

ENVIRONMENTALLY FRIENDLY PRODUCTION TECHNOLOGY OF BIODIESEL

Pavels Karabesko, Maija Strele, Rasma Serzane, Mara Jure

Riga Technical University, Faculty of Material Science and Applied Chemistry,
Department of Chemical Technology of Biologically Active Compounds
mara@ktf.rtu.lv

Abstract. Biodiesel usually is produced by transesterification of various vegetable oils or animal fats with methanol. Unfortunately, methanol is highly toxic and harmful to human health. Application of bioethanol instead of methanol would lead to more environmentally friendly production technology which almost completely would be based on renewable resources. Currently in Europe there are no biodiesel producers using ethanol as a raw material, nevertheless FAEE (Fatty Acid Ethyl Esters) is used as biodiesel in Brazil. Mandate to CEN for standards for FAEE for use in diesel engines and heating fuels (M/393) was set in 2006. We established the optimal conditions for synthesis of rapeseed oil ethyl esters (REE) by transesterification of oil with bioethanol produced by distillery "Jaunpagasts Plus" Ltd. from local wheat. The best results were reached, when molar ratio of oil to ethanol was 1:6 and KOH was used as a catalyst (1.5 wt% from the mass of oil). The ethanolic solution of KOH was added to oil in two steps and the reaction was carried out at room temperature (the yield of reaction reached 97 %). We have found out the optimal conditions for production of REE by ultrasonication (24 kHz). It is well known that ultrasonication allows replacing a batch processing with continuous flow processing and it reduces investment and operational costs. The results of our experiments show that duration of reaction can be reduced twice in comparison with the classical method and is 0.5 h. We examined commercially available adsorbent Magnesol for purification of the synthesized biodiesel. The technical parameters of our REE corresponded to requirements of LVS EN 14214 set for biodiesel.

Keywords: rapeseed oil ethyl esters, bioethanol, ultrasonication, Magnesol.

Introduction

The worldwide worry regarding environmental protection and the conservation of non-renewable natural resources has given rise to the development of alternative sources of energy to substitute traditional fossil fuels. Biodiesel is expected to play an increasingly important role in the fuel market, as its use can reduce depletion of fossil fuels and harmful emissions. Biodiesel is non-toxic and completely biodegradable. Due to its high flash point, it has low flammability and is safe in use.

Biodiesel usually is produced by transesterification of various vegetable oils or animal fats with methanol. Unfortunately, methanol is highly toxic and harmful to human health. Replacement of methanol with bioethanol would lead to more environmentally friendly production technology which almost completely would be based on renewable resources [1]. Properties of ethyl esters of fatty acids [2] are very similar to the properties of the corresponding methyl esters, unfortunately, from the economical point of view, production of REE is not profitable due to relatively high price of anhydrous ethanol.

Different methods for production of FAEE have been described, e.g., two stage syntheses from rapeseed oil and anhydrous ethanol was carried out in the presence of 0.5 % potassium hydroxide at the 80 °C temperature within 1.5 hours; molar ratio of oil to ethanol was 1:4.2 in the first stage and 1:1.1 in the second stage [3]. The ethanolysis of palm kernel oil has been investigated, using 0.1-0.25 molar ratio of ethanol to oil [4]. The best yield (96 %) of FAEE was obtained in the presence of 1 % potassium hydroxide at the temperature 60 °C, when molar ratio of raw materials was 0.175 and duration of reaction was 2 h. The ethanolysis of refined sunflower oil, carried out at 70 °C using molar ratio oil:ethanol=1:12 and 0.3 % sodium hydroxide as catalyst, provided corresponding esters with 97.2 % yield [5]. A comparative study of ethanolysis of sunflower and rapeseed oil showed [6] that the best conditions for reaction can be reached when catalyst is potassium hydroxide (1.5 %), molar ratio of oil to ethanol is 1:5 and 1:6, temperature is 20 °C and 32 °C, correspondingly.

Previously we investigated [7] the optimal settings for production of REE. We found out, that in the case of absolute ethanol, as well as dehydrated technical ethanol transesterification proceeded best at room temperature (18-20 °C) in the presence of catalyst potassium hydroxide (1.7-2.0 % from oil mass), when molar ratio of oil to ethanol was 1:5 and duration of reaction was 2 h.

The improvement of biodiesel production using low frequency ultrasonication (24 kHz) has been studied [8, 9], leading to reduction of duration of reaction and increase of esters' yield. The application

of ultrasonication for transesterification of sunflower seed oil (molar ratio oil:ethanol=1:7) in the presence of 2 % sodium hydroxide provided the high yield (98 %) of esters even within 40 min [8].

The purification of FAEE with orthophosphoric acid and water usually lead to hardly separable emulsions. The development of FAEE treatment procedure applying *Magnesol* - synthetic magnesium silicate adsorbent - has been described [10].

Materials and methods

Raw materials used for the production of REE: commercial absolute ethanol; bioethanol, produced by distillery “*Jaunpagasts Plus*” Ltd. (Latvia) from local wheat; cold-pressed rapeseed oil, purchased from “*Iecavnieks*” Ltd. (Latvia). The ultrasonication was carried out with 24 kHz frequency using ultrasonograph UP200S/UP400S. The methods used for synthesis of REE are described further.

Results and discussion

Our aim was to establish the optimal conditions for the production of REE from renewable resources of Latvia using transesterification of rapeseed oil with bioethanol of local origin.

Initially, several experiments were carried out using commercial absolute ethanol at room (18-20 °C) and higher (75-80 °C) temperature; duration of reaction varied (see Table 1). Obviously, the best results were obtained when the reaction was run 1 h at room temperature in the presence of 1.3-1.7 % KOH catalyst (from oil mass). The quality of biodiesel was controlled by measuring of kinematic viscosity at 40°C. When transesterification was carried out at higher temperature, glycerol layer did not separate after completion of reaction. It seems that at higher temperatures the presence of potassium salts of free fatty acids (soap) and other by-products lead to emulsification of layers of glycerol and ethyl esters; separation of glycerol becomes impossible.

Table 1

Transesterification of rapeseed oil with absolute ethanol in one stage*

N ^o	Conditions of reaction			Properties of synthesized REE		
	Amount of KOH, %	Temperature, °C	Duration, h	Kinematic viscosity at 40°C, mm ² s ⁻¹	Acid value, mg KOH g ⁻¹	Peroxide value, meq O ₂ kg ⁻¹
1	1.7	75-80	1	5.67**	0.48	11.12
2	1.7	18-20	1	4.88	0.38	3.65
3	1.7	18-20	2	4.87	0.35	3.98
4	1.7	18-20	3	4.88	0.41	2.72
5	1.7	18-20	4.5	4.85	0.47	5.02
6	1.5	18-20	1	4.64	0.41	2.50
7	1.3	18-20	1	4.98	0.50	2.96

* Molar ratio oil:ethanol=1:5, acid value of rapeseed oil is 1.5 mg KOH/g, REE purified by washing with H₃PO₄ and water

** Glycerol did not separate; separation with water

When we ran transesterification with bioethanol at room temperature, the yield of biodiesel reached just 71-82 %. Therefore reaction was repeated adding catalyst-alcohol solution in two steps (see Table 2). The best result (yield of reaction 97 %) was obtained in the experiment N^o 2, when potassium hydroxide was added in 1.3 % and 0.2 % (from oil mass) quantity in the 1st and 2nd stages, correspondingly; thus the total amount of potassium hydroxide was 1.5 %.

The purification process of ethyl esters of fatty acids is encumbered in comparison with methyl esters. The traditional consecutive treatment with solution of *o*-phosphoric acid and water lead to hardly separable emulsion, which requires longer time for settling. Therefore, we carried out experiments (Table 3) applying *Magnesol* for purification of REE.

Table 2

Transesterification of rapeseed oil with bioethanol at room temperature in 2 stages*

N ^o	Amount of catalyst KOH, %			Properties of synthesized REE		
	1 st stage	2 nd stage	Total	Kinematic viscosity at 40 °C, mm ² s ⁻¹	Acid value, mg KOH g ⁻¹	Peroxide value, meq O ₂ kg ⁻¹
1	1.3	0.4	1.7	4.72	0.50	12.75
2	1.3	0.2	1.5	4.93	0.50	6.75
3	1.2	0.4	1.6	4.92	0.50	7.33
4	1.2	0.3	1.5	4.93	0.43	9.27
5	1.1	0.2	1.3	5.02	0.49	10.46
6	1.0	Glycerol did not separate after the 1 st step				

* For the 1st stage molar ratio oil:ethanol=1:5, duration of reaction is 1 h; for the 2nd stage molar ratio oil:ethanol=1:1, duration of reaction is 0.5 h)

This synthetic magnesium silicate adsorbent removes different contaminants: glycerol, methanol, water, soaps and others. The quality parameters of REE purified by both methods are compared in Table 3. The total contamination was less in the case when *o*-phosphoric acid was used; nevertheless, biodiesel treated with *Magnesol* still corresponded to the requirements of the standard LVS EN 14214. The application of *Magnesol* is simpler than workup with acid and water.

Table 3

Comparison of quality parameters of REE purified by different methods

Method of purification	Properties of obtained REE		
	Kinematic viscosity 40 °C, mm ² /s	K ⁺ content, mg kg ⁻¹	Total contamination, mg kg ⁻¹
<i>Magnesol</i> , 1.9 %	4.93	3.48	20.51
10 % H ₃ PO ₄ , water	4.94	1.56	5.56

It is well known that ultrasound assisted transesterification of fatty acids proceeds more quickly allowing replacement of batch processes with continuous flow processes and reduction of investment and operational costs. We have found out the optimal conditions for production of REE using ultrasonication (24 kHz frequency). The results of our experiments (see Table 4) show that duration of reaction can be reduced in comparison with the conventional method and is 0.5 h.

Table 4

Transesterification of rapeseed oil with bioethanol using ultrasonication*

N ^o	Conditions of reaction			Properties of REE		Yield, %	Admixtures in REE, %	
	Amount of KOH, %	Temperature, °C	Duration, min	Kinematic viscosity 40°C, m ² s ⁻¹	Acid value, mg KOH g ⁻¹		Ethanol, water	Precipitates
1	1.7	22	60	5.00	0.15	79.4	4.5	4.7
2	1.7	22	30	4.97	0.14	83.7	4.8	6.6
3	1.7	25	20	5.16	0.20	77.0	4.7	8.0
4	1.7	25	10	5.04	0.16	65.2	4.7	6.2
5	1.7	25	6	Glycerol did not separate				
6	1.7	43	30	4.97	0.20	78.5	4.1	8.1
7	1.8	25	30	5.16	0.20	77.0	4.7	8.0
8	1.4	25	30	5.28	0.41	76.4	3.9	8.7

* Molar ratio oil:ethanol=1:5; ultrasonic amplitude 40%, cycle 0.5-1.0; REE purified by *Magnesol*

We measured the main parameters of REE obtained from bioethanol; the properties of this biodiesel corresponded to the demands of the standard EN 14214 (Table 5).

Table 5

Properties of synthesized REE (exp. N^o2, Table 2)

N ^o	Parameter	Unit	Limit	Determined value	Test method
1	Ester content	% (m m ⁻¹)	≥ 96.5	96.5	LVS EN 14103
2	Density 15°C	kg m ⁻³	800-900	880	LVS EN 3675
3	Viscosity 40°C	mm ² s ⁻¹	3.5-5.0	4.93	LVS EN 3104
4	Flash point	°C	≥ 120	169	LVS EN 22719
5	Water content	mg kg ⁻¹	≤ 500	40	LVS EN ISO 12937
6	Total contamination	mg kg ⁻¹	≤ 24	5.56	LVS EN 12662
7	Peroxide value	meq. O ₂ kg ⁻¹	≤ 100	6.75	ISO 3960
8	Acid value	mg KOH g ⁻¹	≤ 0.50	0.50	LVS EN 14104
9	Iodine value	g I ₂ (100g) ⁻¹	≤ 120	106.6	LVS EN 14111
10	Phosphorus content	mg kg ⁻¹	≤ 10	5.04	ISO 10540-1
11	Ash content	% (m m ⁻¹)	≤ 0.02	0.001	LVS EN 6245
12	Carbon residue	% (m m ⁻¹)	≤ 0.30	0.03	LVS EN 10370
13	K ⁺ content	Mg kg ⁻¹	≤ 5.0	1.56	ČSN 656507

Conclusions

1. Bioethanol produced in Latvia from local wheat can be used instead of methanol for the production of biodiesel.
2. The best yield (97 %) of rapeseed oil ethyl esters was reached by consecutive addition of catalyst-alcohol solution to oil in two stages.
3. Ultrasonication reduces the duration of transesterification twice in comparison with the conventional method – the reaction lasts just 0.5 h.
4. Purification of rapeseed oil ethyl esters can be simplified by application of *Magnesol*.

References

1. Makareviciene V., Janulis P. Environmental effect of rapeseed oil ethyl ester. *Renew. Energ.*, 2003, 28, 2395-2403.
2. Encinar J.M., Gonzalez J.F., Rodriguez-Reinares A. Ethanolysis of frying oil. Biodiesel preparation and characterization. *Fuel Process. Technol.*, 2007, 88, 513-522.
3. Cvengrošova L., Cvengroš J., Hronec M. Rapeseed oil ethyl esters as alternative fuels and their quality control. *Petroleum and Coal*, 1997, 39(3), 36-40.
4. Alamu O.J., Waheed M.A., Jekayinfa S.O. Effect of ethanol-palm kernel oil ratio on alkali-catalyzed biodiesel yield. *Fuel*, 2008, 87, 1529-1533.
5. Kucek K.T., Cesar-Oliveira M.A.F., Wilhelm H.M., Ramos L.P. Ethanolysis of refined soybean oil assisted by sodium and potassium hydroxides. *J. Am. Oil Chem. Soc.*, 2007, 84(4), 385-392.
6. Bouaid A., Martinez M., Aracil J. A comparative study of the production of ethyl esters from vegetable oils as a biodiesel fuel optimization by factorial design. *Chem. Eng. J.*, 2007, 134(1-3), 93-99.
7. Strēle M., Seržane R., Bremers G, Gudriniece E. Pētījumi par eļļām un taukiem. 6. Rapšu eļļas pārēsterificēšana ar etilspirtu. *Latvijas Ķīmijas Žurnāls*, 1999, 4, 67-70.
8. Georgogianni K.G., Kontominas M.G., Pomonis P.J., Avlonitis D., Gergis V. Conventional and *in situ* transesterification of sunflower seed oil for the production of biodiesel. *Fuel Process. Technol.*, 2008, 89, 503-509.
9. Hanh H.D., Dong N.T., Okitsu K., Nishimura R., Maeda Y. Biodiesel production by esterification of oleic acid with short-chain alcohols under ultrasonic irradiation condition. *Renew. Energ.*, 2009, 34(3), 780-783.
10. Domingos A.K., Saad E.B., Wilhelm H.M. Optimization of the ethanolysis of *Raphanus sativus* (L. Var.) crude oil applying the response surface methodology. *Biores. Technol.*, 2008, 99, 1837-1845.