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Comparative Study on Biodiesel Synthesis from Different Vegetables Oils

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Abstract: Studies concerning the synthesis and the characterization of biodiesel from palm, soybean and sunflower oils include the influence of temperature, amount of catalyst and reaction time on the conversion of each biodiesel type. Fatty Acid Methyl Esters (FAME) were synthesized by alkali catalyzed transesterification of the oils, using methanol at 6:1 alcohol: oil molar ratio. Several physico-chemical properties of biodiesel were assayed and compared with values established by the European standards for biodiesel. The fatty acid methyl esters have been analyzed by gas chromatography and infrared spectroscopy.

Keywords: biodiesel, alkali-catalyzed transesterification, FAME

1. Introduction

In present, the world's energy needs are met through non-renewable sources that are petrochemicals, naturals gas and coal. As long as the demand and cost of petroleum-based fuel is growing rapidly, and the present consumption pattern continues, these resources will be depleted in the near future. Time is needed to explore alternative sources of fuel energy. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and easily available [1-9].

Fatty acid methyl esters derived from vegetable oils have gained importance as an alternative fuel for diesel engines. Conventional biodiesel mainly comes from soybean and vegetables oils, palm oil, sunflower oil, rapeseed oil as well as from waste edible oil. Vegetable oils contain 98% triglycerides, having chemical structures like in the example given in Figure 1; small amounts of mono and diglyceride can be also present [9].

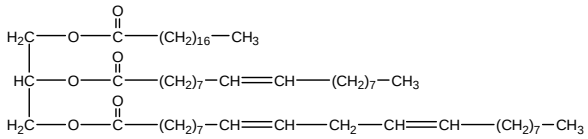


Figure1. Structure of a typical triglyceride molecule

Biodiesel is obtained by the alkali-catalyzed transesterification of the vegetable oils or natural fats with an alcohol (usually methanol, but ethanol is also suitable). Three consecutive reactions are required to complete the transesterification of a triglyceride molecule. A large excess of alcohol is necessary to achieve high conversion and a catalyst is required to obtain reasonable rates. A base catalyst such as sodium or potassium hydroxide is preferred [10-13]. Biodiesel appears to be an attractive energy resource for several reasons. First, biodiesel is made from a renewable resource that could be sustainably supplied. Second, biodiesel appears to have several favorable environmental properties resulting in no net increased release of carbon dioxide and very low sulfur content. The release of sulfur content and carbon monoxide would be cut down by 30 % and 10 %, respectively, using biodiesel as energy source. The gas generated during its' combustion could be reduced, and the decrease in carbon monoxide is the result of the relatively high content of oxygen. Moreover, biodiesel contains no aromatic compounds and other chemical substances which are harmful to the environment. Recent investigation has indicated that the use of biodiesel can decrease 90% of air toxicity and 95% of cancers compared to common diesel source. Third, biodiesel appears to have significant economic potential as a renewable fuel, considering that fossil fuel prices will increase inescapability further in the future. Finally, biodiesel is better than diesel fuel in terms of flash point and biodegradability [3, 4, 14-22].

This work presents the synthesis of biodiesel at different reaction conditions, in order to meet EN 14214 standards for biodiesel. IR spectroscopy, GC and physico-chemical analyses of the product were performed.

2. Experimental

2.1. Materials

Commercial "Olina" palm oil, "Pietro Coricelli" soybean oil and "Floriol" sunflower oil have been used as raw materials. The employed chemicals: absolute methanol, potassium hydroxide powder, anhydrous calcium chloride, diethyl ether, xylene, hexane, hexadecane were p.a. grade, all from Merck. Pure fatty acid methyl esters used as standards for the GC analysis: methyl miristate, methyl stearate, methyl oleate and methyl linoleate, have been purchased from Fluka.

2.2. Syntheses of biodiesel

In a 250 mL flask 100 mL oil were introduced and heated to a temperature selected from 45°C, 50°C, 55°C,60°C. Meanwhile, the designed amount of KOH catalyst: 0.25 g, 0.5 g, 0.75 g, or 1g, was dissolved into 23 g of methanol and poured into the flask. The mixture was maintained under stirring at the reaction temperature for a designated period of time (30, 45, 60, 75, 90, 105, or 120 minutes). Then the reaction was stopped and the flask content placed into a separation funnel. The inferior darker layer (containing glycerin and impurities) has been removed. The remained ester was washed several times with water (to remove traces of glycerin), dried on anhydrous calcium chloride (at room temperature at least 24 h) and then the ester is filtered.

2.3 Physico-chemical analyses

Conventional viscosity was measured using an Engler device. Density was determined by pycnometric method for all samples. Flash point values were assessed using a Pensky-Martens apparatus. Humidity was determined by azeotropic distillation with xylene, using a Dean-Stark device. Acidity indices values were measured by the titrimetric method.

2.4 Gas chromatography

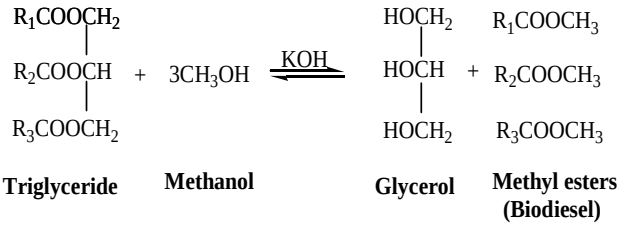
GC analysis of biodiesel composition has been accomplished using a Hewlett Packard 5890 Gas Chromatograph, equipped with a 30 m x 0.32 mm Zebron ZB-5 column and flame-ionization detector. The stationary phase was a mixture of 5% phenyl and 95% polydimethylsiloxane, with 0.50 µm film thickness. The injector and detector temperatures were set at 300°C and 350°C, respectively. Hydrogen was used as a carrier gas, at 1.4 mL/min flow rate. The analysis was performed using a temperature program from 175°C to 195°C, with 3°C/min heating rate, and then to 230°C, with 1°C/min heating rate. Hexane was used as solvent and hexadecane as internal standard. Identification and quantitative analysis were based on calibration for each methyl ester, using pure standards.

2.5 Infrared spectroscopy

The FTIR spectra were recorded on a JASCO FT/IR-410 spectrometer using KBr plates, in the range of 4000-400 cm^{-1}.

3. Results and Discussion

The transesterification reaction between triglycerides of palm, soybean or sunflower oil and methanol in the presence of potassium hydroxide (catalyst) leads to biodiesel. If allowed to go to completion, the net reaction produces three methyl esters mol and 1 mol of glycerol for each mol of transformed triglyceride (Fig.2).



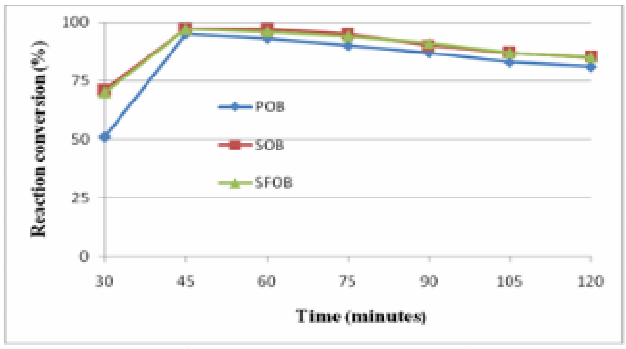
R_1, R_2, R_3 = hydrocarbon chain of fatty acids

Figure 2. Transesterification reaction of triglycerides with methanol

The transesterification reaction requires a catalyst in order to achieve reasonable rates. We used KOH as catalyst, but in fact the metoxid ions (formed by the reaction between the potassium hydroxide and methanol) were the active species.

3.1. Influence of reaction time

The optimal conversions for palm oil, soybean oil and sunflower oil biodiesel were obtained at 45 min reaction time (Fig. 3). We can notice that for reaction times smaller than 45 minutes the conversions were lower, due to incomplete transesterification. If the reaction time exceeded 45 min, the conversion values decreased, too. This fact can be explained by a possible higher degree of the reverse reaction. The conversions of soybean oil biodiesel were similar to the values obtained for sunflower oil biodiesel and slightly higher than for palm oil biodiesel (Fig. 3).



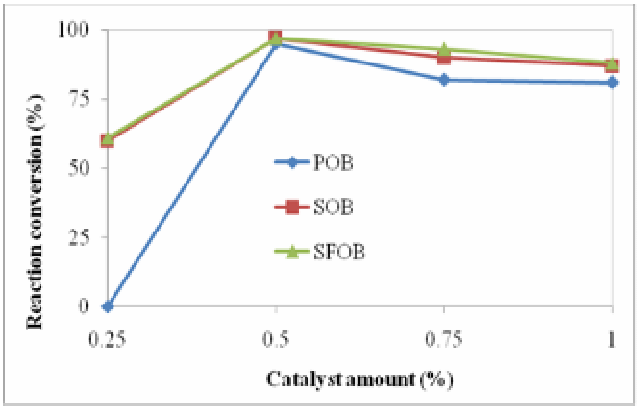
POB = Biodiesel from palm oil, SOB = Biodiesel from soybean oil
SFOB = Biodiesel from sun-flower oil

Figure 3. Reaction time influence on reaction conversion

3.2 Influence of the catalyst amount

As results from Fig. 4, in the case of palm oil biodiesel a catalyst amount of 0.25% (weight of KOH/weight of oil) was insufficient, thus the transesterification reaction did not succeed. Soybean and sunflower oils biodiesel showed a conversion around 60% at the same catalyst amount. These results can be explained by the higher acidity of palm oil (0.6 mg KOH/g) compared to soybean and sunflower oil (0.2 mg KOH/g and 0.25 mg KOH/g, respectively). The

highest conversions for all types of biodiesel were obtained at 0.5% catalyst amount (Fig. 4**)**. In all cases, increase of the catalyst amount beyond this optimal value resulted in decrease of the conversion rate of fatty acid methyl esters, due to formation of soap (potassium salts of the fatty acids). The conversions obtained for soybean and sunflower oils biodiesel were higher than the values for the palm oil biodiesel.



POB = Biodiesel from palm oil, SOB = Biodiesel from soybean oil
SFOB = Biodiesel from sun-flower oil

Figure 4. Influence of the catalyst amount on reaction conversion

3.3. Temperature influence

Biodiesel obtained at temperatures between 55ºC and 60ºC presented higher conversions that biodiesel synthesized at lower temperatures (Fig. 5). The biodiesel conversion values obtained at temperatures between 55ºC and 60ºC were almost the same for all three oils, while at temperatures lower than 55ºC, the methyl esters conversion decreased. At the same temperature, palm oil biodiesel exhibited lower conversion values compared to the two others. This fact can be explained considering that palm oil is solid at room temperature, having higher viscosity in comparison with the others two oils. High viscosity leads to less effective mixing of phases and thus the transesterification reaction occurs slower.

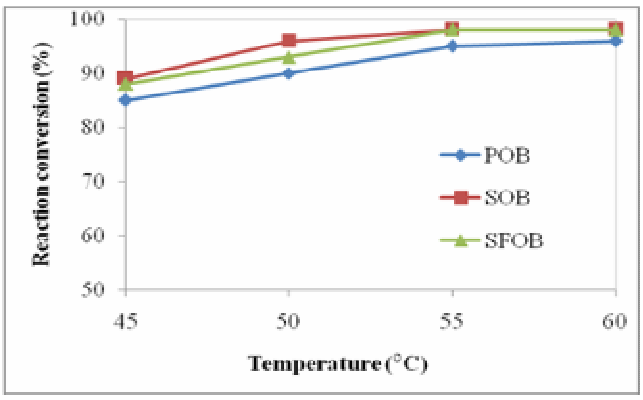


Figure 5. Influence of the temperature on reaction conversion

3.4. Physico-chemical analyses

The kinematic viscosity values of palm oil biodiesel (4.9 mm^2/s) are different from the viscosity values of soybean oil biodiesel (3.65 mm^2/s) and sunflower oil biodiesel (3.55 mm^2/s). It may be noticed that decrease of reaction time and catalyst amount resulted in higher viscosity in all three cases of biodiesel. Viscosity values for biodiesel from palm, soybean and sunflower oil are according the European standard.

For the acidity index of biodiesel, the EN 14214 European Standard requires a maximum value of 0.5 mg KOH/g. For all our analyzed samples, the acidity values varied between 0.1-0.2 mg KOH/g; this value fits in the limits specified by the standards. The acidity values of all biodiesel types were influenced by the reaction time and amount of catalyst, increasing at higher reaction time and catalyst amount. Flash point was determined for each sample. Different flash point values were obtained for each biodiesel type. All flash point values were higher than the lower limit stated by the standard (Table 1).

Regarding the water content, all samples were analyzed and the percentage of water in biodiesel was found below the detection limit.

TABLE 1. Physico-chemical properties of the synthesized biodiesel products, compared to European standards

Property	*EN 14214*		*Biodiesel**		
	Lower limit	Upper limit	Palm oil	Soybean oil	Sunflower oil
Viscosity [mm^2/s] at 40°C	3.5	5.0	4.90	3.65	3.55
Density [g/cm^3] at 15°C	0.86	0.90	0.880	0.885	0.865
Flash point [°C]	>101	-	164	176	182
Humidity [mg/Kg]	-	500	trace	trace	trace
Acidity [mg KOH/g]	-	0.5	0.1-0.2	0.1-0.2	0.1-0.2

3.5. Fatty acid composition

The synthesized biodiesel products were analyzed by gas chromatography, to determine the composition of fatty acid methyl esters (Fig. 6). Identification and quantitation of individual fatty acid methyl esters were accomplished by the internal standard method. For each fatty acid methyl ester a calibration has been performed with pure standards. Table 2 presents the results for the biodiesel samples obtained at 45 min reaction time, 55°C reaction temperature, and using 0.5% catalyst amount. As it can be seen, for the palm oil biodiesel the main methyl esters are palmitate and the oleate, while for the soybean and sunflower oils biodiesel the major methyl esters are linoleate and oleate. This data are according with the literature [23].

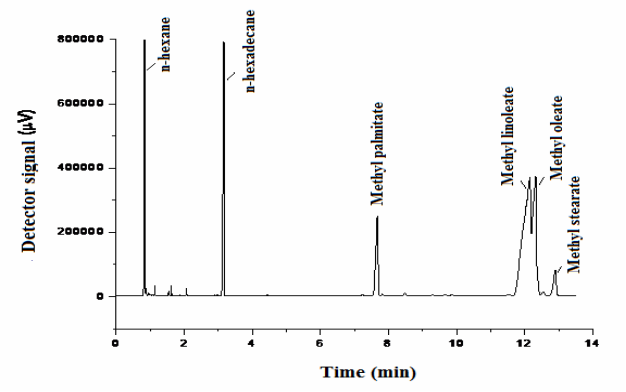


Figure 6. Gas chromatogram of soybean oil biodiesel, synthesized at 45 min reaction time, 55÷60°C, and KOH catalyst amount of 0.5 %

TABLE 2. Fatty acid composition of biodiesel methyl esters

Methyl ester	Composition (%)		
	Palm oil	Soybean oil	Sun-flower oil
Miristate (C14:0)	0.1	-	-
Palmitate (C16:0)	46.5	14.8	7.5
Linoleate (C18:2)	9.7	55.7	68.7
Oleate (C18:1)	36.4	23.1	17.1
Stearate (C18:0)	4.2	3.4	3.9
Others	3.1	2.9	2.8

3.6. Infrared spectroscopy analysis

Figure 7 displays the infrared spectra of biodiesel from palm oil, soybean oil and sunflower oil. It shows strong bands related to the ester carbonyl group stretching vibration at 1740 cm^{-1}, medium intensity bands of the esteric -OCO vibration at 1171 and 1207 cm^{-1}, and the presence of the $(CH_2)_n$ group vibration band at 724 cm^{-1}. The absence of a broad band at the 2500–3300 cm^{-1} region confirms the low moisture and free fatty acid content of the sample. These results are according with the literature data [24-25].

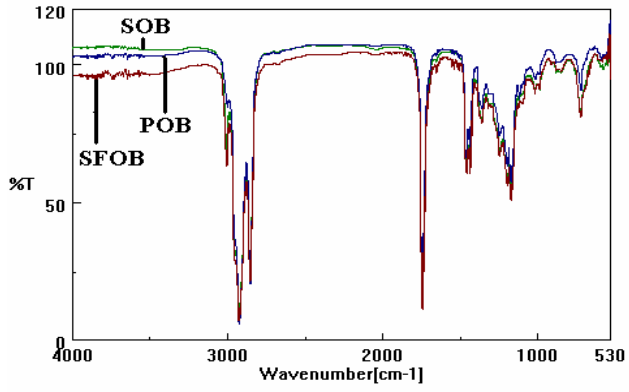


Figure 7. Infrared spectra of biodiesel products obtained from soybean (SOB), palm (POB), and sunflower (SFOB) oils

4. Conclusions

Optimization of reaction conditions: reaction time, temperature, and catalyst amount has been accomplished for biodiesel synthesis from palm oil, soybean oil and sunflower oil. The best conversion values (palm oil 96%, soybean and sunflower oils 98%) were registered for a 45 minutes reaction time, 0.5 g KOH catalyst amount and temperature between 55-60ºC. To sum up, in all cases considered, higher than optimal values of reaction time and amount of catalyst have lead to the decrease in conversion. In the same time, if the amount of catalyst, reaction time and temperature decreased, the reaction conversions were lower as in optimal conditions.

Biodiesel viscosity, density, flash point, humidity and acidity were according to the European Standard for biodiesel (EN14214). The infrared analysis confirmed the structure of expected products, and fatty acid compositions obtained from GC data were according with the literature.

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REFERENCES

1. Ivanoiu (Basa), A., Bandur, G. and Rusnac, L.M., *Rev. Chim. (Bucharest)*, 61(8), **2010**, 793-798.
2. Ahmad, M., Khan, M.A., Zafar, M. and Sultana, S., *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 32, 2, **2010**, 189-196.
3. Huang, G., Chen, F., Wei, D., Zhang, X. and Chen, G., *Applied Energy*, 87(1), **2010**, 38-46.
4. Antolin, G., Tinaut, F.V. and Briceno, Y., *Bioresour. Technol*., 83, 2002, 111-114.
5. Bunyakiat, K., Makmee, S., Sawangkeaw, R. and Ngamprasertsith, S., *Energy Fuels*, 20, **2006**, 812-817.
6. Al-Widyan, M.I. and Al-Shyoukh, A.O., *Bioresour. Technol*., 85, **2002**, 253-256.
7. Peterson, C.L., Reece, D.L., Thompson, J.C., Beck, S.M. and Chase, C., *Biomass Bioenergy*, 10, **1996**, 331-336.
8. Bouaid, A., Martine, M. and Aracil, J., *Fuel*, 86, **2007**, 2596-2602.
9. Kahraman, B., *Renewable and Sustainable Energy Reviews*, 12, **2008**, 542-552.
10. Bita, M.G., Grecu, D.R., Tutunea, D., Popescu, A. and Bica, M., *Rev. Chim. (Bucharest)*, 60(10), **2009**, 1090-1093.
11. Dusescu, C., Borcea, A., Matei, V., Popa, I., Radulescu, I. G., *Rev. Chim. (Bucharest)*, 59(11), **2008**, 1271-1275.
12. Stavarache, C.E., Morris, J., Maeda, Y., Oyane, I., Vinatoru, M., *Rev. Chim. (Bucharest)*, 59(6), 2008, 672-677.
13. Ivanoiu (Basa), A. and Rusnac, L.M., *Chem. Bull. "POLITEHNICA" Univ. (Timişoara)*, 54(68), 2, **2009**, 89-92.
14. Vicente, G., Martinez, M. and Aracil, J., *Bioresour Technol*, 92, **2004**, 297-305.
15. Ma, F. and Hanna, M.A., *Bioresour. Technol*., 70, **1999**, 1-15.
16. Tomasevic, A.V. and Siler-Marinkovic, S.S., *Fuel Process. Technol*., 81, **2003**, 1-6.
17. Ramadhas, A.S., Muraleedharan C. and Jayaraj, S., *Renew. Energy*, 30, **2005**, 1789-1800.
18. Al-Zuhair, S., *Biofuels, Bioprod. Bioref*., 1, **2007**, 57-66.

19. Gryglewicz, S., Piechocki, W., Gryglewicz, G., *Bioresour. Technol.*, 87, **2003**, 35-39.
20. Knothe, G., Van Gerpen, J.H. and Krahl, J., The Biodiesel Handbook, AOCS Press, Champaign, IL **2005**.
21. Ivanoiu (Basa), A., Bandur, G. and Rusnac, L.M., *Rev. Chim. (Bucharest)*, 61(9), **2010**, 872-876.
22. Lotero, E, Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., and Goodwin, J.G.JR, *Industrial & Engineering Chemistry Research*, 44, **2005**, 5353-5363.
23. Demirbas, A., *Energy Convers and Manag*, 44, **2003**, 2093-2109.
24. Dantas, M.B., Almeida, A.A.F., Conceicao, M.M., Fernandes, V.J.Jr., Santos, I.M.G, Silva, F.C., Soledade, L.E.B. and Souza, A.G., *J. Therm. Anal. Cal.*, 87, 3, **2007**, 847-851.
25. Souza, G., Danta, H.J., Silva, M.C.D., Santos, I.M.G., Fernandes, V.J., Sinfronio, F.S.M., et al., *J. Thermal Anal Calorim*, 90, **2007**, 945-953.

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