Isotope Ratio Measurements in the Classification of Carbonaceous Fuels

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Brief: Determination of ^{14}C / ^{12}C carbon isotopic ratios is an established technology currently in regulatory use for the apportionment of biogenic (renewable fuel) carbon and fossil (non-renewable fuel) carbon in municipal waste derived fuels, allowing proper allocation of renewable energy credits to thermal power plants operating on blends of renewable and fossil fuels.

Introduction

As set forth in Presidential Executive Orders 13101[1] , 13123[2] and 13134[3] , as well as Public Laws (106-224) and other legislative actions, federal agencies in the US are required to develop procedures to identify sustainable and carbon neutral fuel resources and to promote the infrastructure for, and encourage greater use of, these renewable resources. The USEPA has determined that refuse derived fuel (RDF) produced from sorted Municipal Solid Waste (MSW), from which metals and recyclables have been removed, is renewable.[4]. Notwithstanding these rulings, there remains some inconsistency in the policies of various federal and state agencies in the designation of fuels derived from MSW as renewable. Because of this inconsistency, facilities that use MSW as a fuel source may not receive proper attribution of renewable energy credits and carbon credits. The technical issue of designating fuel sources as either renewable, or non-renewable, has been effectively addressed in several European countries by application of radiocarbon (^{14}C / ^{12}C) isotope ratio measurements.

This document describes a scientific justification for the policies set forth in the above cited Executive Orders, USEPA directives, public laws, and in the European Union [5] , to the effect that MSW derived fuels are to be considered, all or in part, as renewable.

Carbon Isotopic Ratio Background

Cosmic rays entering earth's upper atmosphere create free neutrons that can react with abundant Nitrogen-14 (^{14}N) atoms. These atoms can eject a proton from the nucleus to form Carbon-14 (^{14}C). ^{14}C is unstable, with a half life of 5730 years, and eventually decays to ^{14}N. Carbon in atmospheric CO_2 has a ^{14}C / ^{12}C ratio of approximately $1.3 \times 10^{-12}/1$. This ratio is fairly constant in the atmosphere over geological time and is reflected in the carbon isotope content of terrestrial organisms, since they continually take up carbon from the biosphere. Upon the death of the these organisms, uptake stops and the ^{14}C / ^{12}C ratio begins to change due to beta decay of the ^{14}C back to ^{14}N. Eventually, the radioactive ^{14}C will have decayed to the point that none can be detected in the remains of the dead organism. This aspect of the carbon cycle underlies radiocarbon dating methods. The terms *radiocarbon dating* and *carbon isotope ratio dating* refer to the same general method. ^{14}C can be measured directly by detecting its radioactive decay, or the ^{14}C / ^{12}C ratio can be determined by mass spectrometry (MS).

Because the time required to form fossil fuels from organic matter is thousands of ^{14}C half lives, fossil fuels contain essentially no ^{14}C. In contrast, carbon from renewable resources such as wood and other biomass will have been fixed within the last few hundred years, and therefore its ^{14}C to ^{12}C ratio will very nearly reflect that of the CO_2 currently in the earth's atmosphere. As described below, ^{14}C / ^{12}C ratios can be determined by using liquid scintillation counting (LSC) or isotope ratio MS.

ASTM and ISO Standard Methods for Carbon Isotope Ratio Measurement

The ratio of ^{14}C to ^{12}C in a specific fuel blend (and in the stack gas CO_2 resulting from combustion of that fuel) depends on the source of the fuel. Fuel sources are referred to as either biogenic (renewable) or fossil (non-renewable) and their associated carbon is referred to here as biogenic carbon or fossil carbon. In isotope ratio MS, biogenic carbon CO_2 shows masses of (m/e) 44, 45 and 46 (for ^{12}C, ^{13}C and ^{14}C respectively), while the fossil carbon CO_2 only shows only masses of (m/e) 44 and 45 (see below). General methods of radiocarbon dating by isotope ratio have been in use since the 1950s. The American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO), respectively, have published standard methods for radiocarbon and ^{14}C / ^{12}C ratio measurements.

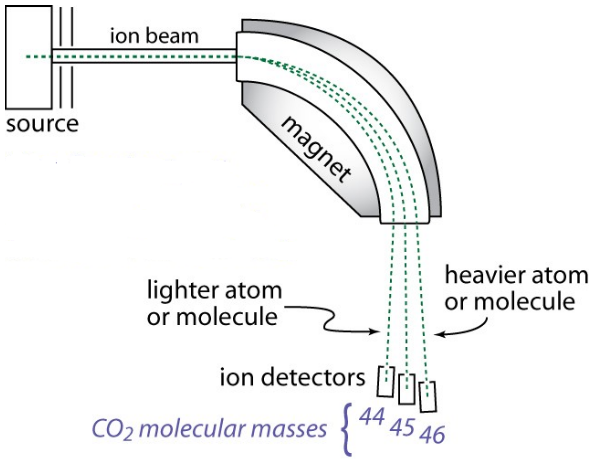
ASTM D6866 - 12: Standard Test Methods for Determining the Bio-based Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis Active Standard ASTM D6866 | Developed by Subcommittee: D20.96 Book of Standards Volume: 08.03. ASTM D6866 testing is required for fuels from municipal solid waste where the renewable portion of the fuel cannot be determined based on the relative energy content of the renewable biomass and fossil feedstock.

ISO 13833:2013(en) Stationary source emissions — Determination of the ratio of biomass (biogenic) and fossil-derived carbon dioxide — Radiocarbon sampling and determination. This International Standard gives sampling and analysis methods for the determination of the ratio of biomass and fossil fuel-derived CO_2in the total emitted CO_2 from exhaust gases of stationary sources, based on the radiocarbon (^{14}C isotope) method. Sample strategies for integrated sampling for periods from 1 h up to 1 month are given. Radiocarbon determination procedures include accelerated mass spectrometry (AMS), beta-ionization (BI), and liquid scintillation (LS) measurement procedures for the determination of the radiocarbon content.

Carbon Isotope Ratio Measurements to Determine Biogenic Fuel to Fossil Fuel Ratios

Use of municipal solid waste (MSW) to produce refuse derived fuel (RDF) to fire boilers for steam generation of electrical power is mature technology. In Europe, there has been relatively strong interest in developing and deploying carbon isotopic ratio MS, or radiocarbon counting, measurements to determine the amount of fossil carbon that is being released from thermal plants operating on MSW.

Thermal treatment of MSW by incineration or gasification to generate power and reduce waste volume to landfill is strictly mandated in several European jurisdictions. ^{14}C measurement is used to determine the ratio of renewable fuel carbon (mainly from woody biomass, and fiber) to fossil fuel carbon (mainly from plastics) in granting renewable energy credits and carbon credits to these facilities.



The most accurate means of determining ^{12}C /^{14}C ratios is by magnetic sector (accelerator) mass spectrometry, which is carried out in the laboratory. From such studies done in Sweden[6] for example, it has been estimated that total measurement uncertainty (i.e. the sum of the random and systematic errors) is approximately 3 % of the fossil carbon content in flue gas samples. In these same studies, it was also found that, on average, only about 33% of the carbon in MSW derived fuels can be attributed to fossil sources.

In these and other studies on carbon source attribution in MSW derived fuels, approximately 60% to 70 % of the carbon was contemporary (renewable). Application of these carbon source attribution methods in the US could help clarify the issue of whether MSW should be considered a renewable fuel, or at least what proportion of MSW derived fuels should be considered renewable. Such an approach would bring the US into line with science based international practices for determining abatement of CO_2 (especially fossil carbon CO_2) emissions. Another potential advantage of deploying this technology is that it could assist in demonstrating compliance with the newly adopted EPA Clean Power Plan 2015 [7] (40 CFR Parts 60, 62, and 78).

Final Word

The USEPA has classified sorted MSW as a renewable fuel[4],[7],[8], regardless of whether the combustible fraction is cellulosic or non-cellulosic, so long as the recyclable fiber and plastic products have been removed. The EPA has further publicly acknowledged that thermal conversion of MSW generates less greenhouse gas (GHG) equivalent (mainly CO_2 + CH_4) than does the placement of organic MSW in landfills. This is because, in addition to CO_2, anaerobic metabolism of organics in landfills generates methane (CH_4), which is more than 20 times as potent as CO_2 as a GHG. Classification of MSW derived RDF, or at least the renewable carbon portion thereof, as a renewable fuel will help keep this biodegradable material out of landfills, and thereby serve to further reduce GHG equivalent emissions.

References

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5. http://ec.europa.eu/eurostat/statistics-explained/index.php/Glossary:Renewable_energy_sources

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