COMPARISON OF METHODS FOR DETERMINATION OF BIOGENIC FRACTION IN LIQUID FUELS

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ABSTRACT

A method of direct measurement of ^{14}C activity concentration via liquid scintillation counting (LSC) is recognized as good and fast methodfor determination of biogenic component in liquid fuels. Two laboratories that used this ^{14}C technique participated in this survey: Laboratory from University of Novi Sad (UNS), Serbia and Laboratory from Ruđer Bošković Institute (RBI), Croatia. Each laboratory used its own calibration methods on the same set of samples (produced diesel-based bio-fuels and commercially available domestic oils).

From the obtained results it can be concluded that eachmethod which uses ^{14}C technique for determination of biogenic component in liquid fuels has its advantages and disadvantages. RBI data evaluation method is based on two calibration curves, for purely biogenic and purely fossil liquids, and the calibration does not depend on the exact chemical composition of the organic liquid. The limits of the method are defined by the SQP(E) of approximately 690. Below this value the count rates of biogenic and fossil liquids become close to each other or even indistinguishable from one another and the obtained results for biogenic fractions are not reliable. In this intercomparison UNS used two different methods, one for produced bio-diesels and the other one for domestic oils. UNS data evaluation method is very dependent on the composition of the examined fuels, so the obtained results with the "two-step" method were relatively good in the case of diesel mixtures with biogenic component. In the case of biogenic oil samples (bought on market), UNS "two-step" method didnot give realistic results, and with the "one-step" method the limitation is largequenching in the samples, so for the samples with SQP(E) less than 700 this method could not give expected results. Samples prepared with liquid fuels are usually colored and the main challenge for determination of biogenic component in both laboratories is handling of highly quenched liquids.

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. In order to address this issue few laboratories worldwide developed methods for exact, effective and reliable quantification of biodiesel content.Determination of biogenic fraction in liquid fuels by direct measurement of the ^{14}C activity concentration via liquid scintillation counting (LSC) technique is fast, simple, accurate and sensitive determination procedure for the mass assessment of biogenic fraction in biofuels [1,2]. Great variety of biogenic matrices in fuels available on the marketenable preparationof calibration curves for different bio-components in various fossil fuels matrices. Laboratory for radioactivity measurements and dose assessment at the Department of

Physics, University of Novi Sad (UNS), Serbia, performed two different methods of calibration: one-step and two-step methods, both described in detail in [1].Laboratory for low-level radioactivities of the Ruđer Bošković Institute (RBI) in Zagreb, Croatia, uses liquids of different colors to construct modern and background calibration curves, MCC and BCC, respectively, by measuring count rates and SQP(E) values of various modern and fossil liquids [2,3]. Since the laboratories use different calibration methods, their results should be compared by interlaboratory comparison measurements. A preliminary comparison of the two techniques applied to the same set of mixtures with the known fractions of the biogenic component is described in [4], and within this paper suitability of the methods for various oils is discussed.

2. Materialsandmethods

Both laboratories used the same type of measuring equipment, Ultra Low Level Liquid Scintillation Spectrometer Quantulus1220. It has low background count rates and a possibility of measurement of quench indicating parameter SQP(E), Spectral Quench Parameter of the External Standard. The SQP(E) represents channel number of 99^{th} percentile of spectrum generated by external standard ^{152}Eu stored in Quantulus. Samples with higher quench level have lower SQP(E) values, which is a consequence of spectra shifting towards lower channels in the presence of quench. SQP(E) values at UNS were measured for each sample for 10 min which is reported to be optimal measurement time for precise quench determination [1], while at RBI 1-minute measurement of SQP(E) preceded each 30-minute measurement of a sample, usually 10 cycles in a run. Spectra were acquired by WinQ software and evaluated by Easy View.

UNS used Ultima Gold F scintillation cocktail and 10 ml to 10 ml volume ratio of the sample to scintillation cocktail in plastic vials. For calibration UNS used blends of commercial diesel with winter and summer additives prepared with biodiesel in volume ratios 99:1 %, 97:3 %, 95:5 %, 93:7 %, 90:10 % and 0:100 % as calibration samples. As biodiesel, FAME (Fatty Acid Methyl Esters) obtained from either sunflower or from lard fat were used. FAME are the most common forms of biofuels [5]. “One-step” calibration method assumes simple correlation between biogenic content of fuel (i.e., mass percentage of biofuel in certain fuel blend) and corresponding measured count rates in beta spectrum. With the “two-step” calibration procedurequench correction curve (efficiency vs. SQP(E) correlation) enables activity concentration calculation and its dependence on biogenic content in fuel, followed with activity concentration vs. biogenic content in fuel correlation [1].

RBI used 10 ml of Ultima Gold F scintillation cocktail mixed with 10 ml of liquid sample in low-potassium glass vials. Several types of fossil fuel, pure benzine and benzene (used as ^{14}C-free background for ^{14}C dating) were used for BCC construction. Various types of commercial domestic oil (vegetable, sunflower, olive, pumpkin), bioethanol and benzene prepared from modern samples were used for MCC construction [2]. The BCC and MCC curves represent relations between the SQP(E) values and count rates of the background and modern samples, respectively. The procedure for the unknown sample consists of: 1) measurement of the count rate and the SQP(E) value, 2) calculation of background and modern count rates corresponding to the measured SQP(E) value based on the BCC and MCC curves, respectively, and 3) the ratio of net count rates of the unknown sample and the modern net count rate at the same SQP(E) represents the fraction of the biogenic component in the liquid. The count rate of the biogenic samples was indistinguishable from the background count rate at

SQP(E) values below 570 [2].
The same sets of prepared blends of commercial fuels (based on diesel with either winter or summer additives) andvarious types of domestic oils (sunflower, olive, peanut, corn sprouts, etc.) are usedfor testing and comparison of calibration methods and measurement techniques developed at RBI and UNS.

3. Results

Diesel with either winter or summer additives was used to check the applicability of the BCC curve developed at RBI. Interestingly, the diesel with winter additives gave higher SQP(E) values and higher countrate (788 channel and 2.5 min^{-1}, respectively) than the diesel with summer additives (720 channel and 2.3 min^{-1}, respectively) (Figure 1 a and b), both results being in accordance with the previously determined BCC curve [2].
Mixtures of diesel with summer additives and FAME produced from either lard fat or sunflower oil in the whole range of concentration were used for testing the behavior of SQP(E) and count rate. The addition of small fraction of sunflower FAME caused a sudden decrease of SQP(E), and the minimal value of SQP(E) = 510 was obtained for 5 % of the biogenic component. At higher biogenic concentrations SQP started to increase again showing some peculiar irregularities, while at biogenic concentrations above 70 %, SQP(E) increased linearly (Figure 1a). Countrate displayed similar characteristics (Figure 1b). The addition of FAME produced from lard fat also caused a decrease of SQP(E) with increasing biogenic concentration, the minimal values SQP(E) = 550 were observed at 30 % and 50 %. The countrateremained very low, in accordance with low SQP values. We had no mixture with lard fat FAME concentration >50 %.
Mixture of diesel with winter additives and FAME produced from lard fate, on the opposite, showed a linear change of both SQP and count rate values with the increase of the biogenic component concentration (Figure 1, line). Such behavior should be checked by mixture containing higher fractions of lard fatFAMEin diesel with winter additives.

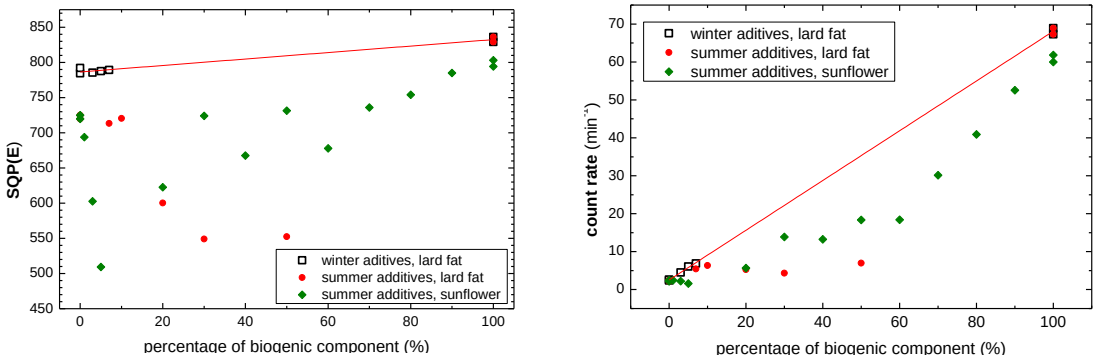

Figure 1.Dependence of SQP(E) values (left) and count rate (right) on a mixture composition obtained at RBI. Fossil component was diesel with either summer or winter additives. Biogenic component was FAME obtained from either sunflower oil or from lard fat.

UNS used "two-step" method for determination of biogenic fraction in prepared mixtures of diesel with additives and FAME. The same matrices were used also for calibration purposes in UNS. SQP(E) values are increasing constantly with the addition of biogenic component in the sample (both for sunflower oil and for lard fat).It may be noticed that the SQP(E) values measured at UNS are higher than those measured at RBI and this could be explained by different type of vials used (plastic and glass vials, respectively).

The obtained results of intercomparisonmeasurements of various mixtures of diesel with either winter or summer additives and FAME obtained from either sunflower oil or lard fat are presented in Table 1. The results obtained at RBI for samples that were used for calibration at UNS are also presented.

Table 1. Biogenic fraction of various mixtures with referent biomass fraction determined by the two methods of data evaluation at UNS and RBI

Referent biomass fraction (%)	**UNS biogenic fraction** (%)	**UNS SQP(E)** (channel)	**RBI biogenic fraction** (%)	**RBI SQP(E)** (channel)
Biogenic component – sunflower oil				
1 summer	- *	-	1.6 ± 0.4	694
3 summer	- *	-	10.8 ± 1.5	603
5 summer	- *	-	-**	510
20 summer	25.8 ±1.3	729	45.2 ± 1.5	622
30 summer	39.0 ± 1.9	736	35.2 ± 0.7	724
40 summer	49.9 ± 1.7	744	63.8 ± 1.3	667
50 summer	51.7 ± 2.0	748	44.9 ± 0.7	731
60 summer	60.4 ± 2.2	778	81.5 ± 1.3	678
70 summer	78.1 ± 2.7	783	75.6 ± 1.0	736
80 summer	81.4 ± 2.9	802	89.8 ± 0.9	754
90 summer	85 ± 3	838	91.7 ± 0.7	785
Biogenic component – lard fat				
3 winter	- *	-	3.5 ± 0.4	786
5 winter	- *	-	6.3 ± 0.4	788
7 winter	- *	-	7.7 ± 0.4	789
7 summer	- *	-	10.9 ± 0.5	713
10 summer	- *	-	13.0 ± 0.5	720
20 summer	20.7 ± 0.7	691	-**	600
30 summer	33.4 ± 1.9	700	-**	549
50 summer	55.8 ± 1.1	705	-**	553

* used for calibration

** forSQP< 600, count rate of a liquid is not distinguishable from the count rate of fossil liquids

By the presented comparisonof the obtained results (Table 1) at RBI with the real biogenic component, the limitations of the RBI evaluation technique have been elucidated. The limit when the count rates of the biogenic and the fossil samples become indistinguishable has been moved from SQP(E) < 570 [2] to SQP(E)< 600. Moreover, large discrepancies were obtained for the SQP(E) values between 600 and 690 – the lower the SQP(E), the larger the relative differences between the measured and the expected biogenic fraction. The biogenic fraction can be successfully determined at SQP(E) > 690. On the other hand, UNS had slight advantage in this intercomparison as they used the samples with the same matrices for calibration purposes. "Two-step" calibration procedure that UNS used implements quench correction and therefore offers more reliable ^{14}C determination in fuels in comparison to "one-step" calibration method [1]. The limitation of this method is that application of these calibration curves is limited to samples with chemically identical bio and fossil

components. It can be used for precise biogenic fraction determination in examined fuel samples if the components of the fuel mixture are well known in advance [4].
In addition, some biogenic oil samples were compared.For biogenic oil samples UNS could not use "two-step" calibration curves because of the differences in the matrix of those samples and samples used for calibration purposes, which was concluded as a constrain of this method [4]. The presented results for biogenic oil samples (Table 2) measured at UNS are calculated by "one-step" calibration curve, although application of this calibration does not include quench considerations and corrections [1]. The SQP(E) values at UNS and RBI follow each other, although there are not the same, because of different types of vials used. Oil samples with high SQP(E) values (>800) gave expected result of 100 % biogenic component by both measurement techniques at UNS and RBI. According to the results presented in Table 2, a limitation of the UNS "one-step" method is the SQP(E) value less than 700, if the SQP(E)<700 (for highly colored samples) then "one-step" method could not be used.The results in Table 1 have shown that at RBI the limit of biogenic fraction determination is defined by SQP(E) ≈ 600, and that for 600 <SQP(E) < 690 large relative differences are obtained. Such a conclusion is also corroborated with the biogenic oil samples (Table 2).Table 2 presents also some oil brands that were used at RBI only. It may be seen that two brands of corn sprouts oils gave different results for the biogenic component, although their SQP(E) values were similar. Two brands of olive oil gave different SQP(E) values due to different oil colors. Olive oil A gave SQP(E) < 600 at both institutions, i.e., in both cases it was below the limit for acceptable results. Olive oil B with SQP(E) = 660 resulted in to high but almost realistic value of biogenic component. The explanation for obtained values of the biogenic component >100 % may be the age of the organic material from which the oil is produced, but such a conclusion should be carefully checked. In Figure 2 we show the modern calibration curve MCC [2] and the new modern oil samples from Table 2 are compared with the MCC. Deviations of the datapoints for corn sprout oil A and palm oil from the MCC are clearly visible.

Table 2.Biogenic fraction of biogenic oil samples determined by the two methods of data evaluation at UNS and RBI.A and B refer to different brands of the same type of oil.

	UNS		RBI	
Sample	SQP(E)	biogenic component %	SQP(E)	biogenic component %
1. sunflower oil A	837	100 ± 6	816	101 ± 2
2. sunflower oil B	845	101 ± 6	824	104 ± 2
3. corn sprout oil A	763	93 ± 4	771	120 ± 2
4. olive oil A	586	-*	597 **	26 ± 2
5. flax(linen) oil	612	-*	614	89 ± 3
6. peanut oil	849	101 ± 6	821	96 ± 2
7. palm oil	-	-	710	127 ± 3
8 . olive oil B	-	-	660	112 ± 3
9. rapeseed oil	-	-	812	98 ± 2
10. sesame oil	-	-	580 **	55 ± 4
11. corn sprout oil B	-	-	781	102 ± 2

* SQP< 700 **SQP< 600

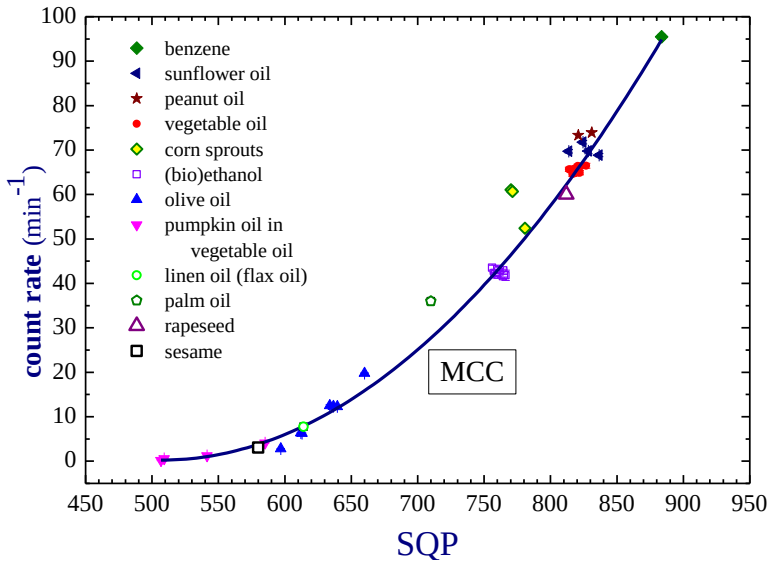

Figure 2.Comparison of various biogenic oil samples with the modern calibration curve MCC [2]. All samples are supposed to be 100%-biogenic.

4. Conclusion

RBI data evaluation method is based on two calibration curves, for purely biogenic and purely fossil liquids, and the calibration does not depend on the exact chemical composition of the organic liquid. The limits of the method are defined by the SQP(E) of approximately 690. Below this value the count rates of biogenic and fossil liquids become close to each other or even indistinguishable from one another and the obtained results for biogenic fractions are not reliable. UNS data evaluation method is very dependent on the composition of the examined fuels, so the obtained results with "two-step" method were relatively good in the case of diesel mixtures with biogenic component. In the case of biogenic oil samples (bought on market), UNS "two-step" method didnot give realistic results, and with the "one-step" method the limitation is largequenching in the samples, so for the samples with SQP(E) less than 700, this method could not give expected results. Similarly, the RBI method for modern biogenic liquids with low SQP(E) values (olive oil, linenoil) didnot give realistic results while modern oil samples with high SQP(E) values give acceptable results. The overall conclusion is that eachmethod that can be used for determination of biogenic component in liquid fuels has its advantages and disadvantages. Samples prepared with liquid fuels are usually colored and the biggest problem in determination of biogenic component is the quench correction. But if the matrix of the sample is known in advance, all three mentioned methods could be used for estimation of the biogenic component. The main challenge for further development of methods for determination of biogenic component by direct LSC measurement in both laboratories is handling of highly quenched liquids.

5. Acknowledgment

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POREĐENJE METODA ZA ODREĐIVANJE BIOGENE KOMPONENTE U TEČNIM GORIVIMA

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SADRŽAJ

Prema preporukama Evropske Unije sa ciljem da se koriste obnovljivi i održivi izvori, do 2020.godine zahteva se da se u svim tečnim gorivima koja se koriste nalazi bar 10% sintetisanogbiodizela. Da bi se koncentracija biodizela moglaproveriti, nekoliko laboratorija u svetu je razvilo metode za tačnu, efikasnu i pouzdanu kvantifikaciju sadržaja biogene komponente. Direktno merenje koncentracije aktivnosti ^{14}C tečnim scintilacionim detektorom (LSC), koje podrazumeva određivanje količine ^{14}C u uzorku kao meru prisutnosti biogene komponente u testiranom gorivu, pokazalo se kao dobra i brza metoda. U ovoj interkomparaciji učestvovale su dve laboratorije: Laboratorija sa Univerziteta u Novom Sadu (UNS), Srbija i Laboratorija sa Instituta Ruđer Bošković (RBI), Hrvatska. Svaka laboratorija je koristila sopstvenikalibracionimetod i isti set uzoraka za interkomparaciju (proizvedena bio-goriva bazirana na dizelu i komercijalno dostupna domaća ulja).

Iz dobijenih rezultata može se zaključiti da svaki od prikazanih metoda ima svoje prednosti i mane, što zavisi od samog sastava uzorka. RBImetod se zasniva na upotrebi dvekalibracione krive, za čisto biogena i čisto fosilna goriva, i kalibracija nije zavisna od hemijskogs sastava analiziranog uzorka. Ograničenje ove metode je SQP(E) vrednost niža od 690. Ispod ove vrednosti odbroji biogene i fosilne komponente postaju veoma bliski jedan drugom i samim tim rezultati koji se dobijaju nisu pouzdani. U ovoj interkomparaciji, UNS je koristila dve različite metode kalibracije, jednu za proizvedene bio-dizele, a drugu za domaća ulja. UNS metod evaluacije izmerenih podataka u mnogome zavisi od sastava ispitivanog goriva, pa su rezultati dobijeni sa "two-step" metodom relativno dobri za smeše dizela sa biogenom komponentom. U slučaju biogenih ulja, UNS "two-step" metod nije dao realistične rezultate, zbog toga je korišćen "one-step" metodza koji je utvrđeno ograničenje za SQP(E) parametar na 700. Uzorci koji se pripremaju sa tečnim gorivima su najčešće obojeni i najveći problem koji se javlja je korekcija na prigušenje u samom uzorku, koja mora biti detaljno sprovedena kako bi se dobio pouzdan rezultat, pa najveći izazov daljnjeg razvoja ovih metoda postaje postupak merenjabiogene komponente u jako prigušenim uzorcima.