

THE EFFECT OF OILS QUALITY AND TRANSESTERIFICATION METHOD ON THE DEGREE OF CONVERSION OF THE FATTY ACIDS METHYL ESTERS

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Abstract

The aim of the work was to determine the effect of oils quality and transesterification method on the degree of conversion of the fatty acids. Material consisted of 4 samples of oil: rapeseed oil obtained by the laboratory hot pressing of rape seeds oils in approx. 80 °C, waste rapeseed and palm oils and one refined rapeseed oil. Oils used in the one-stage transesterification were characterized by a lower hydrolysis and oxidation degree than the oils used in two-stage transesterification (double-base and base-acid method). The quality of the obtained crude methyl esters was determined in terms of acid number, peroxide value, the lipid composition by thin layer chromatography. Quantitative testing of the degree of transesterification and the share of individual esters of fatty acids was conducted by gas chromatography. Studies have shown that that degree of conversion of the fatty acid methyl esters is dependent on both the quality of the oil and the method of transesterification. If oils are characterized by a good quality, then a method of transesterification is less important. However, if oils are heavily contaminated, then the right technology for their transesterification should be chosen, e.g. oil with high content of FFA should be subjected to base-acid transesterification. Studies have shown. If oils are characterized by a good quality, then a method of transesterification is less important. However, if oils are heavily contaminated, then the right technology for their transesterification should be chosen, e.g. oil with high content of FFA should be subjected to base-acid transesterification.

Keywords: *oil, fat, free fatty acids, acid value, method of transesterification*

1. Introduction

Refaat reported that any fatty acid source might be used as a raw material for biodiesel production [1]. Currently, main raw materials for the liquid biofuels (biodiesel) are plant oils. In the pilot and laboratory scale research on using animal fats are also carried out. It also added that due to the economic and ecological aspects, it seems to be reasonable to use a residual fats and oils

can also be used as a material for production of this biofuel, but the use of these raw materials are associated with using complicated and costly cleaning operations [2]. It is generally believed that the choice of suitable raw materials depends on availability, the chemistry and economy of the process as well as on the oil content [2-3]. Nowadays there is also observed increasing interest in the use of waste products. Despite the low price that encourages to their use, they are “difficult” raw material for biodiesel production. Waste vegetable oils and animal fats are characterized by a higher content of free fatty acids, water, solid waste, phosphorus compounds and polymers that make the transesterification difficult or impossible [4]. A multitude of raw materials for biodiesel production as well as their varied quality makes that is difficult to optimize the process. Accordingly, the aim of the work was to determine the effect of oils quality and transesterification method on the degree of conversion of the fatty acids.

2. Material and methods

Material consisted of 4 samples of oils. Rapeseed oil obtained by the laboratory hot pressing of rape seeds oils in approx. 80°C. Waste oil, rapeseed oil and palm oil were obtained from a local catering company. Refined rapeseed oil was bought from a local supermarket.

Oils used in the one-stage transesterification were characterized by a lower hydrolysis and oxidation degree (Tab. 1) than the oils used in two-stage transesterification (Tab. 2). Differences in the degree of hydrolysis and the oxidation of oils used in the tests resulted from the fact that a two-stage transesterification was conducted two months later. During the storage of these oils values of acid and peroxide value has increased (Tab. 2). Moreover, refined rapeseed oil that was subjected to one-stage transesterification was used as a reference sample.

Tab. 1. Characteristics of oils subjected to single-base transesterification

Oil	Acid value (mg KOH/g)	Peroxide value (mEq O ₂ /kg)
Hot-pressed rapeseed oil	3.83	0.12
Waste rapeseed oil	2.36	9.50
Hot-pressed rapeseed oil + waste palm oil (70:30)	2.25	0.88
Refined rapeseed oil	0.25	0.44

Tab. 2. Characteristics of oils subjected to two-stage base and acid-base transesterification

Oil	Acid value (mg KOH/g)	Peroxide value (mEq O ₂ /kg)
Hot-pressed rapeseed oil	5.50	3.50
Waste rapeseed oil	7.50	12.00
Hot-pressed rapeseed oil + waste palm oil (70:30)	8.20	5.20

2.1. Types of transesterification

Single-base transesterification

The reaction was carried out in 500 ml glass flasks placed in the Electrothermal heaters. Weighed 200 g of oil were heated to 60°C. Then a solution of potassium methoxide (2.5 g KOH were mixed with 83.3 ml of methanol) was added to the heated oil. The reaction was carried out at 60°C for 60 minutes with stirring at a rate of 250 rpm. A reaction mixture was distilled in a vacuum evaporator Buchi type R-200 to remove residual methanol and then the mixture was

subjected to the separation in the cylinders for 24 h. After the sedimentation, phases were separated and approximate yield of the process based on the percentage of ester and glycerine phases was determined.

Double-base transesterification

The transesterification was carried out with using equipment described above. In first stage of transesterification 200 g of oil was heated to 60 °C and then a solution of potassium methoxide was added (by using methanol in a ratio of oil = 1: 6 (v / v) and KOH in an amount of 1% based on the weight of oil). Reaction was carried out in 60°C for 40 min. In first stage of process $\frac{3}{4}$ of total amount of potassium methoxide was added and in second one $\frac{1}{4}$. Then the reaction mixture was subjected to separation for 24 h. After complete separation, the upper ester phase was poured into glass flasks and the second stage of transesterification was conducted in 60°C for 30 min. After the second step of transesterification, the ester phase was isolated as described above and approximate yield of the process was determined.

Base-acid transesterification

The transesterification was carried out with using equipment described above. In first stage of transesterification 100 g of oil was heated to 60°C and then methanol (in a ratio to oil 30:1) and 1% H₂SO₄ (m/m) were added. Reaction was conducted in 60°C during 90 min. Then the reaction mixture was subjected to separation for 24 h. After complete separation, the upper ester phase was poured into glass flasks and the second stage of transesterification was conducted. In this stage 0.5% KOH (m/m) was dissolved in 13.5 ml and reaction was conducted in 60°C during 30 min. After the second step of transesterification, the ester phase was isolated as described above and approximate yield of the process was determined.

Analytical methods

The quality of the obtained crude methyl esters was determined in terms of acid number (PN-EN14104:2004P), peroxide value (PN-EN ISO 3960:2012P), the lipid composition by thin layer chromatography [5]. Quantitative testing of the degree of transesterification and the share of individual esters of fatty acids was conducted by gas chromatography.

3. Results and discussion

Volume measurements of ester and glycerol phases have been taken to control the progress of transesterification. Share of the ester phase (Tab. 3) turned out to be dependent mainly on the method of transesterification, while type of used oil had lesser impact. Maximum shares of the ester phase (92.7-94.8%) were obtained during the two-stage base-acid transesterification, while the lowest (87.3-89.6%) during the single-base transesterification.

Share of ester phase, as was shown by the results of further analysis, does not prove the effectiveness of the transesterification, but it is rather the result of the different rate of sedimentation of phases with diversified content of compounds other than methyl esters of fatty acid. This is evidenced by the results of thin layer chromatography (Fig. 1.2), indicating the complete conversion of triglycerides to methyl esters in the case of single-base transesterification with the lowest share of ester phase. In turn, higher shares of ester phases after double-stage transesterification were associated with incomplete conversion of triacylglycerol.

The chromatograms of these samples presented visible areas of unreacted lipids, i.e. tri-, di- and monoacylglycerols, which indicate on the disruption of transesterification reaction. One of the alleged reasons could be acid value of oils exceeding 4 mg KOH/g. This value was recognized by Ramadhas al. as the highest value of this parameter that is admissible during single-base transesterification [6]. A high content of free fatty acids interfere with the course of the single-base

transesterification. Responsible for that are soaps, which are formed during contact of base catalyst with free fatty acids, that emulsifying the reaction system. Therefore the reduction of the transesterification efficiency, problem with separation of ester and glycerine phases are observed [6-8]. Further disruptions of the transesterification caused by the high content of free fatty acids may be associated with the separation of water during the saponification reaction, which hydrolysing fat what causes the formation of another portion of the free fatty acids [9].

Tab. 3. Share of ester and glycerol phases after 24 h of the sedimentation

Methyl esters	Share of phase (%)	
	ester	glycerol
<i>Single-base transesterification</i>		
refined rape seed oil	89.6	10.4
hot-pressed rapeseed oil	87.3	12.7
waste rapeseed oil	87.7	12.3
hot-pressed rapeseed oil + waste palm oil (70:30)	88.7	11.3
<i>Double-base transesterification</i>		
hot-pressed rapeseed oil	91.0	9.0
waste rapeseed oil	91.5	8.5
hot-pressed rapeseed oil + waste palm oil (70:30)	92.0	8.0
<i>Base-acid transesterification</i>		
hot-pressed rapeseed oil	94.8	5.2
waste rapeseed oil	93.6	6.4
hot-pressed rapeseed oil + waste palm oil (70:30)	92.7	7.3

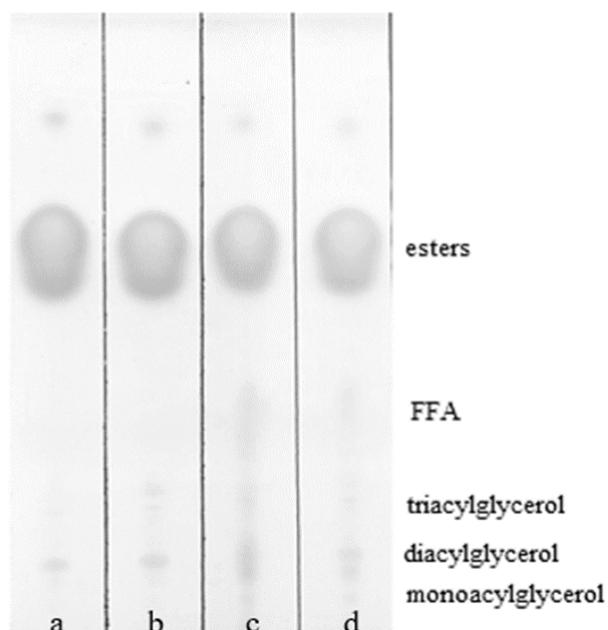


Fig. 1. TLC chromatograms of methyl esters obtained by the single-base transesterification with different oils: a) refined rapeseed oil, b) hot-pressed oil, c) waste rapeseed oil, d) mixture of pressed rapeseed oil and waste palm oil

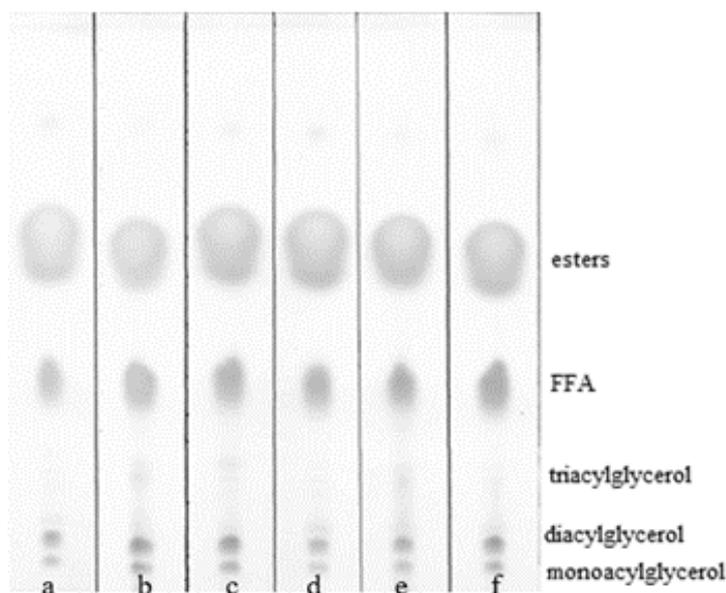


Fig. 2. TLC chromatograms of esters obtained by the double-base and base-acid transesterification with different oils: a) pressed rapeseed oil (base transesterification), b) waste rapeseed oil (base transesterification), c) mixture of pressed rapeseed oil and waste palm oil (base transesterification), d) pressed rapeseed oil (base-acid transesterification), e) waste rapeseed oil (base-acid transesterification), f) mixture of pressed rapeseed oil and waste palm oil (base-acid transesterification)

Tab. 4. Share of fatty acid methyl esters (%) in ester phases after single-base transesterification

Methyl ester of fatty acid	Ester phase from fat			
	Refined rapeseed oil	Hot-pressed oil	Waste rapeseed oil	Hot-pressed rapeseed oil + waste palm oil (70:30)
total	97.0	95.0	90.9	93.3
linolenic	8.6	9.7	4.3	7.2
palmitic	4.4	4.0	9.1	14.4
stearic	1.6	1.7	2.4	2.4
oleic	60.0	59.0	51.4	52.2
linoleic	18.9	17.6	19.8	14.3

The results of these studies showed that during single-base transesterification satisfactory degree of conversion (97% of the fatty acid esters) was observed only for the refined oil. In case of another oils degree of fatty acids conversion ranged from 90.9 to 95.0% (Tab. 4). According to the European standard EN 14 214 the content of fatty acid methyl esters in biodiesel should be $\geq 96.5\%$.

The degree of fatty acids conversion reached during double-basic transesterification ranged from 92.1% (esters from hot-pressed rapeseed) to 71.2% (esters from waste rapeseed oil) (Tab. 5). Moreover, the use of base-acid transesterification, in comparison with double-base transesterification, did not changed degree of conversion of fatty acids in hot-pressed and its mixture with palm oil, while improved (by 12 percentage units) in waste rapeseed oil (Tab. 5). Observed increase in the conversion of fatty acids in waste rapeseed oil (with high acid and peroxide values) that was subjected to base-acid transesterification, confirmed the adverse effects of products of lipid transformation on the yield of process. At the same time, it stresses the need for proper purification of oil prior to transesterification or use other conditions of process [2].

Tab. 5. Share of fatty acid methyl ester in ester phases (%) after double-stage transesterification

Methyl ester of fatty acid	Ester phase from fat		
	Hot-pressed oil	Waste rapeseed oil	Hot-pressed rapeseed oil + waste palm oil (70:30)
<i>Double-base transesterification</i>			
total	92.1	71.2	85.1
linolenic	9.7	4.4	7.3
palmitic	3.9	7.0	12.7
stearic	1.7	1.9	2.2
oleic	57.1	40.4	47.8
linoleic	17.1	15.5	13.3
<i>Base-acid transesterification</i>			
total	92.3	83.4	82.5
linolenic	9.7	4.3	7.3
palmitic	3.9	8.1	12.1
stearic	1.8	2.2	2.2
oleic	57.2	47.4	46.6
linoleic	17.1	18.2	12.9

Conclusion

Studies have shown that degree of conversion of the fatty acid methyl esters is dependent on both the quality of the oil and the method of transesterification. If oils are characterized by a good quality, then a method of transesterification is less important. However, if oils are heavily contaminated, then the right technology for their transesterification should be chosen, e.g. oil with high content of FFA should be subjected to base-acid transesterification.

References

- [1] Refaat, A. A., *Different techniques for the production of biodiesel from waste vegetable oil*, International Journal of Environmental Science and Technology, Vol. 7, No. 1, pp. 183-213, 2010.
- [2] Karmakar, A., Karmakar, S., Mukherjee, S., *Properties of various plants and animal feedstocks for biodiesel production*, Bioresource Technology, Vol. 101, No. 19, pp. 7201-7210, 2010.
- [3] Sharma, Y. C., Singh, B., *Development of biodiesel: Current scenario*, Renewable and Sustainable Energy Reviews, Vol. 13; pp. 1646-1651, 2009.
- [4] Tańska, M., Rotkiewicz, D., Bączek, N., *Adsorpcyjne oczyszczanie tłuszczów posmażalnicych przeznaczonych do produkcji bioediesla*, Nauka Przyroda Technologie, Vol. 6, No. 4, pp. 1-11, 2012.
- [5] Ackman, R. G., *Application of thin-layer chromatography to lipid separation: neutral lipids*, Chapter 3 in: Analyses of fats, oils and derivatives, Ed. E.G. Perkins, AOCS Press, Champaign, pp. 60-82, Illinois 1991.
- [6] Ramadhas, A. S., Jayaraj, S., Muraleedharan, C., *Biodiesel production from high FFA rubber seed oil*, Fuel, Vol. 84: pp. 335-340.
- [7] Meher, L. C., Sagar, D. V., Naik, S. N., *Technical aspects of biodiesel production by transesterification – a review*, Renewable and Sustainable Energy Reviews, Vol. 10, No. 3, pp. 248-268, 2006.

- [8] Lu, H., Lu, Y., Zhou, H., Yang, Y., Chen, M., Liang, B., *Production of biodiesel from *Jatropha curcas* L. oil*, Computers and Chemical Engineering, Vol. 33, pp. 1091-1096, 2006.
- [9] Walisiewicz-Niebalska, W., Lipkowski, A. W., Kijeński, J., *Aspekty technologiczne i ekonomiczne wytwarzania biopaliwa estrowego*, In: Materials of the Conference Zintegrowane, inteligentne systemy wykorzystania energii odnawialnej, pp. 1-9, Częstochowa – Podlesice 2005.

