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Biogenic fraction determination in fuels – Optimal parameters survey

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HIGHLIGHTS

- Direct LSC method development for bio-component quantification in fuels is presented.
- Optimal parameters and measurement conditions on LS counter Quantlus are discussed.
- Two simple calibration procedures for ^{14}C determination in biofuels were carried out.
- Fuel blends 1–100% FAME were produced from two feedstock and two fossil matrices.
- Minimal detectable biogenic content assessed is (0.47–1.1)%m for 300 min of counting.

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ABSTRACT

The novel method for biogenic component determination in liquid fuels by direct measurement of the ^{14}C activity concentration via liquid scintillation counting (LSC) technique has been used in few laboratories worldwide. This paper presents results of the development of method for bio-component quantification in fuel mixtures in the Nuclear Physics Laboratory Novi Sad, Serbia, as well as their comparison to established methodology in literature with intent to define optimal parameters and measurement conditions for ^{14}C determination in biofuels. Therefore, the purpose of the paper is to give comprehensive overview of optimal parameters such as scintillation cocktail and vial selection, fuel/cocktail ratio and best calibration procedure of liquid scintillation counter Quantulus 1220™, with practical information for laboratories that intend to develop this technique. Biodiesel produced from two different feedstock materials was mixed with two commercial fossil matrices to produce fuel blends containing 1–100% FAME (Fatty Acid Methyl Esters), which were analyzed for calibration purposes. Analytical study of relation between the detected released energy and quench level led to establishment of calibration curves specific to the fuel types produced in this moment on the market in Serbia.

1. Introduction

European Union's promotion of the use of sustainable and renewable resources reflected to requirement of at least 10% of synthesized biodiesel in liquid fuels by the year 2020 [1]. This legislation has stimulated various types of petrodiesel and bio-based component blends production, which triggered development of methods for exact, effective and reliable quantification of biodiesel content. Biogenic and fossil materials cannot be distinguished by classical analytical technologies such as HPLC, GC, IR or UV, the only difference is based on the amount of radioactivity measured by LSC or AMS instruments [2].

The novel method for biogenic component determination in liquid fuels by direct measurement of the ^{14}C activity concentration via liquid scintillation counting (LSC) technique has been developed in few laboratories worldwide and the results of the implementation were published recently [3–9]. The direct LSC method is based on different ^{14}C signatures of the biogenic and the fossil components: while the biogenic (recent-grown) component reflects the modern atmospheric ^{14}C activity, no ^{14}C is present in fossil fuels [9], which means that the quantity of ^{14}C in the sample is the criterion for bio-fuel presence in the fuel [7]. The purpose of this paper is to present results of experiments that established LSC technique in procedural manner for direct quantification of biogenic levels in fuel mixtures in the Nuclear Physics Laboratory Novi Sad, Serbia. Optimal parameters obtained through the experiments

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have been also discussed and compared to the previous published works of various authors.

2. Methods and instrumentation

2.1. Equipment

Measurements were performed on Ultra Low Level Liquid Scintillation Spectrometer Wallac 1220 Quantulus manufactured by PerkinElmer. Besides low background count rates, one other advantage of Quantulus 1220™ is automatic measurement of quench indicating parameter SQP(E), Spectral Quench Parameter of the External Standard. It represents channel number of 99th percentile of spectrum generated by external standard ^{152}Eu stored in Quantulus. Samples with higher quench level have lower SQP(E) parameters, which is a consequence of spectra shifting towards lower channels in the presence of quench. SQP(E) had been measured for each sample for 10 min which is reported to be optimal measurement time for precise quench determination [10].

Spectra were acquired by EasyView and WinQ software, where optimal window was selected according to highest Figure of Merit (FOM) values.

2.2. Materials

A standard radioactive source activity (aqueous ^{14}C solution) produced from PerkinElmer, was used for instrument's calibration, certified activity $A(^{14}C) = (9.19 \cdot 10^5 \pm 3\%)$ dpm ml^{-1} on reference date 9th July 2008.

Both, polyethylene and glass vials were tested in order to determine their influence on background level. The sample:scintillation cocktail volume ratio was explored with highest FOM values demanded.

2.2.1. Calibration samples

For calibration purposes two different PerkinElmer scintillation cocktails suitable for organic sample measurements were used, Opti Fluor O and Ultima Gold F.

Background determination was done with different fossil matrices – diesel from column of hydro treatment without additives (ultra-low sulfur content), commercial diesel fuels with additives (standard EN 590) that improve fuel's characteristics (friction modifiers, paraffin dispersants and flow improver additives), "premium quality" diesel (with cetane improver, detergent-dispersant additives, anticorrosion compounds, deemulgator, antifoam additives, paraffin dispersants and flow improver additives), distilled water, gasoline, petroleum ether and oil. All fossil diesel fuels were produced in national refinery NIS Petrol and were tested according to SRPS EN 590:2010 standard (Table 1). Results indicate that all fossil samples - except fuel without additives - comply with SRPS EN 590 standard. Fuel samples without additives have poor lubricity (above 460 μm), which is the consequence of hydrodesulphurization process, therefore require use of improving lubricity additives.

Calibration of instrument was carried out with two commercial fossil fuels with additives for winter and summer season added. FAME (Fatty Acid Methyl Esters) are the most popular and common forms of the biofuels on the global market at the moment [11]. Blends of commercial diesel with winter and summer additives were prepared with biodiesel in ratio 99:1%(v/v), 97:3%(v/v), 95:5%(v/v), 93:7%(v/v), 90:10%(v/v) i 0:100%(v/v) as calibration samples. FAME biodiesel was produced by conventional, homogeneous transesterification of fatty acids in methyl alcohol, in the presence of KOH as a catalyst with two feedstock materials, hybrid sunflower oil and lard fat. Residual methanol was removed after gravitational separation of glycerine by vacuum distillation from obtained FAME. Residual impurities (soaps and salts) were removed with water and the remaining water was removed by the silica gel. After filtering, compliance of FAME obtained was tested with the standard EN 14214:2009. Results of analysis are given in Table 2.

Sunflower seed selection as raw material was based on the fact that it represents a typical oleaceous plant from the region [12]. Sunflowers are grown on an average area of 178,000 ha and achieve average yield of 2.54 t ha^{-1} in the Republic of Serbia [13]. Favorable climatic conditions, long tradition, mastered production technology and large number of domestically produced hybrids are all advantages for the sunflower production. Other advantages of sunflower are high energy value of sunflower cake and good sources of protein with amino acid availabilities similar to those of soybean meal. Also, sunflower meal does not have anti-nutritional factors such as those found in soybean and rapeseed meals [14]. Domestic sunflower hybrid "Somborac" was used

Table 1
Properties of used fossil diesel (SRPS EN 590:2010).

Property	Units	Method	Limit		Value			
			min	max	No additives	ED with summer additives	ED with winter additives	ED premium quality
Density 15 °C	kg m^{-3}	SRPS EN ISO 3675:2007	820.0	845.0	828.8	822.3	834.8	826.9
Cetan index	–	SRPS ISO 4264:2011	46.0	–	52.8	52.8	52.9	54.1
Polycyclic aromatic hydrocarbons	%(m/m)	SRPS EN 12916:2012	–	8.0	3.4	5.3	6.7	7.1
Sulfur content	mg kg^{-1}	SRPS EN ISO 20846:2012	–	10.0	6.2	7.2	7.2	<3.0
Flash point	°C	SRPS ISO 2719:2008	55	–	66	63	68	66
Carbon residue remnant (at 10% distillation remnant)	%(m/m)	SRPS ISO 10370:2003	–	0.30	0.01	0.01	0.01	0.01
Sulfated ash content	%(m/m)	SRPS EN ISO 6245:2008	–	0.01	0.003	0.004	0.004	0.003
Water content	mg kg^{-1}	SRPS EN ISO 12937:2011	–	200	60	44	34	21
Total contamination	mg kg^{-1}	SRPS EN 12662:2012	–	24	2.9	3.6	3.4	3.2
Copper band corrosion (3 h at 50 °C)		SRPS EN ISO 2160:2012	Class I		1a	1a	1a	1a
Oxidation stability	g m^{-3}	SRPS ISO 12205:2005	–	25	/	16	13	2
Lubricity	μm	SRPS EN ISO 12156-1:2012	–	460	490	418	413	366
Viscosity at 40 °C	mm^2 s^{-1}	SRPS ISO 3104:2003	2	4.50	2.531	2.436	2.833	2.511
Distillation at 250 °C	%(v/v)	SRPS EN ISO 3405:2012	–	65	22.7	49	36.2	48.1
Distillation at 350 °C	%(v/v)		85	–	97.3	96	95.3	95.6
95%(v/v) distillation	°C		–	360	330.6	347.8	352.3	347.4
Cold filter plugging point	°C	SRPS EN 116:2010	Class B					
			–	0	−6	−7	−19	−10
Blur point	°C	SRPS ISO 3015	–	–	−4	−4	−5	−5