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PRODUCTION OF VEGETABLE OIL FATTY ACID METHYL ESTERS FROM USED FRYING OIL BY COMBINED ACIDIC/ALKALI TRANSESTERIFICATION

J. Hancsók, F. Kovács, M. Krár

University of Veszprém, Dept. of Hydrocarbon and Coal Processing
H-8201, Veszprém, Po. Box. 158, E-mail: hancsokj@almos.vein.hu

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Abstract

In this paper the actual driving forces of the research, production and utilization of biofuels are listed for directing attention for these. The authors try to find a solution to utilize the greatly available spent frying oils as engine fuels. These spent frying oils have high free fatty acid content and are ranked as dangerous substances. In the experimental part a combined (acid and alkali catalyzed) transesterification process is presented where the promoting effect of the applied co-solvents during pre and main esterification and of the fatty acid methyl ester content of the product mixtures was investigated. Considering 2-4 h acidic transesterification (depending on the free fatty acid content of the feeds) followed by 2 h alkali catalyzed transesterification, the authors were able to find process parameters and solvents promoting the esterification, resulting in 97-98% methyl ester content within relatively short time. All products obtained by the combined transesterification have met the requirements of the currently valid EU standard.

***Key words**: fatty acid methyl ester, esterification, transesterification, frying oils*

1. Introduction

Recently, research and production of biofuels is in the focus of mankind, due to the non-uniform distribution and depletion of crude oil reserves, the periodically and rapidly changing prices of crude oil, the utilization of renewable energy sources, substitution of the polluting fossil energy sources, replacing import energy carriers, reducing the import dependence, the political potential to support rural population, moderating the agricultural overproduction crises, utilization of fallow lands, the lower lifecycle carbon-dioxide emission and the contribution to the protection of soil and water sources [1-4].

Besides, Directive 2003/30/EC of the European Council and European Parliament, finalized in May 2003 calls for the following [5]:

- Member States should ensure that a minimum proportion of biofuels and other renewable fuels is placed on their markets, and, to that effect, shall set national indicative targets. A reference value for these targets shall be 2 %, calculated on the basis of energy content, of all petrol and diesel fuel for transport purposes placed on their markets by 31 December 2005;
- the reference value shall be increased to 5.75% by 31 December 2010 (0.75%/year increase) for the Member States;
- the transportation fuels blended with biofuels shall meet the requirements of the valid national and EU standards for engine gasoline (EN 228) and for diesel fuel (EN 590), too;

- for percentages of biofuels, blended into mineral oil derivatives, exceeding the limit value of 5% fatty acid methyl ester, a specific labelling at the sales points shall be imposed;
- Member States shall report to the Commission before 1 July each year on the measures taken to promote the use of biofuels, on the national resources allocated to the production of biomass for energy uses other than transport, on the total sales of transpiration fuel and the share of biofuels.

Blending of 5 v/v% of biodiesel into the diesel fuel is authorized from 1 May 2004, so long as the biodiesel is in accordance with all requirements of EN 14214:2003 standard (Automotive fuels – Fatty acid methyl esters (FAME) for biodiesel engines – Requirements and test methods).

Vegetable oil fatty acid methyl esters can be produced from vegetable oils, animal fats and used frying oils. Application of the latter two is not so general, because their availability is lower than that of various types of vegetable oils. Animal fats are mainly used to produce fat powder while collection and adequate treatment of used frying oils is not wide-spread. Although used frying oils are classified as dangerous substances according to the 102/1996 Executive Decree of the Hungarian Government, even the great consumers (restaurants, fast food restaurants etc.) only return the half of their used volume to the collecting companies.

Other possibilities of the utilization of used frying oils are the following:

- engine fuel after chemical transformation,
- animal feed; significant amount was used earlier, although the utilization of culinary garbage is not permitted in the member countries of the EU in order to prevent epidemics,
- chemical industry, e.g. soap, detergents, etc.,
- component of plasticizers [6],
- mixing into asphalt,
- heating oil, fuel oil [7], etc.

The significance of the application of vegetable oils and their derivatives in the mentioned areas arises from environmental aspects, mainly from their good biodegradability. The most important application area would be the utilization as fuel of internal combustion engines. It is a generally accepted opinion that vegetable oils can not directly be used in modern engines, only their conversion products, especially mono alkyl methyl esters.

Chemical transformation of used frying oils is not possible by conventional method (alkali catalyst), because of its high free fatty acid content (5-35%). The alkali catalyst immediately reacts with the free fatty acids contained in used frying oils resulting in soaps and it is not able to catalyse the reaction. A possible way is the conversion of the used frying oils with acid catalyst (chlorhydric acid, sulphuric acid, acid ion-exchange resin). Substantial amount of acid catalyst and significantly higher reaction time is necessary for the transesterification, compared with the alkali catalysed method [8]. Another option is the conversion of used frying oils by combined acid and alkali catalyzed transesterification. In this process the free fatty acid content of the used frying oils are first pre-esterified in the presence of acid catalyst, then the transesterification is finished by alkali catalyst [9].

The high free fatty acid content of the spent frying oils can also be reduced by mixing unused vegetable oil. On the basis of the quality characteristics of used frying oils, the amount of unused vegetable oil to be mixed into the spent oil has to be determined to ensure the suitability of the mixtures for the two step transesterification. The objective of our research work was to determine the favourable ratio of the spent frying oil and the unused vegetable oil resulting in practically complete conversion during the combined transesterification. Besides, our aim was to study the effect of free fatty acid content of the used frying oil and of the operating conditions of the combined transesterification on the yield of methyl esters. During the combined transesterification a solvent is used to increase the rate of reaction at the interphase.

Experimental

According to the previous, our experimental work was focused on the investigation of the transesterification of different feeds based on sunflower oil: spent frying oil; unused vegetable oil and various mixtures of the previous (to obtain different free fatty acid contents). We also studied the effect of acidic pre-esterification on the yield of methyl esters and the promoting effect of the solvent(s) applied in the pre- and main transesterification steps.

Materials

Methanol; concentrated sulphuric acid; sodium methylate; tetrahydrofuran (THF) and dioxane (solvents for increasing interphase); feeds based on sunflower oil: spent frying oil; unused vegetable oil and various mixtures of the previous.

Free fatty acid content of the various mixtures of the used frying oil and unused sunflower oil is given in Table 1, their fatty acid composition in Table 2 and their main characteristics in Table 3.

Table 1 Free fatty acid content of the various mixtures of spent frying oil/unused sunflower oil

Sample name	HFFA*	A	B	C	D	SF**
Free Fatty Aicd content, %	32,5	19,1	12,7	6,5	0,5	<0,1

** HFFA: high free fatty acid, ** SF: unused vegetable oil*
A, B, C, D: various mixtures of the previous

Table 2 Fatty acid composition of the unused vegetable oil and spent frying oil

Fatty acid composition, %	Sunflower oil	
	unused	spent
C14:0	-	0,1
C16:0	6,3	8,2
C16:1	0,1	0,2
C18:0	3,6	3,6
C18:1	28,5	27,7
C18:2	60,3	58,4
C18:3	0,1	0,5
C20:0	0,2	0,2
C20:1	0,2	0,2
C22:0	0,7	0,6
C22:1	-	-
C24:0	-	0,2

Table 3 Main properties of the unused vegetable oil, spent frying oil and their mixtures

Properties	HFFA*	**A**	**B**	**C**	**D**	SF**
Density at 15°C, g/cm^3	0,9231	0,9229	0,9225	0,9219	0,9214	0,9212
Kinematical viscosity at 40°C, mm^2/sec	36,4	36,2	34,2	32,6	31,9	31,5
Kinematical viscosity at 100°C, mm^2/sec	5,33	5,67	6,39	6,96	7,58	7,63
Flash point, open cup, °C	> 300					
Iodine value, g Iodine/100g	126	123	120	117	115	115
Acid value, mg KOH/g	65	39	25	13	1,0	0,9
CFPP, °C	+19	+18	+16	+13	+12	+11

** HFFA: high free fatty acid, ** SF: unused vegetable oil*
A, B, C, D: various mixtures of the previous

2.3. Methods

Evaluation of the feed and products was performed according to methods specified by EN 14214:2004 (Automotive fuels – Fatty acid methyl esters (FAME) for biodiesel engines – Requirements and test methods) standard, complying with the precision data of the standard.

Properties	Unit	Test method
Ester content	% (m/m)	EN 14103
Density at 20°C	kg/m^3	EN ISO 3675 EN ISO 12185
Kinematical viscosity at 40°C	mm^2/s	EN ISO 3104
Flash point, closed cup,	°C	EN ISO 3679
Sulphur content	mg/kg	EN ISO 20846
Conradson carbon (from 10% distillation residue)	% (m/m)	EN ISO 10370
Cetane number		EN ISO 5165
Cold filter plugging point, CFPP	°C	EN 116
Sulfated ash content	% (m/m)	ISO 3987
Water content	mg/kg	EN ISO 12937
Total contamination	mg/kg	EN 12662
Copper strip corrosion (3 h at 50°C)	rating	EN ISO 2160
Oxidation stability, 110°C	hours	EN 14112
Acid value	mg KOH/g	EN 14104
Iodine value	g Iodine/ 100 g	EN 14111
Linolenic acid methyl ester	% (m/m)	EN 14103
Polyunsaturated methyl ester (>=4 double bonds)	% (m/m)	-
Methanol content	% (m/m)	EN 14110
Monoglyceride content	% (m/m)	EN 14105
Diglyceride content	% (m/m)	EN 14105
Triglyceride content	% (m/m)	EN 14105
Free glycerol	% (m/m)	EN 14105 EN 14106
Total glycerol	% (m/m)	EN 14105
Group I. metals (Na+K) Group II. metals (Ca+Mg)	mg/kg mg/kg	EN 14108 EN 14109 prEN 14538
Phosphorus content	mg/kg	EN 14107

2.4. Experimental method

Tetrahydrofuran (THF) and dioxane co-solvent was added to the methanol in a ratio of 40:1 in order to improve the solubility of methanol in the vegetable oil and attaining better phase contacting. Conditions of the combined transesterification were as follows: *1.step:* 60°C, ratio of methanol+THF/vegetable oil: 4:1, 15% concentrated sulphuric acid (related to the amount of vegetable oil), reaction time: 0.5-6 h; *2. step:* 60°C, ratio of methanol+THF/vegetable oil: 4:1, 3.0% Na methylate (related to the amount of vegetable oil), reaction time: 2 h. The transesterification experiments were also carried out with dioxane co-solvent under the same conditions.

After the desired reaction time the products were immediately cooled in water containing ice while stochiometric amount of sodium hydroxide dissolved in water was added to the reaction mixture to neutralize the sulphuric acid. The volume of dilution water was equal to that of the base reaction mixture. Afterwards, the obtained reaction mixtures were extracted with dichloromethane three times. The volume of the extracting medium was four times as much as that of the base reaction mixture. After separating the organic phase and drying it by anhydrous sodium sulphate, dichloromethane was removed by vacuum distillation. The same process was performed after the alkali catalyzed transesterification, too, where hydrochloric acid was used to neutralize sodium methylate.

2.5 Results and discussion

During our experiments alkali catalysed transesterification of all 6 feeds with a reaction time of 2 hours was carried out without acidic pre-esterification. Based on the obtained results (Figure 1) it was established that there were no significant differences between the characteristics of the products obtained by transesterification of the unused sunflower oil and those of the mixture having 0.5% free fatty acid content. Fatty acid methyl ester content of higher than 96.5% could only be attained by using these two feeds. Accordingly, fatty acid content of the feed practically does not influence the alkali catalysed transesterification if it is present in low concentration (≤0.5%). In case of the other feeds, the applied catalyst formed soaps with the free fatty acids and it was not able to catalyse the transesterifying reactions (Table 4). Separation of the products was more complicated and sulphate ash content of the products became significantly higher when soaps had been formed. Additionally, Group I metal content (Na+K) of products became higher, too. Therefore if it is necessary for reduce the free fatty acid content of the mixtures of spent frying oils and sunflower oils. A possible way is to apply an acid catalysed pre-esterification step prior to the main transesterification. Feeds “HFFA”, “A”, “B” and “C” were pre-esterified by using acid catalyst, first without solvents, then in the presence of THF co-solvent. The high reaction time experienced at the acid catalysed transesterification (Figure 2) substantially decreased with the application of solvent (Figure 3). Free fatty acid content of feed “HFFA” was still ca. 4% after 2 hours of reaction time. Fatty acid contents in case of feed “A”, “B” and “C” were all below 0.1% after 4 hours of reaction time (Figure 3).

Figure 1 Change of fatty acid methyl ester content during the alkali catalyzed transesterification (without pre-esterification)

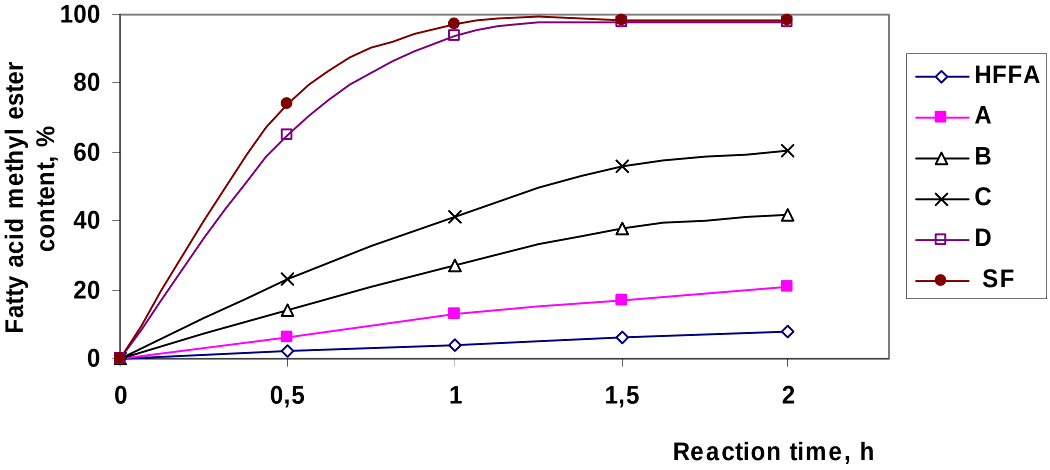


Figure 2 Change of free fatty acid content during the acidic pre-esterification in the absence of co-solvent

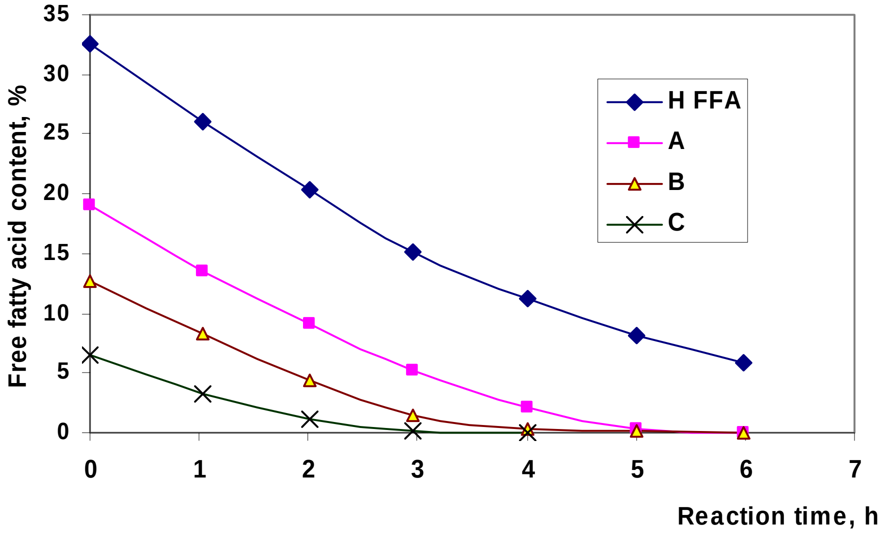


Figure 3 Change of free fatty acid content during the acidic pre-esterification in the presence of THF co-solvent

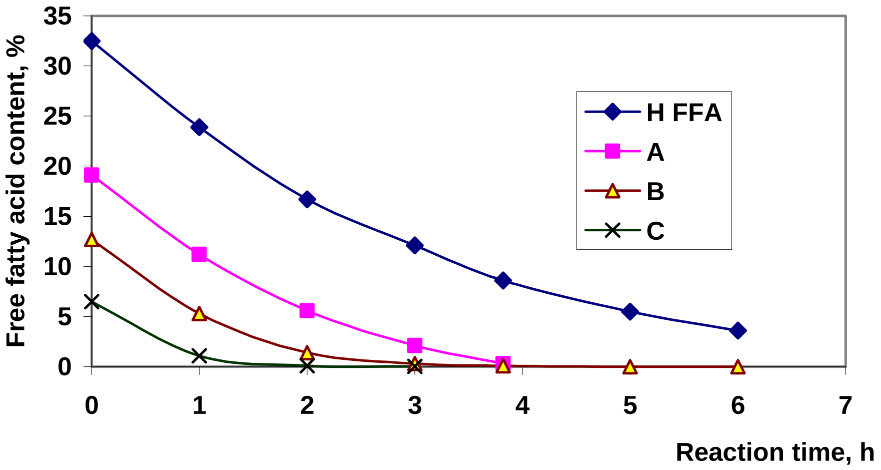
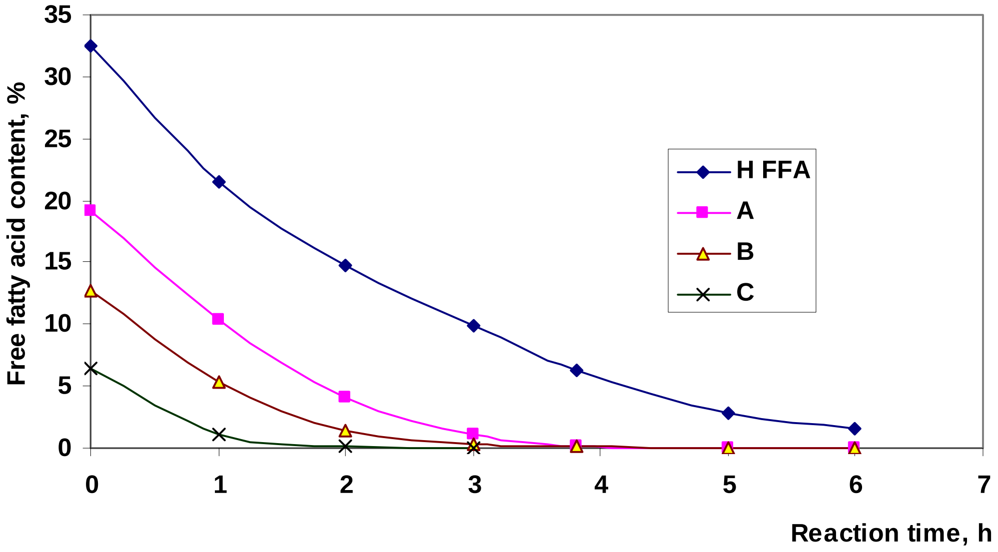


Table 4 Mass balance of the alkali catalyzed transesterification (without pre-esterification)

	HFFA	A	B	C
Feed composition, %				
Triglyceride content	57,42	68,82	74,27	79,54
Free fatty acid content	27,65	16,25	10,80	5,53
Methanol	12,37	12,37	12,37	12,37
Na-methylate	2,55	2,55	2,55	2,55
Total feed	100,00	100,00	100,00	100,00
Product composition, %				
Methyl ester	4,60	17,87	35,77	51,62
Glycerol	0,48	1,86	3,73	5,38
Monoglicerid content	0,58	0,77	0,97	0,77
Diglyceride content	1,74	5,61	4,64	4,45
Triglyceride content	47,56	43,12	31,52	21,95
Soap	14,25	10,51	8,76	5,84
Methanol	14,42	12,31	10,05	7,80
Free fatty acid content	14,42	6,50	2,68	0,12
Na-methylate	0,00	0,67	0,99	1,51
Other	1,95	0,78	0,90	0,56
Total product, %	100	100	100	100

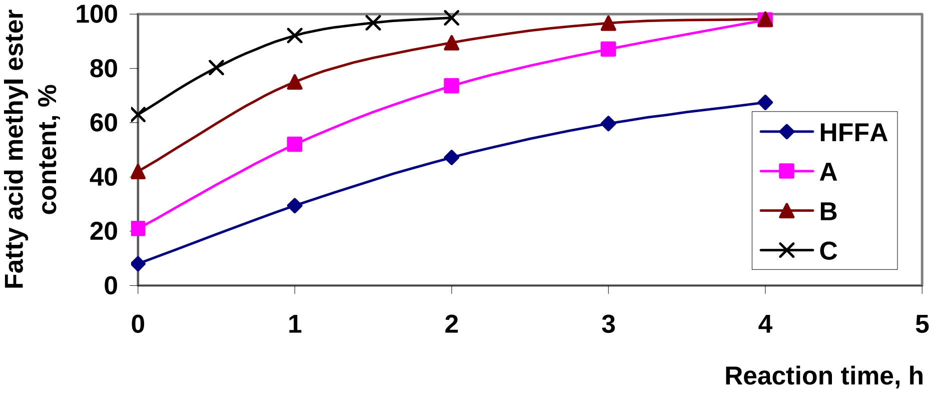
The same pre-esterification experiments were carried out using dioxane co-solvent. On the basis of the results we concluded that the rate of esterification reaction is significantly higher (Figure 4), the reaction time is lower by about half an hour compared with the case when THF was used. By applying this solvent we were not able to reduce the free fatty acid content of feed “HFFA” below 0.1% within 6 h of reaction time. Although transesterification was faster in the presence of dioxane it has to be noted that the price of dioxane is twice as much as that of the THF.

Figure 4 Change of free fatty acid content during the acidic pre-esterification in the presence of dioxane co-solvent



Mixtures of used frying oils/unused sunflower oil of <0.1% free fatty acid content obtained by acidic pre-esterification, transesterification experiments were carried out in the presence of Na-methylate catalyst for 2 hours of reaction time. Figure 5 illustrates that fatty acid methyl ester content of the products obtained by the combined transesterification (reaction time: 4 h pre and 2 h main) of feed "HFFA" was only ca. 60% due to high free fatty acid content of the feed. Fatty acid methyl ester content of several products was higher than 96.5% specified by the currently valid EU standard. In case of feed "C" the mixture produced by combined transesterification with a pre-esterification time of 2 h, the yield of fatty acid methyl esters was higher than 98%.

Figure 5 Change of fatty acid methyl ester content of the end product during the combined transesterification as a function of the reaction time of pre-esterification (reaction time of alkali transesterification: 2 h)



Quality and performance characteristics of biodiesel produced by transesterification of various feeds (spent frying oil, unused sunflower oil and mixtures of the previous) are summarized in Table 5. Based on the results it was established that– excluding feed "HFFA" – we were able to find a conversion process and process conditions suitable for the production of biodiesel which comply with the requirements of the currently valid EU standard. The products met the CFPP specifications of standard by applying additive.

Conclusions

Based on the results of our experiments carried out without the pre-esterification step, we concluded that fatty acid methyl ester mixtures complying with the currently valid standard can be produced by alkali catalyzed transesterification from vegetable oils of ≤0.5% free fatty acid content and from mixtures of spent frying oil/unused sunflower oil. Consequently, free fatty acid content of lower than 0.5% does not significantly affect the transesterification in the presence of alkali catalyst.

In case of feeds "HFFA", "A, "B" and "C" an acidic pre-esterification was necessary to attain a reasonable fatty acid methyl ester content. During the pre-esterification dioxane proved to be more effective from the two investigated solvents (THF and dioxane); the statistically variant differences were not too high and the price of dioxane is the double THF's. The application of solvents significantly reduces the reaction time during the acid catalysed transesterification providing an opportunity to capacity increase or to the reduction of the size of transesterification plant and thus of the investment cost, too.

During the alkali catalysed transesterification of the intermediates produced in the acidic transesterification step a methyl ester yield of only ca. 60% could be attained in case of the combined transesterification (4 h pre-esterification followed by 2 h alkali transesterification) of feed "HFFA" of high free fatty acid content (32.5). With the other combined transesterification >96.5% methyl ester yield could be attained. We were able to find process parameters of the transesterification suitable to produce product mixtures which comply with the specifications of the currently valid EU standard (except in case of feed "HFFA").

Table 5 Main characteristics of fatty acid methyl esters (end products)

Characteristics	Name of biodiesel sample						Standard EN 14214
	HFFA	A	B	C	D	SF	
Ester content, %	67.5	97.9	98.2	98.6	97.8	98.3	>96.5
Density at 15°C, g/cm^3	0.9106	0.8869	0.8861	0.8875	0.8871	0.8868	0.860-0.900
Kinematical viscosity at 40°C, mm^2/sec	4.56	4.35	4.28	4.32	4.38	4.34	3.5-5.0
Flash point, closed cup, °C	132	121	122	125	122	120	>101
Sulphur content, mg/kg	5	6	5	5	6	5	<10
Conradson carbon (from 10% distillation residue), %	0.5	0.22	0.20	0.20	0.18	0.11	<0.3
Cold filter plugging point, CFPP, °C	+5	-5	-5	-5	-6	-5	-20
Water content, ppm	296	276	280	274	285	257	<500
Copper strip corrosion (3 h at 50°C)	Class 1						Class 1
Oxidation stability, 110°C, hours	5.2	9.5	9.4	9.4	9.6	10.4	>6.0
Acid value, mg KOH/g	3.1	0.1	0.1	0.1	0.1	0.10	<0.5
Iodine value, g I_2/100g	124	120	119	117	114	114	<120
Methanol content, %	0.1	0.1	0.1	0.1	0.1	0.1	<0.2
Monoglyceride content, %	1.8		0.20	0.32	0.41	0.28	<0.8
Diglyceride content, %	4.3		0.10	0.13	0.14	0.11	<0.2
Triglyceride content, %	24.7		0.15	0.11	0.1	0.12	<0.2
Free glycerol content, %	0.03		0.015	0.015	0.015	0.011	<0.02
Total glycerol content, %	0.4		0.14	0.13	0.12	0.11	<0.25
Phosphorus content, mg/kg	<1	<1	<1	<1	<1	<1	<10
Group I. metals (Na+K), mg/kg	<1	<1	<1	<1	<1	<1	<5

REFERENCES

[1] Dimming, Th., Haupt, J., Radig, W.: Freiberger. Forschungshefte.A, **1999**., A852, 34-60.

[2] Reinhardt, G.A., Gärtner S.O.: 4th International Colloquium on Fuels 2003, Technische Akademie Esslingen, Ostfildern (Germany), 15-16., January **2003.**, 111-114.

[3] Krahl, J., Munack A., Schröder O., Stein, H., Dutz M., Bünger J.: 4th International Colloquium on Fuels 2003, Technische Akademie Esslingen, Ostfildern (Germany), 15-16., January **2003.**, 115-123.

[4] Hancsók, J.; Kovács, F.: The Biodiesel. Essay, BME OMIKK Environmental Papers, , Budapest, January, 2002, 56.

[5] Directive 2003/30/EC of the European Parliament and of the Council on the promotion of the use of biofuels or other renewable fuels for transport, May, 2003.

[6] Wehlmann, J.: Freiberger. Forschungshefte.A, **1999**., A852, 61-75.

[7] Karaosmanoglu, F., Kurt, G.: Energy Sources, 20(9), **1998**., 867-574.

[8] Canakci, M., Gerpen, J.V.: Transaction of the ASAE, 42(5), **1999**, 1203-1210.

[9] Boocock, D.G.B. Biodiesel: Myths, Challenges, Solutions and Luck. 2003. „53rd Canadian Chem. Eng. Conf." 26-29. October 2003.