COMPARISON OF METHODS FOR DETERMINATION OF BIOGENIC FRACTION IN LIQUID FUELS

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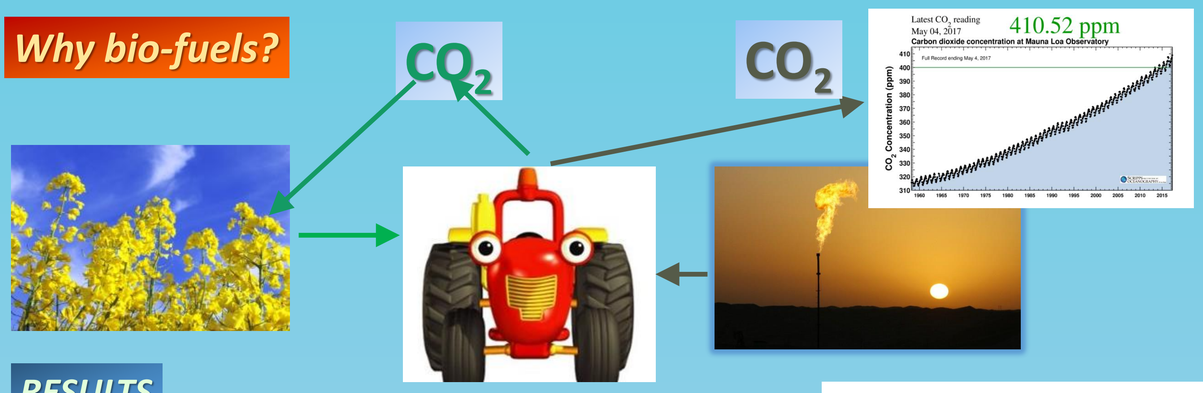
INTRODUCTION

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 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. Great variety of biogenic matrices in fuels available on the market enable preparation of 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, and Laboratory for low-level radioactivities, Ruđer Bošković Institute (RBI), Zagreb, Croatia, use different calibration methods, and interlaboratory comparison of their results is presented in this work.

Why bio-fuels?



METHODS AND INSTRUMENTATION

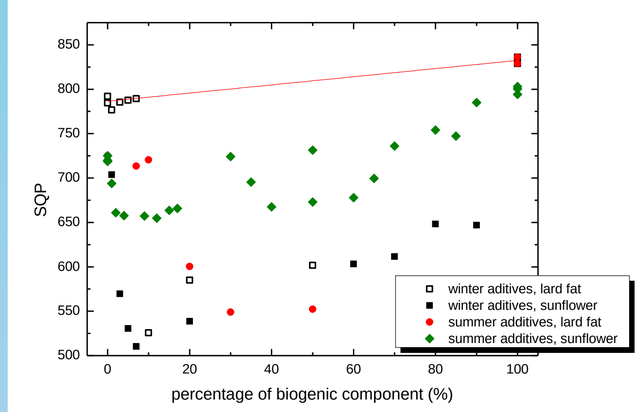
Both laboratories used the same type of measuring equipment, UltraLow Level Liquid Scintillation Spectrometer Quantulus1220 and same measurement geometry (10 mL sample + 10 mL scintillant) and the same scintillation cocktail – Ultima Gold F. Nevertheless, methods from two laboratories differ in calibration methods and measurement vials. IRB 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 in low potassium glass vials. UNS performed two calibration methods: 1) the „one-step" method assumes simple correlation between biogenic content of fuel and count rate), and 2) the „two-steps" method - quench correction curve enables activity concentration calculation and its dependence on biogenic content in fuel, followed by activity concentration vs. biogenic content in fuel correlation.
Mixtures of fossil fuels and biogenic additives were prepared. The fossil component was based on diesel with either winter or summer additives. The biogenic component was FAME (Fatty Acid Methyl Esters) obtained from either sunflower oil or from lard fat. The same sets of samples were analyzed in both laboratories (Table 1). In addition, various types of domestic oils were used for testing the measurement techniques developed at RBI and UNS (Table 2).

RESULTS

Table 1. Biogenic fraction of various mixtures with referent biomass fraction

Referent biomass fraction (%)	UNS biogenic fraction (%)	UNS SQP(E) (chan)	RBI biogenic fraction (%)	RBI SQP(E) (chan)
Biogenic component – sunflower oil				
Type of additive				
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
** for SQP < 600, count rate of a liquid is not distinguishable from the count rate of fossil liquids



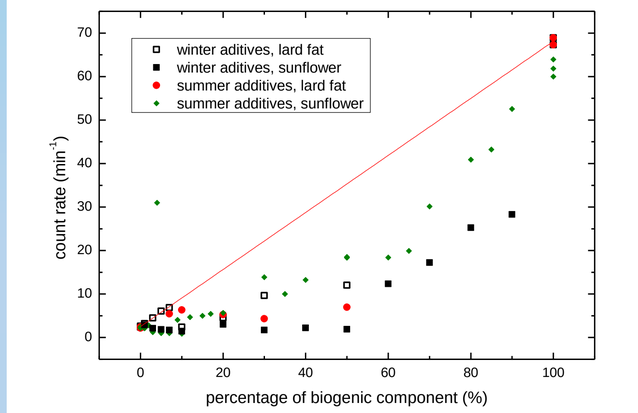


Figure 1. Dependence of SQP(E) values and count rate on a mixture composition obtained at RBI. Fossil component was diesel with either summer or winter additives. Biogenic component was FAME (Fatty Acid Methyl Esters**) obtained from either sunflower oil or from lard fat.**

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

	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**

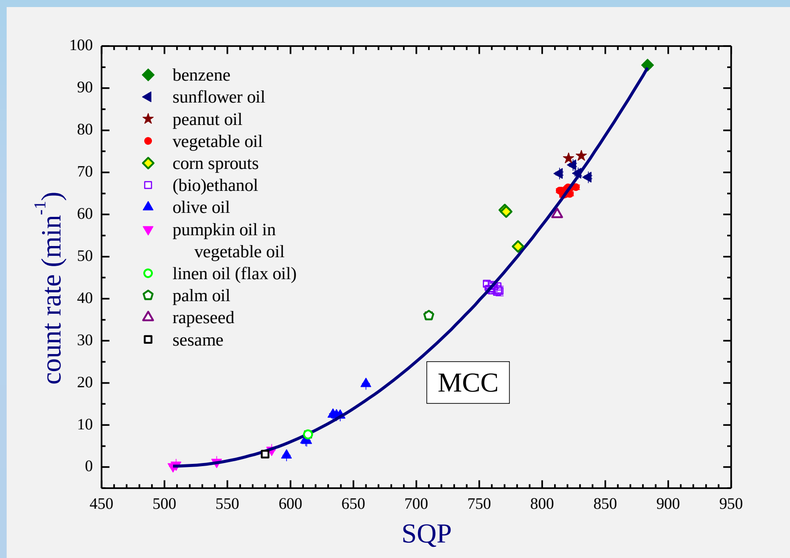


Figure 2. Comparison of various biogenic oil samples with the modern calibration curve MCC. All samples are supposed to be 100%-biogenic.

CONCLUSIONS

Each described method 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, SQP < 700. Additionally, the „one-step" method from UNS showed better measurement performances for all tested samples, while the „two-step" method gave unreliable results for oil samples.

Acknowledgement: The paper is a part of the research done within the Bilateral project Serbia-Croatia 2016-2017.