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PRODUCTION AND CHARACTERIZATION OF BIODIESEL FROM RAPESEED OILS

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ABSTRACT. The main objective of the present work was to investigate the influence of rapeseed oil type upon the biodiesel quality. For this purpose eleven types of rapeseed oil were used to obtain biodiesel by alkaline transesterification. The produced biodiesels were examined for several physico–chemical characteristics in order to evaluate and compare their quality with the specifications for biodiesel according to the EN 14214:2004 European standard.

Keywords: *rapeseed oil, biodiesel, alkaline transesterification*

INTRODUCTION

Biodiesel is gaining more and more importance as an attractive alternative fuel due to the depleting nature of fossil fuel resources. The most common method to produce biodiesel, industrially applied, is catalytic transesterification of vegetable oils and animal fats using a homogeneous acid or base catalyst (Fig. 1a). Alkaline-catalyzed transesterification process is normally adopted for biodiesel production because alkaline catalysts are the most effective transesterification catalysts compared to the acid catalysts and also for economic reasons [1, 2]. The basic catalyst reacts with methanol to form sodium methoxide (Fig. 1b) that reacts with the triglycerides to produce biodiesel (fatty acid methyl esters, FAMEs). The main by-product is glycerol which, after purification, can be used for pharmaceutical and cosmetic purposes. Free fatty acids, water and unreacted alkaline catalyst are also present. Thus, complicated purification steps are needed in order to obtain a pure biodiesel achieving the standard requirements. When the acidity of a feedstock is high the reaction between the free fatty acids and the basic catalyst produces soap (Fig. 1c). Since soap is a surfactant it forms emulsions and makes the separation between FAMEs and glycerol difficult. Thus, in the presence of a high content of free fatty acids an acid-catalyzed process is used.

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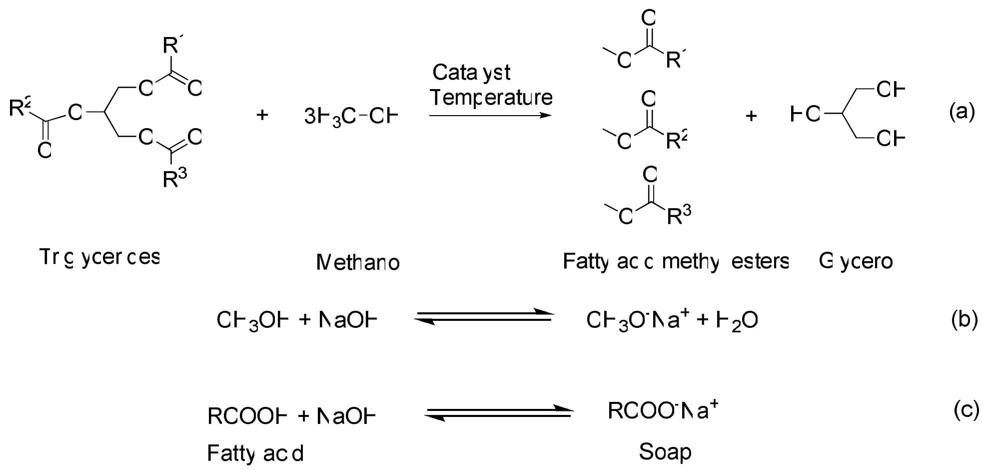

Figure 1. (a) Methanolysis reaction of triglycerides for the production of Fatty Acid Methyl Esters(biodiesel); (b) Methoxide formation; (c) Unwanted reaction of soap formation due to the presence of free fatty acids

Rapeseed (*Brassica napus*) is widely cultivated throughout the world for the production of animal feed, vegetable oil and biodiesel. Rapeseed oil is one of the preferred oil stocks for biodiesel production, partly because rapeseed produces more oil per unit of land area compared to other oil sources, ranking fourth in the world with respect to production, after soybean, palm and cottonseed [3]. The properties of the biodiesel fuel are strongly influenced by the structure and distribution of the component fatty acid methyl esters which vary depending on the source.

The main objective of the present work was to investigate the influence of rapeseed oil type upon the biodiesel quality. For this purpose eleven types of rapeseed oils were used to obtain biodiesel by alkaline transesterification. The reaction conditions used for methanolysis of rapeseed oils were: 1.5 % (w/w by oil weight) KOH as catalyst, methanol/oil molar ratio 6:1, reaction temperature 60℃, rate of mixing 300 rpm and a reaction time of 1 h. The produced biodiesel was examined for several physico–chemical characteristics in order to evaluate and compare its quality with the specifications for biodiesel according to the EN 14214:2004 European standard (Table 1) [4].

Table 1. Generally applicable requirements and related test methods for several physico-chemical characteristics necessary for FAME use as diesel fuel

Property	**Unit**	**Limits**		**Test method**
		Minimum	**Maximum**	
Density, 15℃	Kg/m ^{3}	860	900	EN ISO 3675
Viscosity, 40℃	mm ^{2}/s	3.50	5.00	ASTM D 2983-04a

Property	Unit	Limits		Test method
		Minimum	Maximum	
Acid value	mg KOH/g		0.50	EN 14104
Iodine value	gI_2/100g	-	120	EN 14111
Sulfur content	mg/Kg	-	10.0	prEN ISO 20846
Water content	mg/Kg	-	500	EN ISO 12937
Flash point	°C	120		prEN ISO 3679
Ester content	% (m/m)	96.5		EN 14103
Linoleic acid methyl ester	% (m/m)	-	12.0	EN 14103

RESULTS AND DISCUSSION

The biodiesel yield was considered as the ratio between the produced biodiesel weight and the initial rapeseed oil weight, % (w/w). The yields obtained for the transesterification of rapeseed oils are shown in Table 2.

Table 2. The yields obtained for the transesterification reactions of rapeseed oils

Rapeseed biodiesel	Martor I	Martor II	Aviator	Karibik	Formula	Nelson	Octans	Toccata	Petrol	Smart	Speed
Yield, wt %	93.2	93.9	92.9	90.6	57.3	91.3	92.4	92	91.2	93.3	93.4

As shown in the table above, the yields for the alkaline transesterification reactions were greater than 90 % except for FORMULA rapeseed oil, with a yield of only 57.3 %. The reason was the high content of free fatty acids which in the presence of potassium hydroxide determined the formation of soaps, making difficult the conversion of triglycerides to methyl esters and also the separation of reaction products.

The products of above transesterification processes were analyzed, taking into consideration several specifications for biodiesel as fuel in diesel engines. Most of these parameters comply with the limits prescribed in the EN 14214:2004 standard for biodiesel.

For each studied physico-chemical characteristic the values obtained were graphically presented compared with the minimum and/or maximum limits recommended by the quality specifications according to EN 14214:2004 (see Figure 2).

DENSITY

Density is an important property of biodiesel. It represents the weight of a unit volume of fluid. Fuel injection equipment operates on a volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel. The density values for the rapeseed derived biodiesels are schematically presented in Figure 2a. It is noted that only the biodiesel obtained from FORMULA rapeseed oil has exceeded the maximum permissible. This was due to low yield of reaction; much of the oil remained untransformed. The density values for other rapeseed oils were comparable to those reported in the literature [5].

VISCOSITY

Viscosity is a measure of the internal friction or resistance of an oil to flow. As the temperature of oil is increased, its viscosity decreases and it is therefore able to flow more readily. Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The viscosity may be used not only as the indicator of impurities in biodiesel, but also as the control parameter of the transesterification process [6].

The values of the kinematic viscosity at 40°C for the rapeseed oil biodiesels were represented in Figure 2b. Due to low conversion efficiency, the viscosity value for biodiesel obtained from FORMULA oil was higher than the maximum recommended (out of the plotting scale). Biodiesel produced from AVIATOR and MARTOR I oils have slightly exceeded the maximum, but in the literature the viscosity values for rapeseed biodiesel are up to 5.7 mm^2/s [7].

ACID VALUE

High fuel acidity is associated with corrosion and engine deposits, particularly in the fuel injectors. The acid number or acid value indicates the quantity of free fatty acids (FFA) and mineral acids (negligible) present in the sample. According to EN 14104, the acid value is expressed in milligrams (mg) potassium hydroxide (KOH) required to neutralize 1 g of sample.

The acid value of the analyzed biodiesels was ranged 0.09 – 0.42 mg KOH/g. The EN 14214:2004 biodiesel standard approved a maximum acid value for biodiesel of 0.5 mg KOH/g which was fulfilled by all of the produced rapeseed methyl esters (Figure 2c). The highest value of 0.42 mg KOH/g sample was obtained for the FORMULA oil biodiesel, indicating a high content of free fatty acids.

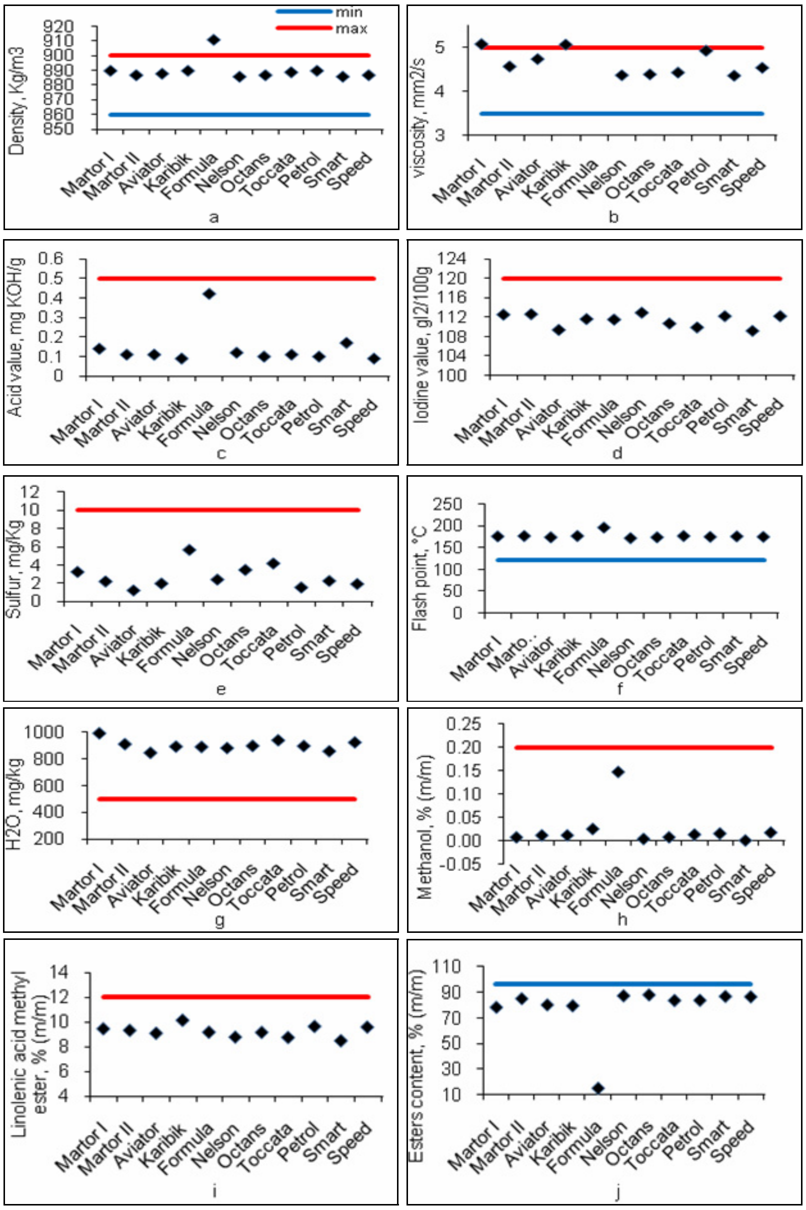

Figure 2. Physico-chemical characteristics of rapeseed derived biodiesels compared with the minimum and/or maximum limits recommended by the quality specifications according to EN 14214:2004 (minimum limit – blue line, maximum limit – red line); **a** - density; **b** - viscosity; **c** - acid value; **d** - iodine value; **e** - sulphur content; **f** - flash point; **g** - water content; **h** - methanol content; **i** - linoleic acid methyl ester content; **j** - ester content

IODINE VALUE

Iodine value depends on the feedstock origin and greatly influences fuel oxidation tendency. Consequently, in order to avoid oxidation, special precautions must be taken during the storage of biodiesel from rapeseed oil with high iodine values, According to EN 14214 European standard methyl esters used as diesel fuel must have an iodine value less than 120 g I_2 per 100 g of sample. Methyl esters obtained in this study had iodine value in the range 109.2 – 112.9 g I_2/100 g (Figure 2d), thus the variations were not considerable.

SULFUR CONTENT

The presence of sulfur in biodiesel samples may be from vegetable oils, for example, from phospholipids present in all vegetable oils or glucosinolates present in rapeseed derived biodiesel [8].The sulfur content of the biodiesels was analyzed by EN ISO 20846 test method, using ultraviolet fluorescence spectrometry. The values were ranged from 1.23–5.64 mg/Kg, as shown in Figure 2e. Values for sulfur content for the rapeseed biodiesels were all situated below the recommended maximum of 10.0 mg/Kg.

FLASH POINT

The flash point of a substance represents the lowest temperature at which it can vaporize to form flammable mixtures when exposed to air. It is a parameter to consider in the handling, storage and safety of fuels and flammable materials. A higher value of flash point decreases the risk of fire. In the case of biodiesel, the flash point (FP) decreases with increasing amounts of residual alcohol and other low-boiling solvents [9]. In this study, only residual methanol can be present in biodiesel. Therefore, the flash point was presupposed to be depending only on the methanol content. For all rapeseed biodiesel samples, the flash point was much higher than the minimum recommended value of 120 °C. The results are plotted in Figure 2f.

WATER CONTENT

The water content in biodiesel is an important factor in the quality control. Water can promote microbial growth, lead to tank corrosion, participate in the formation of emulsions, and cause hydrolysis or hydrolytic oxidation [8]. Therefore, the content of water is limited to 0.05 % (w/w) according to EN 14214. The water content of the rapeseed biodiesel samples was measured using EN ISO 12937 standard test method and in all experiments, the values were higher than the recommended maximum of 500 mg/Kg, as presented in Figure 2g. This indicates an incomplete purification process and the need for additional steps for biodiesel drying.

METHANOL CONTENT

The residual methanol in biodiesel can cause corrosion of metal, mainly of aluminium, and decreases the biodiesel flash point. Besides, it is responsible for cetane number and lubricity decreasing of fuel. The values for the methanol content were situated below the maximum recommended of 0.20% (w/w), for all the types of rapeseed biodiesel submitted to analysis (Figure 2h). The highest value of 0.1469 % (w/w) was obtained for FORMULA oil biodiesel that demonstrated once again the difficulties caused by the formed soaps on the conversion and purification processes.

ESTER CONTENT. LINOLENIC ACID METHYL ESTER CONTENT

The values for ester content of rapeseed biodiesels were all situated below the recommended minimum of 96.5% (w/w). This requires additional steps of purification and drying to achieve a more efficient removal of water and of by-products (mono-, di- triglycerides, and glycerol) to obtain a product that meets the quality specifications. Values for ester content are presented in Figure 2j. In the case of biodiesel obtained from FORMULA oil the ester content was only 14.9 % (w/w), indicating a very low conversion of triglycerides into methyl esters. The values for linolenic acid methyl ester content were all situated below the maximum recommended value of 12% (w/w) (Figure 2i).

A complete purification scheme of crude biodiesel in order to obtain a finished product that meets EN 14214 quality specifications is proposed in Figure 3.

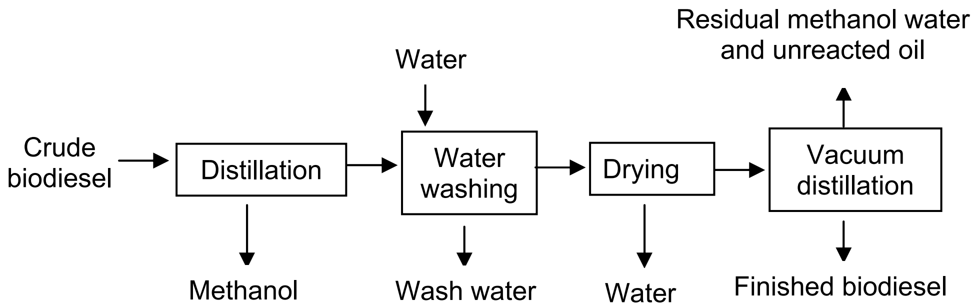

Figure 3. Purification scheme of crude biodiesel in order to obtain a finished product that meets EN 14214 quality specifications.

Crude biodiesel is first submitted to a distillation process in order to remove methanol from other components. Then a water washing step is used to remove remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel. After the wash process, the remaining water is removed from the biodiesel by a drying process. A final vacuum distillation is required to remove any residual methanol, water and unreacted oil and to obtain a biofuel purity that meets EN 14214 specifications. Vacuum operating conditions are required in order to keep the temperature low enough to avoid the biofuel degradation.

HIGHER HEATING VALUE

Higher heating value (HHV) is an important property defining the energy content and thereby efficiency of fuels that determines in the case of biodiesel its suitability as an alternative to diesel fuels. As it can be observed from Table 3, the values were ranged from 38.8 to 40.1 MJ/kg. Higher HHVs were obtained for experiments in which the yields of ester were higher while the lowest value was obtained for FORMULA oil due to low conversion of triglycerides. For the other rapeseed biodiesels the variations were not considerable. The European standard EN 14214 approved a suitable heating value for biodiesel of 35 MJ/kg.

Table 3. High heating values for rapeseed derived biodiesels

Rapeseed biodiesel	Martor I	Martor II	Aviator	Karibik	Formula	Nelson	Octans	Toccata	Petrol	Smart	Speed
HHV, MJ/Kg	39.9	39.9	39.9	38.9	38.8	40.0	39.9	39.9	40.1	39.9	39.9

CONCLUSIONS

The results obtained in the present study regarding the production of biodiesel using alkaline transesterification of eleven varieties of rapeseed oil as feedstocks together with the physico-chemical characterization of the biodiesels obtained, showed that only the rapeseed oil from the FORMULA hybrid proved inadequate for the alkaline transesterification process due to high levels of free fatty acids that led to the formation of soaps. The consequence was a low yield for the transesterification process of only 57.3% due to incomplete conversion of triglycerides into esters. The formed soaps caused many difficulties also in the purification steps of crude biodiesel that included: separation, washing and drying, ester content of the final product being only 14.9% (w/w). The other rapeseed oils tested: control sample variety oils (MARTOR I, MARTOR II), AVIATOR, KARIBIK, NELSON, OCTANS, TOCCATA, PETROL, SMART, SPEED gave yields higher than 90% and the physico-chemical characterization of these biodiesels demonstrated that these rapeseed oils can be successfully used as feedstocks for biodiesel production using alkaline transesterification.

EXPERIMENTAL SECTION

Materials and methods

11 types of rapeseed oil: two rapeseed oils from DEXTER control sample variety named further MARTOR I and MARTOR II (obtained from Saaten-Union) and eight oils obtained from rapeseed hybrids: AVIATOR, KARIBIK, FORMULA, NELSON, OCTANS, TOCCATA, PETROL, SMART, SPEED (obtained from Syngenta). The fatty acid profiles of rapeseed oils are summarized in Table 4. Pure standards of fatty methyl esters (FAMEs) were obtained from Sigma Chemicals Co. (St. Louis, MO, USA). Methanol, n-hexane, potassium hydroxide, and anhydrous magnesium silicate were of Merck (Darmstadt, Germany). All the chemicals used were analytical reagent grade.

Table 4. Fatty acid composition for the rapeseed oils used for biodiesel production

Fatty acids Abr.		Cultivar										
		Dexter control sample variety (Saaten-Union)		Hybrids (Syngenta)								
		Martor I	Martor II	Aviator	Karibik	Formula	Nelson	Octans	Tocatta	Petrol	Smart	Speed
C10	%	0.014	0.013	0.013	0.015	0.013	0.013	0.016	0.014	0.016	0.017	0.015
C12	%	0.010	0.010	0.011	0.009	0.010	0.009	0.009	0.010	0.009	0.009	0.009
C14	%	0.057	0.058	0.065	0.055	0.056	0.056	0.051	0.058	0.051	0.051	0.051
C16	%	4.32	4.24	4.42	4.3	4.18	4.13	4.23	4.06	4.29	3.98	4.23
C16:1	%	0.186	0.191	0.185	0.197	0.176	0.184	0.186	0.174	0.186	0.17	0.193
C18	%	1.67	1.57	1.70	1.66	1.56	1.53	1.69	1.66	1.53	1.85	1.64
C18:1	%	58.2	58.9	59.1	59.17	57.5	58.8	58.3	59.8	59.1	61.4	59.5
C18:2	%	19.4	18.8	18.5	17.31	19.5	19.4	18.5	18.9	18.2	17.2	17.6
C18:3	%	9.27	9.26	8.98	10	8.46	8.67	9.01	8.65	9.5	8.28	9.51
C20	%	0.530	0.474	0.496	0.512	0.474	0.472	0.502	0.488	0.512	0.535	0.495
C22:0	%	0.261	0.220	0.227	0.236	0.224	0.23	0.226	0.224	0.275	0.225	0.229
C22:1	%	-	-	-	-	-	0.048	0.076	0.029	-	-	-
C24:0	%	0.093	-	0.071		0.069	0.091	0.078	0.071	0.096	0.076	-

Alkaline catalyzed transesterification

Single-stage laboratory esterification was carried out in a 250 ml conical flask equipped with a magnetic stirrer. 1.5 g potassium hydroxyde dissolved in 20 ml methanol was added to 100 g vigorously stirred oil. Stirring was continued for 1 h at 60°C. After this time the reaction was stopped, the mixture was transferred to a separatory funnel and the glycerol was allowed to separate for a minimum of 3 h. After separation of the two layers by sedimentation, the upper methyl esters layer was purified by distilling the residual methanol at 80°C. The remaining catalyst was removed by successive rinses with distilled water. Finally, the residual water was eliminated by treatment with anhydrous magnesium silicate at 60 °C for 60 min with stirring. After cooling, the biodiesel was filtered and its quality was tested.

Gas Chromatographic Analysis of Fatty Acid Methyl Ester

The fatty acid methyl ester contents in the reaction mixture were determined using an Agilent 7890A GC gas chromatograph equipped with a DB-WAX capillary column (30m × 0.25mm × 0.25μm) and a flame ionization detector. The column oven temperature was kept at 50 °C for 1 min, heated to 200 °C at 25°C/min, then to 230 °C at 3°C/min and finally maintained for 18 min. The injector and detector temperatures were set to 250 and 280 °C, respectively. Helium was utilized as a carrier gas. The gas chromatography calibration was conducted via the analysis of standard solutions of methyl esters and heptadecanoate methyl ester was used as internal standard.

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