Limitation and comparison of two methods for determination of biogenic fraction in liquid fuels by ^{14}C

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INTRODUCTION

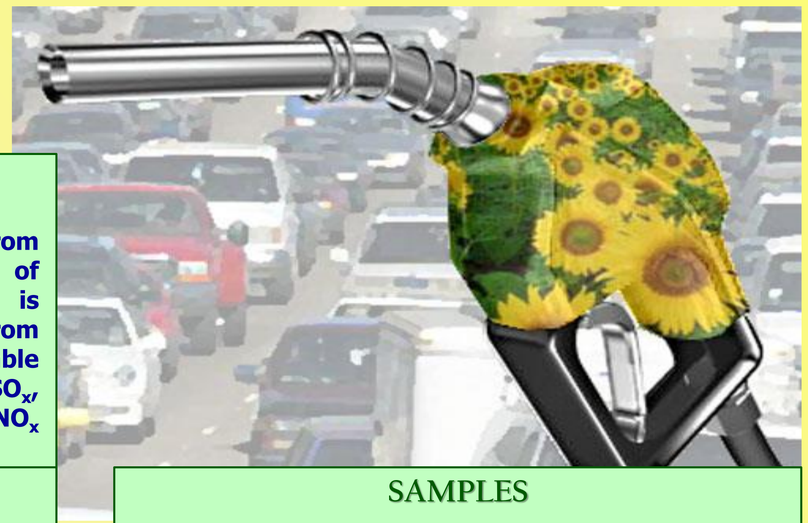
Determination of biogenic fraction in liquid fuels by direct measurement of the ^{14}C activity concentration via liquid scintillation counting (LSC) technique has been adopted in few laboratories worldwide. This method is regarded as fast, simple, accurate and sensitive determination procedure for the mass assessment of biogenic fraction in biofuels. There are some variations in the calibration techniques used by different laboratories that should be compared by intercomparison measurements. There is a great variety of biogenic matrices in fuels available on the market, so the calibration curves should work well for a variety of bio-components in various fossil fuels matrices.

Two laboratories participated in this study:
- **Laboratory for low radioactivity at the Department of Physics, University of Novi Sad (UNS), Serbia, and**
- **Laboratory for low-level radioactivities of the Ruđer Bošković Institute (RBI) in Zagreb, Croatia.**

In order to compare two calibration methods, we used the same set of mixtures with the known fractions of the biogenic component.

BIODIESEL BENEFITS

Biodiesel is a non-toxic biodegradable fuel produced from vegetable oil triglycerides during the process of transesterification with methanol. Biodiesel is environmentally friendly and renewable fuel produced from biomass. Emission of CO_2 is low according to renewable nature. In comparison to fossil diesel emissions of CO, SO_x, unburned hydrocarbons and soot is very low, and NO_x emissions are slightly higher.



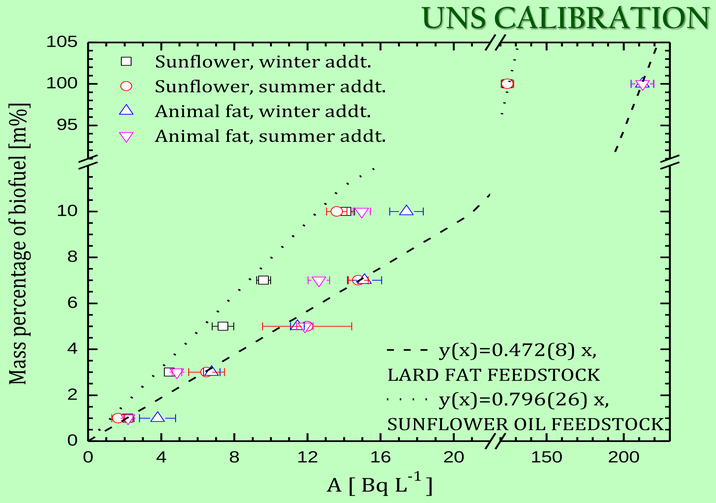
METHODS AND INSTRUMENTATION

Both laboratories used the same type of measuring equipment, Ultra Low Level Liquid Scintillation Spectrometer Quantulus 1220.
UNS used UltimaGold F scintillation cocktail and 10ml:10ml volume ratio of the sample:scintillation cocktail in plastic vials.
RBI used 10 ml of UltimaGold F scintillation cocktail mixed with 10 ml of liquid sample in low-potassium glass vials.

SAMPLES

For intercomparison purpose the following mixtures were used: commercial fossil fuels mixed with FAME – biogenic component produced from sunflower oil – with the reference biomass fractions of 20 %, 30 %, 40 %, 50 %, 60 %, 70 %, 80 % and 90 %, and FAME produced from lard fat with the reference biomass fractions 20 %, 30 % and 50 %, as well as 3 %, 5 %, 7 % and 10 % with summer or winter additives.

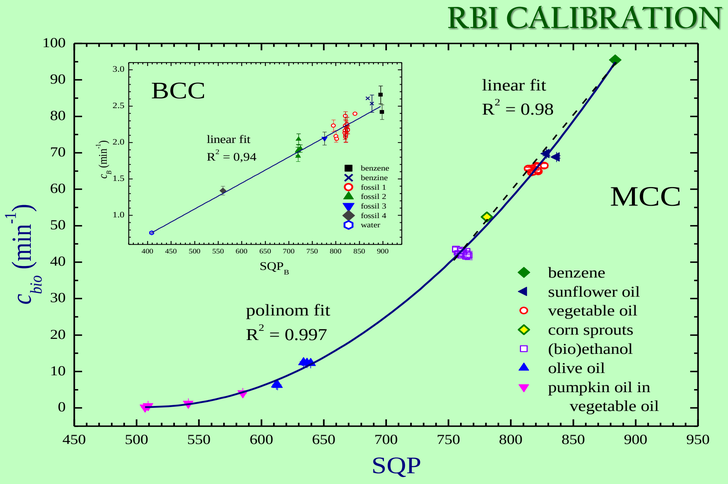
UNS CALIBRATION



UNS performed a two-step method for calibration. The procedure assumes application of previously established efficiency vs. SQP(E) correlation, followed with activity concentration vs. biogenic content in fuel.

SQP(E) = standard quench parameter

RBI CALIBRATION

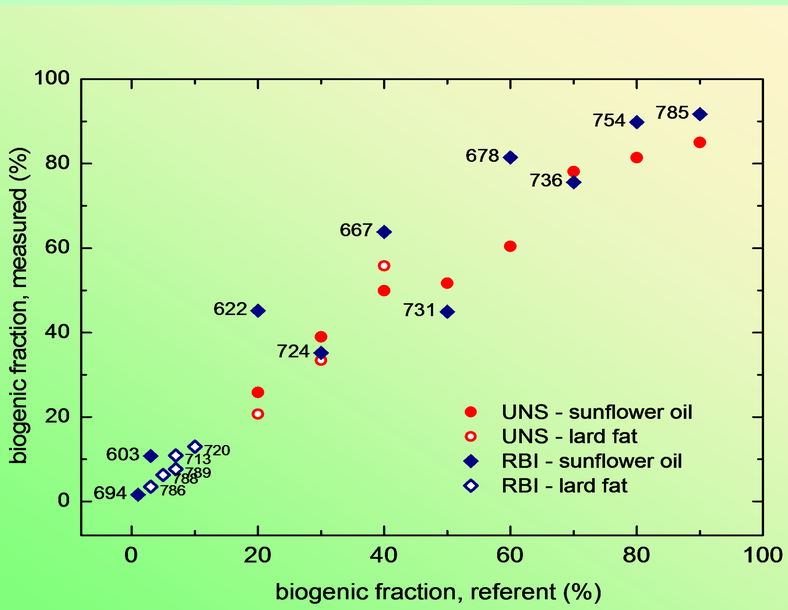


RBI callibration technique uses liquids of different colours to construct modern and background calibration curves, MCC and BCC, respectively, by measuring count rates and SQP(E) values of various modern and fossil liquids.

RESULTS

Referent biomass fraction (%)	UNS biogenic fraction (%)	RBI biogenic fraction (%)	RBI SQP(E) (channel)
Biogenic component – sunflower oil			
1	- *	1.6 ± 0.4	694
3	- *	10.8 ± 1.5	603
5	- *	-**	510
20	25.8 ±1.3	45.2 ± 1.5	622
30	39.0 ± 1.9	35.2 ± 0.7	724
40	49.9 ± 1.7	63.8 + 1.3	667
50	51.7 ± 2.0	44.9 ± 0.7	731
60	60.4 ± 2.2	81.5 ± 1.3	678
70	78.1 ± 2.7	75.6 ± 1.0	736
80	81.4 ± 2.9	89.8 ± 0.9	754
90	85 ± 3	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	20.7 ± 0.7	-**	600
30	33.4 ± 1.9	-**	549
50	55.8 ± 1.1	-**	553

* used for calibration
** for SQP < 600, count rate of purely biogenic liquids is not distinguishable from the count rate of fossil liquids



Correlation between the biogenic fraction measured at RBI and UNS and the referent biogenic fraction. The numbers represent the SQP(E) values of the corresponding samples measured at RBI.

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 700. Below this value the count rate of biogenic and fossil liquids become close to each other or even indistinguishable from one another.**
- ✓ **UNS data evaluation method is very dependent on the composition of the examined fuels, so the obtained results in this case were relatively good, but the future investigation should test also whether this calibration method is suitable for some other fuel matrices, for example for various types of domestic oil (vegetable, sunflower, olive, pumpkin, flax, peanut, corn sprouts, palm, rapeseed) used in everyday life. This will be further step in this joint intercomparison in testing advantages and limitations of the RBI and UNS methods.**

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