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EA-IRMS: Tracing botanical origin of biofuels with hydrogen isotope fingerprints

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Goal

Demonstrate how hydrogen isotope fingerprints provide a framework for botanical origin detection of biofuels.

Introduction

Energy collected from renewable sources such as wind, sunlight, waves and geothermal heat is increasingly replacing the traditional electricity energy fossil fuel sources. In the light of the growing environmental concerns, and with fossil fuels making up most of our energy demand, we are facing a trend of replacing traditional fossil fuels with biofuels, which are consequently contributing to the reduction of carbon dioxide emissions. This trend is supported by worldwide initiatives and energy policies that are focused on lower-carbon fuels usage, especially for transportation, and monitoring and reporting of greenhouse gas emissions.

Biofuels are divided in three main generations. The first generation includes traditional energy crops such as sugar plants or vegetable oil seeds; the second generation derives from agricultural and forestry waste; and the third generation is related to biofuel production from micro and macro algae[1].

Increasing biofuel production using traditional energy crops can have severe consequences for global food supply, therefore the second and third generation biofuels are considered a more favorable approach to generating biofuels, particularly in terms of carbon dioxide neutral production. Thus, having information on the origin of biofuels could support understanding the environmental impact of the biofuel products in question.

In this study, a range of biofuels have been analyzed for hydrogen isotope ratios, in an EU related project, for the assessment of the geographical and botanical origin of the raw materials. The biofuel matrix ranged from greasy to liquid with different states of viscosity, which required different approaches for sample introduction.

Hydrogen isotope fingerprints of biofuels

Hydrogen isotope fingerprints of biological material have a fingerprint, a unique chemical signature which can be used to identify their origin and bio-productivity. Hydrogen isotopes are influenced by different natural processes acting on biomass and can help differentiating between biomass derived products from fossil-based feedstocks.

This is possible because plants carry a local-regional fingerprint primarily derived from the hydrological cycle, which is associated with local-regional rainfall, but can also be influenced by cultivation practices, soil processes and geological characteristics of the local area, altitude and proximity to the shoreline. The hydrogen (and oxygen) isotope fingerprints change in rainfall as you move further inland from the shoreline and with increasing altitude because the heavier isotopes are the first to be released from the clouds[2]. These effects can be tracked in the hydrogen isotopic fingerprints of organic material used for biofuels production.

Analytical configuration

The biofuel samples were injected as a liquid using a 0.5 µl syringe in the Thermo Scientific™ AS 1310 Liquid Autosampler, while viscous and rather solid samples were analyzed in silver capsules using Thermo Scientific™ MAS Plus Autosampler. Analyses were undertaken with the Thermo Scientific™ Elemental Analyzer IRMS System for OH analysis, equipped with a bottom feed connector for reverse Helium flow. The H_2 gas produced was then analyzed by the Thermo Scientific™ DELTA V™ Isotope Ratio Mass Spectrometer. Analytical time per sample was 210s. A wide linearity range of the IRMS system allows for fast and simple sample preparation by easy transfer of small sample amount in the silver capsules using a small rod dipped into the sample and transferred touching the bottom of the capsule without contacting the walls. Approximately 100 µg of sample material was used for analysis when undertaken using the MAS Plus autosampler.

Results

For testing the two different sample introduction approaches (liquid and greasy/viscous), the liquid samples were also analyzed in special hard silver capsules. The obtained δ^2H values showed remarkable agreement demonstrating excellent reproducibility of the data. This implies that evaporation of volatile components during the transfer into the capsules is negligible, as well as the storage in the autosampler carousel prior to analysis. Data accuracy is supported by analysis of standard NBS 22.

The samples analyzed include biodiesel and bioethanol. Biodiesel is produced from oil rich plants (e.g. rapeseed, sunflower), whereas bioethanol is produced from cereals (e.g. wheat, maize) or sugary feedstocks (sugar cane, sugar beet). We report here that the different production sources of biofuels have different hydrogen isotope fingerprints (Table 1). This suggests that a framework for differentiating different sources of biofuels, and potentially also differentiating biomass derived products from fossil-based feedstocks, exists and can be further pursued.

Table 1. Hydrogen isotope fingerprints of different oils. SD: standard deviation based on 10 repetitions for liquid samples and 5 repetitions for solid/viscous samples. Hydrogen isotopes Delta values are referenced against V-SMOW2 and GISP, as well as NBS 22.

Biofuel type	δ^2H vs. VSMOW [‰]	SD
Bio diesel*	-204.33	0.96
Chip fat*	-182.69	2.11
Distilled biodiesel*	-209.42	0.21
Distilled biodiesel	-211.37	0.87
Olive oil residue*	-144.77	1.14
Mixed oil*	-177.59	0.36
Unknown A*	-180.11	0.60
Unknown A	-179.95	1.62
Refined palm oil	-225.34	1.45
Refined rape oil	-171.43	0.47
Refined soy oil	-180.24	0.60
Unknown B	-204.50	1.59
Soybean oil	-114.23	1.78
Refined grease	-227.03	3.23
Oil residue	-206.24	0.84
Distilled frying oil	-196.07	2.72

* Samples injected by syringe with liquids autosampler, all others measured in capsules.

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Summary

There is a trend in replacing fossil fuels by biofuels in order to meet the growing energy demand and to reduce the negative impact of fossil fuels on greenhouse gas emission. However, the feedstock and the production process of fossil fuels impacts the acceptance and the benefit of the use of biofuels from the economic, environmental and social perspective. Information on the origin of biofuel products can help better understand their environmental impact.

Using isotope fingerprints of hydrogen, often combined with isotope fingerprints of carbon, nitrogen, oxygen and sulfur, helps to distinguish different sources of biofuels and provides a viable framework for correct labeling of products, protecting producers, consumers, and our environment. Further work should be undertaken to gather more isotope fingerprint data on biofuels and further enhance this framework. With the EA IsoLink IRMS System, laboratories gain an effective analytical solution for petroleum investigations which provides fast and reliable analysis with full automation.

Literature

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