Enzymatic transesterification of Hungarian rapeseed and sunflower oils

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Abstract

Application of transportation fuels containing biomass-derived components has emerged into focus in the last years. The main reason of this tendency is the energy policy of the European Union, declared in Directive 2003/30/EC of the European Council and Parliament. A major recommendation of this Directive is that member states are asked to ensure that a minimum proportion of biofuels and other renewable fuels are blended into transportation fuels. This proportion is proposed to be 2%, calculated on the basis of energy content of all gasoline and diesel fuel for transport purposes placed on their markets by 31 December 2005. The proportion of biofuels shall be increased to 5.75% by 2010. According to the latest proposal, the share of biomass derived components should be increased to 10% by 2020.

This target can be achieved with the application of biodiesel, which is produced from triglycerides. Quite a number of feedstocks are available for the production of biodiesel. Out of them a very important one is the rapeseed oil obtained from rape, which can be cultivated with high yield in the western part of Europe. Another important raw material is the sunflower, which can be efficiently cultivated in the climate and geographical conditions of the Central European Region. The two vegetable oils are reasonable for Hungary as feedstocks for biodiesel production.

During the research work, Hungarian vegetable oils produced by pressing were refined under identical conditions. Biodiesels were produced by batch technology of enzymatic catalysis (Novozym 435) from the refined oils using identical process condition. Quality properties of biodiesels were determined by standard test methods according to EN 14214. Monoester content of the biodiesels produced with the above described method was above 98.5. The most favorable results of the different analytical tests were observed in case of the biodiesel of highest oleic acid methyl ester content, which was produced from the sunflower oil, obtained from an improved type of sunflower species.

Keywords: Hungarian vegetable oils, enzymatic transesterification, biodiesel

1. Introduction

The European Union facilitated the penetration of biofuels with the establishment of Directive 2003/30/EC, which resulted in a biofuels share of 1% in the EU by 2005, calculated on the total amount of transportation fuels consumed [COM (2006) 845]. The most recent proposal of the European Union is to raise the share of biofuels to 10% by 2020. This proposed value can be accomplished by utilization of different vegetable oils and its derivatives as fuels. The application of triglycerides as fuels are the following:

- direct blending into diesel fuels,
- transesterification to biodiesel fuels,
- fuel blending component by different cracking processes (engine fuel, jet, diesel fuel).

Recently, among these methods the use of biodiesels gained by the transesterification of triglycerides by methanol is the most preferred (Fig. 1) (Anon., 2006).

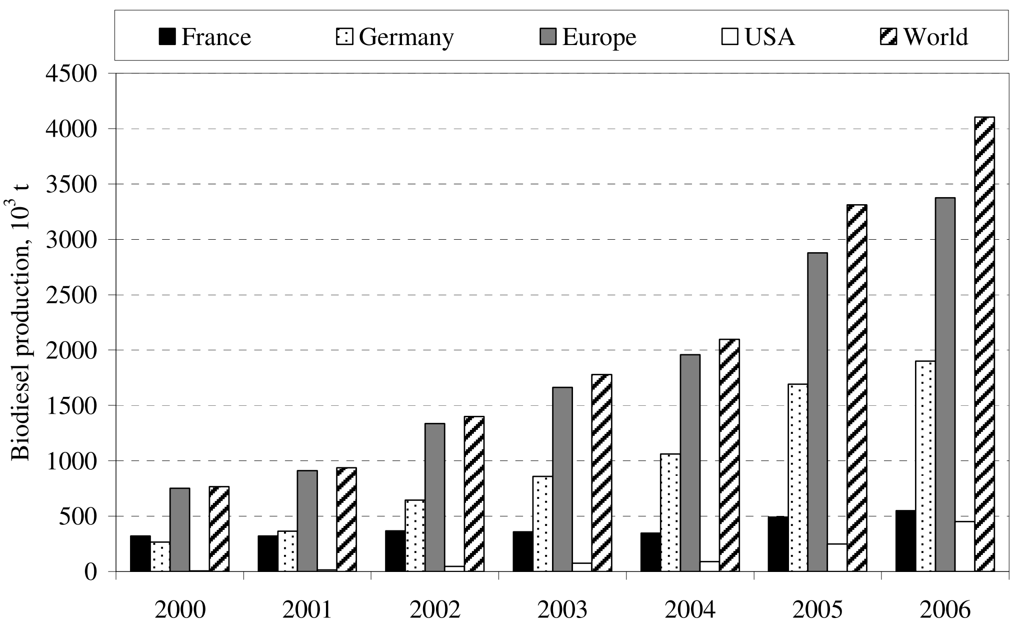

Figure 1: The quantity of biodiesels produced

Quite a number of feedstocks are available for the production of biodiesel (Körbitz, 1999): vegetable oils produced from different plants, animal fat and used frying oil, but fuel is produced from a few of them. There is a significant difference between the distribution of the produced vegetable oils and the distribution of biodiesel feedstocks. Nowadays soybean oil, palm oil and palmkerneloil are produced in highest amount in the world (Fig. 2/left; Mielke, T. (2007), but mainly rapeseed oil and sunflower oil are used as biodiesel feedstock (Fig. 2/right), because the soybean oil, palmoil and palmkernel oil are mainly used for food and cosmetic purposes.

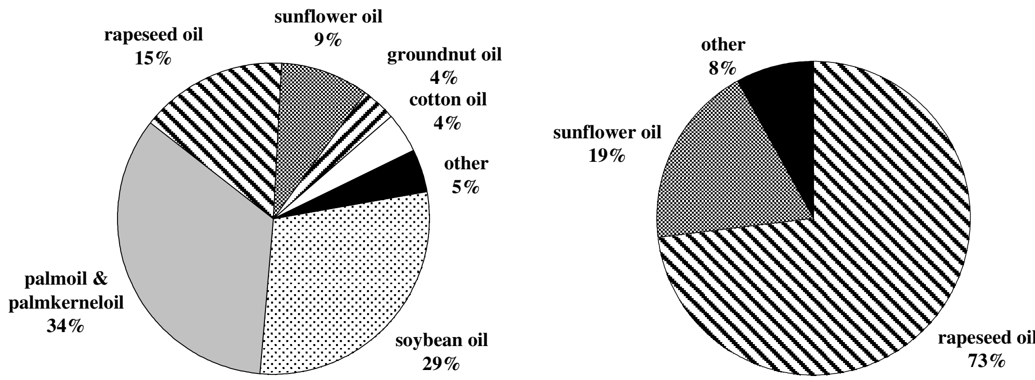

Figure 2. Share of biodiesel – purpose vegetable oils (right side) in the total vegetable oil production (left side)

In the western part of Europe (Germany, France) the main feedstock of biodiesel production is the rapeseed oil obtained from rape, which can be cultivated with high yield. At sufficient climatic and geographical conditions a yield of 3-4 t rapeseed/ha can be obtained in case of winter rape which is harvested usually at the end of July (Bendz, K., 2006). The yield of spring rape, which is usually harvested in September, is lower by aprox. 1 t rapeseed/ ha (Bendz, K., 2006).

Another important raw material is the sunflower, which can be efficiently cultivated in the climate and geographical conditions of the Central European Region. At the begining warm and wet weather is needed for growing of sunflower. At the begining of blooming humid and warm weather is required, while needs maturation dry and sunny weather is needed. The avarage yield of sunflower seed is between 1.8-2.0 t/ha in the European Union (Bendz, K., 2006).

In the last couple of years expediently improved sunflower plant with high oleicacid content came into front. This is because the oil from the conventional sunflower contains bigger amount of polyunsatureted fatty acids (linoleic acid C18:2, linolenic acid; C18:3), which have adverse effect of the iodine number of biodiesel. In general, the iodine number limit of EN 14214: 2004 standard can not be achieved with biodiesel which produced from conventional sunflower oil, so it can not be used directly as diesel fuel.

These two vegetable oils are reasonable for Hungary as feedstocks for biodiesel production (Bélafi-Bakó, 2002; Hancsók, 2005). In Hungary the cultivated area of rape was between 70000-140000 ha. The amount of harvested rapeseed was between 100000-300000 t/year, and the obtained rapeseed oil was aprox. 50000-120000 t/year in 2005 (Nemes, F., 2006). In 2007 the cultivation area of the winter and spring rape is aprox. 340000 ha because biodiesel production has started. The amount of harvested sunflower seed (1,0-1,2 million t) is bigger than the rapeseed, but a part of this amount is used for food purpose (Bendz, K., 2006). In 2007 the area of the improved sunflower was aprox. 60000 ha, the area of conventional sunflower was aprox. 340000 ha in Hungary.

2. Experimental

The aim of our experimental work was to investigate the possibilities of producing high quality fatty acid methyl-ester blends. In our research work, the possibility of the transesterification of different vegetable oils was investigated by using Candida antartica lipase enzyme. Furthermore, the effect of fatty acid composition of the feeds on the characteristics of biodiesel products was studied. Suitability of biodiesel products considering the requirements of the standard (EN 14214) was also investigated.

The transesterification was carried out in the presence of Candida Antarctica (Novozym 435) immobilized lipase enzyme. The operational parameters during our experimental work were based on our previous results (Krár, M., 2005; Kovács, F., 2003). The transesterification was conducted at 50±1 °C in the presence of 12 % (of the total amount of reactants) Candida Antarctica (Novozym 435) immobilized lipase enzyme. Methanol was fed in 8 equal portions. The reaction time was 3, 6, 9, 12, 16 hours. When choosing the methanol:triglyceride ratio for the reaction a small methanol excess was considered. Thus the theoretical 3:1 methanol:triglyceride molar ratio was raised to 4:1.

2.1. Experimental apparatus

The transesterification was carried out by the use of the New Brunswick G24 type shaker. Simultaneously all feedstock could be put into the shaker, thus the same parameters could be assured.

2.2. Materials

During our experimental work rapeseed oil (R) and sunflower oils were used as feeds. Two sunflower oils were conventional species (S-1 and S-2), the another is improved one (HOS). Their fatty acid composition can be found in Table I.

Immobilized lipase enzyme, Novozyme 435 – received as a kind gift from Novo Nordisk, Denmark – was used for the transesterifying experiments. The enzyme obtained from Candida antarctica was immobilized on macroporous resin support, diameter 0.3-0.9 mm, its reported activity was 7000 PLA/g (Bélafi-Bakó, K., 2002).
Methanol of analytical grade was also used for the transesterification.

2.3. Test methods

Properties of the feed and products were determined by standard test methods specified by EN 14214: 2004. (Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods), complying with the specified precision data.

Table I: Fatty acid composition of vegetable oils

Fatty acid composition*, %	**S-1**	**S-2**	**HOS**	**R**
C16:0	7.6	6.6	2.4	4.0
C16:1	0.1	0.1	0.1	0.2
C18:0	3.2	4.0	2.5	1.7
C18:1	20.4	26.4	91.8	75.5
C18:2	67.6	61.7	1.2	12.3
C18:3	0.1	0.1	0.6	5.2
C20:0	0.2	0.2	0.8	0.3
C20:1	0.1	0.1	0.5	0.7
C22:0	0.5	0.6	0.1	0.1
C24:0	0.2	0.2	0.0	0.0

*The first number represents the number of carbon atoms and the second means the number of double bonds in the molecule

3. Results and discussion

After the reaction time of 16 hours we found only a few percent of difference in the methyl-ester content of the different samples. Methyl ester content of the products gained through enzimcatalytic transesterification was higher than 98.5%. The highest methyl ester content was achieved with the transesterification of the sunflower oil of high oleic acid content (Fig. 2).

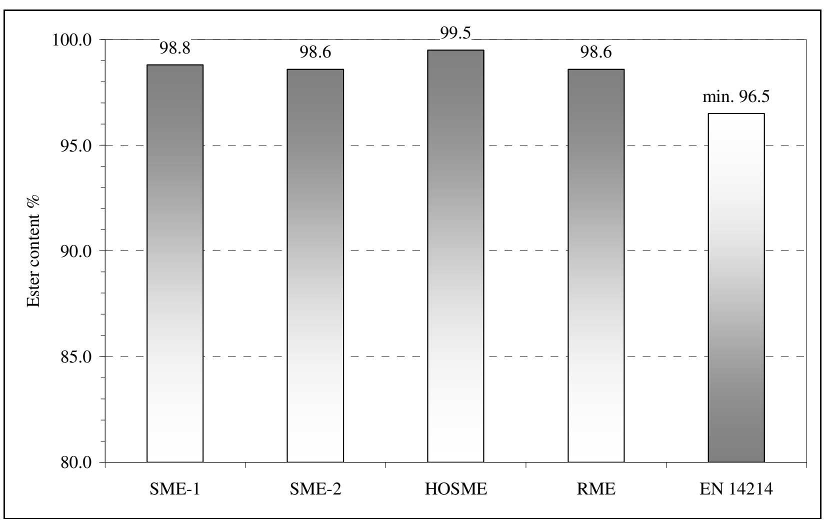

Figure 3. Methlyester content of biodiesels

The kinematical viscosity at 40 °C, the density and the flash point of all feedstock types were only slightly different, and decreased significantly during the transesterification reactions. These values have met the specification of the EN 14214: 2004 biodiesel standard.

On the basis of the melting point of the individual fatty acid methyl esters it is clear, that the more double bonds the molecule contains (i.e. the more unsaturated it is), the lower melting point it has (Table 3; Dimming, Th., 1999.). In case of the saturated fatty acid methyl ester molecules, the melting point significantly increases with the carbon number and the difference in the melting point of the saturated stearic acid methyl ester and that of the unsaturated oleic acid methyl ester of same carbon number (one double bond) is nearly 60°C, which can be considered as very high. Therefore, regarding the cold flow properties of the biodiesels the carbon number and the degree of saturation of the methyl ester molecules are very important.

Table 4. Melting point of several fatty acid methyl esters contained in biodiesels

Name	Symbol	Melting point, °C
Lauric acid methyl ester	C12:0	+ 5.2
Myristic acid methyl ester	C14:0	+19.0
Palmitic acid methyl ester	C16:0	+30.0
Stearic acid methyl ester	C18:0	+39.1
Oleic acid methyl ester	C18:1	-19.9
Linoleic acid methyl ester	C18:2	-35.0
Linolenic acid methyl ester	C18:3	-46.0
Eurcic acid methyl ester	C22:1	-1.2

Biodiesel containing high amount of oleic acid and low quantity of saturated fatty acids (HOSME) has the most favourable cold filter plugging point (CFPP) (Fig. 3.). The samples prepared from the conventional sunflower (SME-1, SME-2) had the worse CFPP value due to their unfavourable fatty acid composition (high content of saturated fatty acids). CFPP of the RME value is between that of the SME and HOSME. Although CFPP values of all the samples comply with requirements of the summer grade (grade A) biodiesel standard for temperate climate regions; they are inappropriate as a winter grade biodiesel.

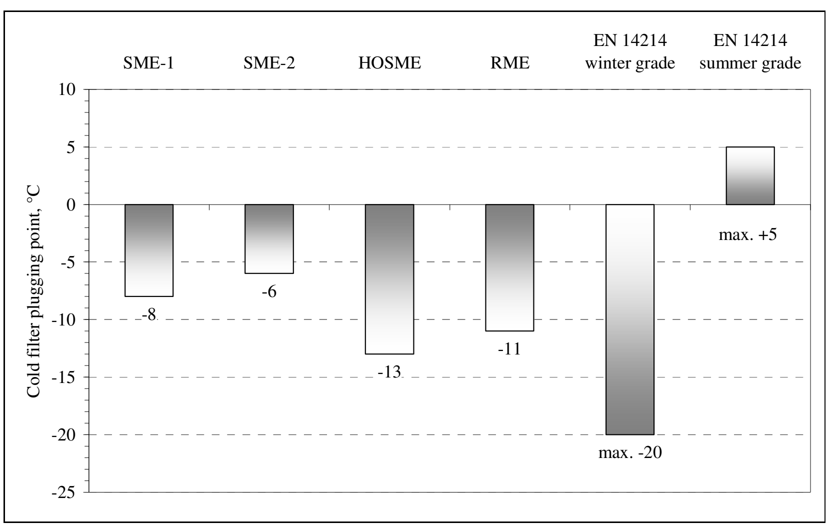

Figure 4. CFPP of biodiesels

The iodine number of fatty acid methyl esters is an important performance property, because it has definite relation between the iodinen umber and number of double bonds in the methyl ester molecule. The higher iodidenumber the biodiesel has, the more methyl esters with unsatureted bonds it contains (Table 5.). The iodine numbers of the saturated methylesters are 0.

Table 5. Iodine number of several fatty acid methyl esters contained in biodiesels

Name	Symbol	Iodine number, g I_2/ 100 g
Lauric acid methyl ester	C12:0	0
Myristic acid methyl ester	C14:0	0
Palmitic acid methyl ester	C16:0	0
Palmitoleic acid methyl ester	C16:1	95
Stearic acid methyl ester	C18:0	0
Oleic acid methyl ester	C18:1	86
Linoleic acid methyl ester	C18:2	173
Linolenic acid methyl ester	C18:3	262
Arachidic acid methyl ester	C20:0	0
Eicosenoic acid methyl ester	C20:1	79
Behenic acid methyl ester	C22:0	0
Eurcic acid methyl ester	C22:1	72

Iodine numbers of biodiesels prepared from the sunflower oil of high oleic acid content and from conventional rapeseed oil have met the specification (max. 120 g I_2/ 100 g) of EN 14214 biodiesel standard (Fig. 5.). Those prepared from conventional sunflower oil, however were off-specification from the point of view of iodine number. Thus they are not suitable to be used directly as a biodiesel fuel.

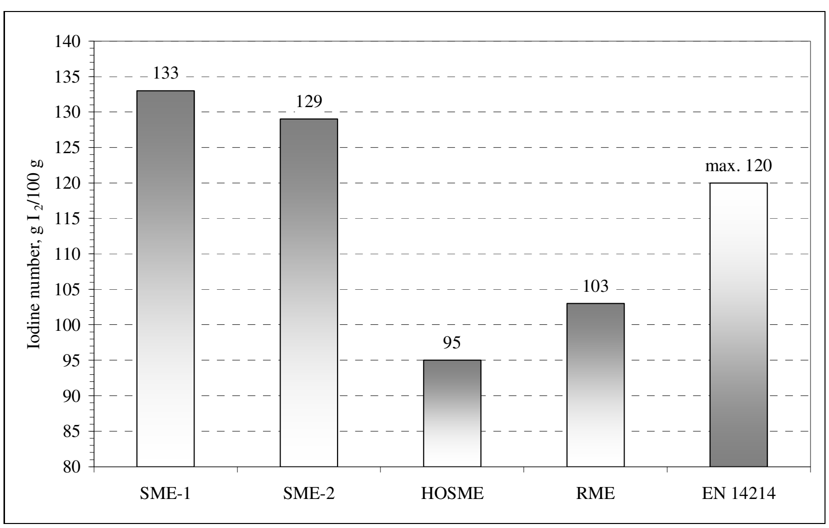

Figure 5. Iodine number of biodiesels

The main properties of biodiesels derived from different Hungarian vegetable oils are shown in Table 2.

Table 2. Main characteristics of selected products (* winter grade diesel fuel; ** summer grade diesel fuel)

Property	SME-1	SME-2	HOSME	RME	EN 14214
Ester content %	98.8	98.6	99.5	98.6	min. 96.5
Density, 15°C, g/cm^3	0.8843	0.8830	0.8861	0.8882	0.860-0.900
Kinematic viscosity, 40°C, mm^2/s	4.64	4.42	4.21	4.32	3.50-5.00
Sulphur content, mg/kg	8	7	5	6	max. 10
Nitrogen content, mg/kg	5	4	3	8	-
Flash point, °C	130	137	122	132	max. 120
Acid value, mg KOH/g	0.3	0.4	0.08	0.15	max. 0.50
Iodine value, g Iodine/100g	133	129	95	103	120
Cold filter plugging point, °C	-8	-6	-13	-11	max. -20*/+5**
Methanol content, %	0.11	0.06	0.12	0.16	max. 0.20
Monoglyceride content, %	0.74	0.50	0.35	0.32	max. 0.80
Diglyceride content, %	0.12	0.10	0.14	0.16	max. 0.20
Triglyceride content, %	0.15	0.12	0.07	0.14	max. 0.20
Free glycerol, %	0.16	0.14	0.07	0.12	max. 0.20
Total glycerol, %	0.23	0.15	0.18	0.19	max. 0.25

4. CONCLUSIONS

Through the transesterification of Hungarian vegetable oils of various fatty acid contents, it was concluded that fatty acid composition does not affect enzymatic transesterification.

Biodiesels produced from different vegetable oils were in compliance with all the requirements of the standard, except cold filter plugging point (winter grade) and iodine value in case of biodiesels which were produced from conventional sunflower oils (SME-1, SME-2). The values of CFPP are still inadequate, thus further plant improvement, possibly after-treatment of biodiesel products (e.g. winterization or additivation) is needed.

From the four biodiesel samples having different fatty acid compositions and other characteristics, the sample of high oleic acid content (HOSME) has the best ester content, iodine number and CFPP value. The low CFPP value and iodine number are results of the lower saturated fatty acid content.

Summarized it can be stated, that biodiesels with good iodine number and CFPP value can only be produced from vegetable oils with high oleic acid content. An ideal biodiesel would only contain oleic acid methyl ester. In order to approach this "perfect biodiesel" further plant improvement is needed.

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