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GAS CHROMATOGRAPHIC INVESTIGATIONS OF COMPOSITIONAL PROFILES OF BIODIESEL FROM DIFFERENT ORIGIN

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Abstract

GC investigations of content and distribution of fatty acid methyl esters (FAMEs) in biodiesels were carried out. Samples of five commercial biodiesel and two laboratory synthesized with known feedstock and two commercial with unknown origin were subjected to determine FAMEs compositions. Three methods for quantitation of compositional profiles are applied and compared. The method with internal standard were chosen because of its better precision. Calibration was made for the individual FAMEs using ten replicate analyses of standard mixture C14 – C22 and standard deviation and uncertainty of the method were given. "Characteristic values" that can be used to reflect the origin of biodiesel were calculated from GC data of investigated samples and from literature reference. It was shown their application to distinguish biodiesel fuels produced from vegetable oils or animal fats.

Key words: Biodiesel fuel; free acid methyl esters; gas chromatography; vegetable oil; animal fat.

1. Introduction

Biodiesel fuels are an alternative source of energy and in the present energetic context they continues to simulate interest throughout the world. They generate less greenhouse effect than fossil fuels. A " green " fuel, biodiesel is biodegradable, nontoxic and essentially free of metals, sulfur and carcinogenic aromatics [1- 3]. Biodiesel can be used as a substitute for, or additive to, diesel oils. Pure biodiesel (B100) is generally not used as a fuel, but instead it is blended with petroleum diesel in 2, 5 or 20 volume % (B2, B5, B20) [4].

Biodiesel is defined as a fuel comprised of monoalkyl esters of long – chain fatty acids derived from vegetable oils or animal fats [1, 2, 5]. Various methods have been reported for the production of biodiesel [1, 2, 6, 8]. Among these transesterification of triacylglycerides (contain in vegetable and animal feed stocks) with alcohols in the presence of a catalyst to yield alkyl esters and glycerin, which is removed (by product). The most common alcohol is methanol, so another name for such biodiesel is fatty acid methyl esters (FAME). The "first generation" are biodiesels produced from edible feed stocks (vegetable oils, animal fats). The "second generation" are biodiesels produced from non – feed stocks like lignocellulosic biomass. Most biodiesels in use today are first generation [2, 3]. They contain individual FAMEs from C10:0 to C24:1 in variable quantities. The first number refers to the number of carbon atoms in fatty acid (FA) chain, the second – the number of C – C double bonds in the FA chain.

As far as biodiesel is a mixture of FAMEs, its properties depend on the chemical structure of individual FAMEs and their contents. Also FAME profiles of biodiesel may be dependent on the stocks and origin of oils.

Biodiesel FAMEs can be analyzed directly by gas chromatography – flame ionization detector (GC – FID) [4, 9, 12], gas chromatography – mass spectrometry (GC – MS) [5, 12, 15], two – dimensional gas chromatography [3, 11, 14], high performance liquid chromatography [13].

The purpose of this study was to investigate the compositional FAME profiles of biodiesels from oils and fats by GC – FID, using different quantitative methods, and to determine the most "characteristic values" for recognition the origin of biodiesel.

2. Experimental procedures

2.1. Materials and Standards

FAME Mix C14 – C22 and Fatty acid methyl esters (C14:0; C16:0; C16:1; C18:0; C18:1; C18:2; C18:3; C20:0; C20:1; C22:0; C22:1; C24:0; C24:1) were purchased from Sigma – Aldrich (Switzerland) and Supelco.

2.2. Samples

Five biodiesels were investigated – three commercially – produced biodiesels, labeled as sample 1, 2 and 3, and two were laboratory synthesized by transesterification of sunflower and rapeseed oil using sodium methoxide, labeled as samples 4 and 5. Four samples, named "unknown" (samples 6 to 9) were used to predict biodiesel origin. Samples 6 and 7 were comercially available, sample 8 and 9 were completely unknown.

2.3. Biodiesel sample preparation for GC analysis

Accurately weighed approximately 250 mg of sample is placed in 10 ml vial and 5 ml solution of internal standard (IS) is added. The solution of IS is 10 mg/ml methyl heptadecanoate in heptane [16]. The samples are then analyzed under the chromatographic conditions (2.4).

2.4 GC analysis

GC analysis were carried out on a GC system Agilent Technologies 7890A equipped with FID, split/splitless injector and Agilent 7693 A automated liquid sampler. Column: HP INNOWAX, 30m x 0.32 mm ID, 0.25μm film thickness. Temperature program of the oven: initial temperature 210ºC for 9 minutes, rate 20ºC/min to 230ºC, 10 minutes. Detector temperature: 300ºC, injector temperature: 250ºC. Carrier gas: He, column flow 1.5 ml/min, split ratio 1:80. Hydrogen flow 40 ml/min, air flow 400 ml/min, make-up gas (nitrogen) 40 ml/min. Injection volume 1μl. ChemStation for GC was used for instrument control, data acquisition and data analysis.

3.Results and discussion

3.1.Peak identification

To identify the peaks of the biodiesel gas chromatograms, a comparison of retention times with those in the standard mixture and pure fatty acid methyl esters (2.1) was carried out. Peak symmetry was satisfactory to allow peak identification and quantitation.

For the purpose of reproducibility of retention times, 10 injections of the biodiesel (sample 2) are carried out. The results obtained are shown in Table 1. RSD values demonstrates a good reproducibility of the GC separation under the specified conditions.

Table 1. GC retention times of rapeseed oil FAMEs (sample 2)

Compound	t_R (min)	SD (min)	RSD (%)	GC (%)	SD	RSD
C14:0	2.860	0.0010	0.0349	0.060	0.000	0.000
C16:0	3.879	0.0010	0.0258	5.126	0.006	0.117
C16:1	4.105	0.0015	0.0365	0.181	0.000	0.200
C18:0	5.743	0.0015	0.0261	2.060	0.004	0.194
C18:1	6.154	0.0016	0.0260	46.123	0.112	0.243
C18:2	6.849	0.0016	0.0233	34.550	0.050	0.144
C18:3	7.903	0.0016	0.0202	4.883	0.015	0.310
C20:0	9.110	0.0018	0.0197	0.423	0.008	1.891
C20:1	9.548	0.0017	0.0178	1.110	0.016	1.441
C22:0	12.475	0.0018	0.0144	0.484	0.008	1.653
C22:1	12.959	0.0019	0.0146	0.941	0.017	1.806
C24:0	17.234	0.0020	0.0116	0.0410	0.000	0.900
C24:1	18.178	0.0022	0.0121	0.152	0.001	0.657

SD – Standard deviation, RSD – Relative standard deviation

3.2.Calculations

The total ester content was calculated according to EN 14103 standard [16]. The total peak area from C14:0 to C24:1 and the peak area of internal standard (IS) methyl heptadecanoate were used.

This standard method is not intended for determination of the content of each individual ester (except for C18:3) what is necessary for our investigations.

We compared three quantitative methods to calculate individual FAMEs in biodiesels:

A. Normalization method – reports the area of each FAME peak in the run as a percentage of the total area of all peaks in the run (like C18:3 in EN 14103), supposing that the response factors of FID are 1.0 for all FAMEs.

B. Internal standard calculation (ISTD) – a known amount of IS is added to the calibration and unknown samples. Using IS and compounds amount and peak areas in the calibration sample, appropriate response factors are calculated to compensate for changes in detector sensitivity for different FAMEs.

C. Correction of peak areas of FAMEs with mass correction coefficients F_i by Ongkiehong [17] using Eq. (1):

$$F_i = M_i/n_i \quad (1)$$

where: M_i is the molecule mass of i^{th} compound, n_i is the number of carbon atoms in the molecule of i^{th} compound, and standardized the corrected areas to percent.

In Tables 2 and 3 the results obtained by the above quantitative methods for samples 1 and 3 respectively are shown. The values of SD were calculated from 6 analyses for each sample. The comparison among these 3 methods was carried out using F – criteria of some values, which we named "characteristic". The choice of such values was grounded on the following findings:

In vegetable oils animal fats dominate even – numbered fatty acids: saturated and unsaturated. So, we calculated and compared the following "characteristic values":

- Sum of saturated FAMEs ($\sum_s$ = C14:0 + C16:0 + C18:0 + C20:0 + C22:0 + C24:0)
- Sum of monounsaturated FAMEs ($\sum_{mus}$ = C16:1 + C18:1 + C20:1 + C22:1 + C24:1)
- Sum of polyunsaturated FAMEs ($\sum_{pus}$ = C18:2 + C18:3)
- $\sum_{uns}/\sum_s$ ($\sum_{uns} = \sum_{mus} + \sum_{pus}$)

Table 2 FAME profile of the sunflower oil biodiesel

	Composition						F-criteria			
	Method A		Method B		Method C		F_{cal} A/B	F_{cal} A/C	F_{cal} B/C	$F_{(5,5)}$ α = 0.05
	average	SD	average	SD	average	SD				
C14:0	0.070	0	0.080	0	0.070	0				
C16:0	6.246	0.006	6.403	0.006	6.486	0.010				
C16:1	0.106	0.006	0.130	0	0.110	0				
C18:0	3.046	0.006	3.080	0	3.073	0.006				
C18:1	25.106	0.021	27.353	0.006	25.113	0.015				
C18:2	62.516	0.076	62.060	0.030	62.093	0.045				
C18:3	0.080	0	0.090	0	0.070	0				
C20:0	0.220	0	0.216	0.006	0.216	0.006				
C20:1	0.180	0.010	0.230	0.010	0.170	0				
C22:0	0.670	0.010	0.670	0.010	0.656	0.015				
C22:1	0.070	0	0.080	0	0.056	0.006				
C24:0	0.233	0.006	0.220	0	0.196	0.007				
C24:1	0.020	0.017	0.030	0.017	0.013	0.011				
∑s	10.486	0.012	10.670	0.010	10.700	0.020	1.44	2.78	4.00	5.05
∑mus	25.480	0.020	27.823	0.015	25.463	0.015	1.78	1.78	1.00	5.05
∑pus	62.600	0.066	62.150	0.032	62.163	0.055	4.25	1.44	2.95	5.05
∑uns/∑s	8.396	0.015	8.430	0.010	8.186	0.060	2.25	16.00	36.00	5.05

The comparison by F – criteria of the "characteristic values" from the three quantitative methods results in relation to standard deviation. The calculated F – criteria in Table 2 and Table 3 show that method B gives more reproducible results. We accepted to use ISTD method in our calculations.

Table 3 FAME profile of the rapeseed oil biodiesel

	Composition						F-criteria			
	Method A		Method B		Method C		F_{cal} A/B	F_{cal} A/C	F_{cal} B/C	$F_{(5, 5)}$ α = 0.05
	average	SD	average	SD	average	SD				
C14:0	0.050	0	0.050	0	0.050	0				
C16:0	4.750	0.017	4.536	0.006	4.633	0.009				
C16:1	0.210	0	0.240	0	0.203	0.006				
C18:0	1.736	0.006	1.640	0	1.656	0.006				
C18:1	59.810	0.320	60.790	0.038	57.023	0.025				
C18:2	19.110	0.130	17.690	0.010	18.043	0.030				
C18:3	7.710	0.032	7.910	0.010	7.243	0.006				
C20:0	0.540	0	0.500	0	0.503	0.006				
C20:1	1.260	0.043	1.510	0.063	1.250	0.010				
C22:0	0.300	0	0.283	0.006	0.276	0.015				
C22:1	0.376	0.006	0.380	0	0.350	0				
C24:0	0.120	0	0.106	0.009	0.103	0.006				
C24:1	0.173	0.006	0.180	0	0.146	0.006				
∑s	7.493	0.018	7.116	0.009	7.223	0.018	4.00	1.00	4.00	5.05
∑mus	61.830	0.180	63.100	0.080	58.973	0.035	3.24	26.44	5.24	5.05
∑pus	26.820	0.080	25.600	0.017	25.286	0.035	22.14	5.22	4.23	5.05
∑uns/∑s	11.830	0	12.460	0.015	11.666	0.064	0.00	0.00	18.20	5.05

The precision of the method was determined by 10 replicates of analysis of biodiesel (Table 1) and FAME standard mixture (2.1) spiked with internal standard (Table 4). The estimated standard deviation is from 0.02 to 0.43% for the different FAMEs. Uncertainty was calculated by the methods in [18], using coverage factor of 2 and was from 0.06 to 1.16%.

Table 4 Results of analysis of FAME Mix C14 – C22

	From Certificate of Analysis		Experimentally determined	
	Concentration (%)	STD DEV	Mean of 10 analysis	STD DEV
C14:0	3.50	0.06	3.49	0.02
C16:0	8.50	0.01	8.47	0.04
C18:1	21.10	0.45	20.81	0.34
C18:1	8.80	0.14	8.52	0.07
C18:0	5.10	0.10	5.12	0.06
C18:2	1.70	0.04	1.78	0.07
C18:2	29.00	0.68	29.14	0.43
C18:3	4.30	0.09	4.56	0.04
C20:0	1.70	0.03	1.70	0.02
C22:0	1.70	0.03	1.68	0.02

3.3.Compositional profiles of biodiesels

In Table 5 the composition of FAMEs in biodiesel samples from some vegetable oils and animal fats are given. Data was taken from literature quoted.

One can see that vegetable oils typically contain high levels of unsaturated fatty acids. There is a difference between the levels of mono- and polyunsaturated fatty acids. Rapeseed oils contain higher concentrations of C18:1 (56-60%). Soybean, corn and sunflower oils contain higher concentrations of C18:2 (54-67%). The animal oils contain lower concentrations of unsaturated fatty acids compared with vegetable oils.

Methyl esters of saturated acids in vegetable oils change within 7 and 17%, and in animal oils from 20 to 50%. The content of methyl esters of polyunsaturated acids in vegetable oils varies from 25 to 68%, and in animal oils from 2 to 13%.

"Characteristic values" $\sum_s$ and $\sum_{uns}/\sum_s$ are sufficiently different for oils and fats. Other two values are not so significant in view of the fact that rapeseed oil biodiesel contains higher concentration of monounsaturated than polyunsaturated, while in other vegetable oils it is opposable. We consider that all four "Characteristic values" together would give an information about the type – vegetable or animal – of the feedstock.

In Table 6 the FAME profiles and the "Characteristic values" of the investigated samples are shown.

Data in Table 5 and 6 shows a good possibilities to distinguish biodiesels produced from vegetable oils and animal fats. It is seen that "unknown" samples 6 and 7 may belong to vegetable oils because of higher concentration of unsaturated acid esters and that is right. Sample 8 probably is from vegetable oil, sample 9 is most likely from animal fats in view of higher concentration of saturated acid esters.

We intend to continue our studies to extend the information level applying different pattern recognition methods.

4. Conclusions

Biodiesel fuels produced by transesterification of triglycerides contain individual fatty acid methyl esters (FAME). In view of the fact that fuel properties strongly depend on FAMEs content, the compositional profiles of biodiesel from different origin are investigated. The samples are commercially available and laboratory synthesized.

Gas chromatographic conditions for good separation and correct quantitation of individual FAMEs in biodiesels are established. The used method shows standard deviation less than 0.5% and uncertainty less than 1.2% for all methyl esters.

"Characteristic values" (CV) reflecting the origin of biodiesel were found. Some CV are calculated based upon the chromatographic data of investigated samples and from literature references. Applying them on some known and unknown biodiesel indicates a good ability to distinguish biodiesel fuels from vegetable oils or animal fats.

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Table 5. Composition of FAMEs from literature sources

FAME	COMPOSITION, %													
	Corn oil [15]	Sunflower oil [2]	Sunflower oil [15]	Soya oil [2]	Soya oil [19]	Rapeseed oil [19]	Rapeseed oil [4]	Rapeseed oil [2]	Tallow [15]	Tallow [19]	Tallow [9]	Chicken oil [4]	Pork oil [4]	Lard [15]
C14:0		0.10		0.10	0.21	0.11	0.04		3.18	1.70	7.50	1.12	0.43	1.18
C16:0	10.10	6.40	5.44	11.60	11.20	4.10	4.12	4.20	28.30	25.50	24.90	17.60	15.60	23.70
C16:1	0.07	0.10	0.08	0.20	0.20	0.27	0.05	0.10	2.72	3.27	4.90	2.15	5.28	1.87
C18:0	1.58	3.60	3.08	3.90	4.04	1.80	1.57	1.60	17.60	14.40	17.90	9.91	3.93	13.60
C18:1	26.90	21.70	28.90	23.70	21.90	58.60	55.70	59.50	40.10	40.30	31.10	34.30	28.50	45.30
C18:2	59.90	66.30	61.30	53.80	53.80	22.20	17.80	21.50	2.14	12.00	2.30	7.38	11.90	11.25
C18:3	0.70	1.50	0.08	5.90	7.29	13.30	7.61	8.40		0.99	1.70	0.37	0.48	0.62
C20:0	0.42	0.30	0.20	0.30	0.36	0.79	0.56	0.40		0.40		0.14	0.05	0.27
C20:1	0.26	0.20	0.18	0.30	0.26	1.79	1.31	2.10		1.03	0.20	0.73	0.29	0.72
C22:0		0.60	0.66	0.30	0.45	0.57	0.32	0.30						
C22:1		0.10		0.10		0.13	0.51	0.50						
C24:0		0.20		0.10	0.16	0.30	0.15	0.10		0.34		0.08		
C24:1				0.30		0.54	0.16	0.10		0.17		0.15	0.15	
Σ_s	12.10	11.20	9.38	16.30	16.42	7.67	6.76	6.60	49.08	42.34	50.30	28.85	20.01	38.75
Σ_{mus}	27.23	22.10	29.16	24.6	22.36	61.33	57.73	62.30	42.82	44.77	36.20	37.33	34.22	47.89
Σ_{pus}	60.60	67.80	61.38	59.70	61.09	35.50	25.41	29.90	2.14	12.99	4.00	7.75	12.38	11.87
Σ_{uns}/Σ_s	7.26	8.03	9.65	5.17	5.08	12.62	12.30	13.96	1.36	0.80	1.12	1.56	2.33	1.54

Table 6. Composition of FAMEs in samples 1 – 9

FAME	COMPOSITION, %								
	Known origin					Unknown origin			
	Sample 1 sunflower	Sample 2 rapeseed	Sample 3 rapeseed	Sample 4 sunflower	Sample 5 rapeseed	Sample 6	Sample 7	Sample 8	Sample 9
C14:0	0.08	0.06	0.05	0.05	0.04	0.06	0.06	0.18	11.40
C16:0	6.40	5.13	4.53	5.51	4.60	5.71	5.64	8.53	35.30
C16:1	0.13	0.18	0.24	0.08	0.22	0.15	0.14	0.22	1.28
C18:0	3.08	2.06	1.64	3.48	1.78	2.94	2.85	3.42	10.40
C18:1	27.35	46.00	60.84	22.24	55.87	38.38	34.80	31.09	21.10
C18:2	62.10	34.50	17.69	54.6	17.71	45.90	47.00	48.08	2.30
C18:3	0.09	4.87	7.92	0.05	5.25	2.50	1.96	0.10	0.42
C20:0	0.22	0.42	0.50	0.22	0.57	0.35	0.30	0.25	
C20:1	0.24	1.14	1.58	0.15	1.27	0.60	0.50	0.30	
C22:0	0.67	0.48	0.29	0.60	0.40	0.63	0.52	0.77	
C22:1	0.08	0.94	0.38	0.10	0.58	0.30	0.31	0.23	
C24:0	0.22	0.04	0.11	0.30	0.25	0.25	0.19	0.27	
C24:1	0.01	0.15	0.18	0.08	0.45	0.08	0.07	0.13	
Σ_s	10.67	8.19	7.12	10.16	7.64	9.94	9.56	13.42	51.1
Σ_{mus}	27.81	48.41	63.22	22.64	58.39	39.51	35.82	31.97	22.38
Σ_{pus}	62.19	39.37	25.61	54.65	22.96	48.40	48.96	48.18	2.72
Σ_{uns} / Σ_s	8.43	10.72	12.48	7.61	10.64	8.84	8.87	5.97	0.49