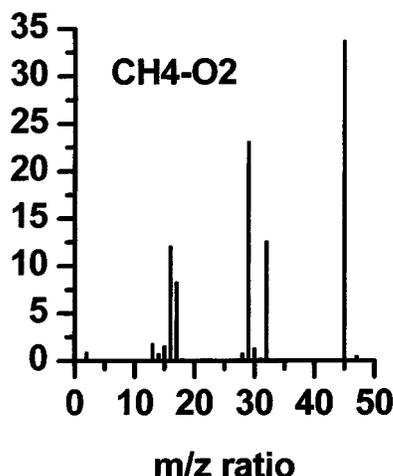


FIG. 3. Background-corrected mass spectrum signals for product gas from spark ignition combustion of methane- ^{13}C and oxygen (in arbitrary units).

Mass spectrometric results show that the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio monotonically rises (to a maximum value) as the reactor is repeatedly combusted and reloaded. Considering the aforementioned sources of $^{12}\text{CO}_2$, the total concentration available from oxygen, methane- ^{13}C , and air leakage is likely <5 ppm vol. All of this evidence indicates that some $^{12}\text{CO}_2$ from the reactor is generated during combustion itself. The suspect sources of oxidizable, natural abundance carbon are the reactor interior walls and spark plug surfaces.

An interesting design aspect of the experimental system is the peak reactor pressure. Since the reactor functions as a static combustion bomb, it was designed to withstand limited rises in pressure and temperature. With regard to this, a mechanical pressure gauge was directly installed on the reactor to estimate peak pressure for methane-oxygen combustion. With the reactor initially at ambient temperature and 45 psia, the combustion pressure was observed to peak near 135 psia on the gauge. In general the reactor body consists of 316L stainless steel of minimum wall thickness, 2 mm. The primary reactor valve incorporates a welded body-bonnet seal for effective gas containment. The electric igniter is a robust automotive-racing spark plug. Previous numerical simulations of methane-oxygen ignition¹⁰ (initial $\text{CH}_4\text{-O}_2$ mole ratio 1:10, pressure 1.0 bar, temperature 27 °C) indicate that the minimum local temperature for induced ignition is ~ 1600 °C, the latter value apparently achievable by spark discharge.

The spark combustion reactor generated a product profile for methane-oxygen typified in Fig. 3. Detected ions of interest in the mass spectrometer include H_2^+ (m/z 2), O_2^+ (m/z 16), $^{13}\text{CH}_4^+$ (m/z 17), HO^+ (m/z 17), H_2O^+ (m/z 18), N_2^+ (m/z 28), $^{12}\text{CO}^+$ (m/z 28), $^{13}\text{CO}^+$ (m/z 29), O_2^+ (m/z 32), $^{12}\text{CO}_2^+$ (m/z 44), and $^{13}\text{CO}_2^+$ (m/z 45). The data show that the major combustion gas products are carbon dioxide, carbon monoxide, and water, along with some nonreacted starting material. In addition to this, traces of carbon powder were recovered from the reactor. This product distribution is typical of chain reaction chemistry.

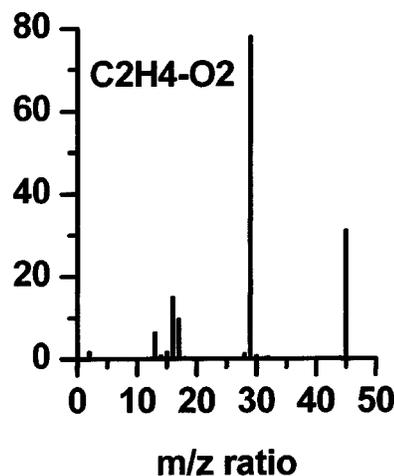


FIG. 4. Background-corrected mass spectrum signals for product gas from spark ignition combustion of ethylene- $^{13}\text{C}_2$ and oxygen (in arbitrary units).

Double labeled ethylene- $^{13}\text{C}_2$ was also tested using the spark reactor. The mass spectrometric data collected for ethylene-oxygen combustion are depicted in Fig. 4. For comparative purposes the reactants ($^{13}\text{C}_2\text{H}_4\text{-O}_2$) were loaded at the same pressure relative to that of $^{13}\text{CH}_4\text{-O}_2$. In general, ethylene spark combustion resulted in a profile related to methane combustion, although the major signal was instead observed at m/z 29 (at 100 eV electron ionization this would include $^{13}\text{CO}^+$ and $^{13}\text{C}_2\text{H}_3^+$ ions). In the case of ethylene combustion the initial reactant ratios were stoichiometric for carbon monoxide production.

Assuming that oxygen gas used for combustion is natural abundance, then a small subset of the mass spectrometric data for all CO_2^+ species can be used to estimate ^{13}C enrichment. It is clear that the m/z 44 ion signal corresponds to $^{12}\text{C}^{16}\text{O}_2$ species. However, the m/z 45 signal includes contributions from both $^{12}\text{C}^{17}\text{O}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}_2$. Considering that ^{17}O natural abundance is about 0.04 at. %, assigning the m/z 45 peak entirely as $^{13}\text{C}^{16}\text{O}_2$ does not introduce significant calculational error. Thus, with natural abundance oxygen, the following simple equation approximates ^{13}C enrichment:

$$^{13}\text{C} \text{ at. \%} = m/z \ 45 / (m/z \ 44 + m/z \ 45) * 100\%. \quad (1)$$

Of course, a more complete treatment of the CO_2^+ mass spectrometric data could include the ion signals from m/z 44 through 49. Equation (1) discarded the information encoded in peaks m/z 46 through 49. To utilize this mass spectrometric data, one can define the sum of squares error (SSE) parameter and next perform a least squares search. Given the variable assignment of $x = ^{12}\text{C}$ at. %, then $1 - x = ^{13}\text{C}$ at. %; similarly, $y = ^{16}\text{O}$ at. %, $z = ^{17}\text{O}$ at. %, and $1 - y - z = ^{18}\text{O}$ at. %. The ion signals from m/z 44 to 49 can be normalized, such that signal summation from m/z 44 to 49 is unity. The SSE parameter is given as

$$\begin{aligned}
\text{SSE} = & [mz_{44} - xyy]^2 + [mz_{45} - 2*xyz - (1-x)*yy]^2 + [mz_{46} - 2*xy*(1-y-z) - xzz - 2*(1-x)*yz]^2 \\
& + [mz_{47} - 2*xz*(1-y-z) - 2*(1-x)*y*(1-y-z) - (1-x)*zz]^2 + [mz_{48} - 2*(1-x)*z*(1-y-z) \\
& - x*(1-y-z)*(1-y-z)]^2 + [mz_{49} - (1-x)*(1-y-z)*(1-y-z)]^2.
\end{aligned} \tag{2}$$

Minimizing the SSE parameter results in best-fit 12-carbon, 13-carbon, 16-oxygen, 17-oxygen, and 18-oxygen at. % values. A comparison of the results obtained from Eqs. (1) and (2) reveals that if the oxygen used for combustion is natural abundance, then both ^{13}C at. % values are very close. However, if the oxygen reactant were somehow isotopically enriched, then Eq. (1) is not valid, and Eq. (2) should be applied instead.

ACKNOWLEDGMENTS

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