

UTILIZATION OF USED OILS AND FATS FOR FAME BIOFUELS PRODUCTION

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Summary. The research aimed at the determination of the effectiveness of transesterification of used oils and fats. The raw materials used for the experiments were: palm oil, rapeseed oil, sunflower oil and animal fat. Pure potassium hydroxide p.a. was used as the catalyser and methanol was used for methanolysis. The process was conducted in single and two step stages. The transesterification process was conducted in two stages. Depending on the raw material after the first stage of transesterification between 69 and 81% (v/v) conversion degree was obtained, i.e. transformation of oils and fats into FAME. Application of the second stage of transesterification allowed to reach a considerable improvement of the efficiency of the transesterification process.

Key words: Biodiesel, transesterification, alkaline and acid catalyzers

INTRODUCTION

So far the main raw materials for biofuels manufacturing for auto-ignition engines have been raw or refined plant oils. Plant oils are composed of about 95% of glycerides, which in turn are composed of fatty acids. Oil contains also sterols, phospholipids, free fatty acids, water and other impurities. Fuel properties of oil and biofuels depend on the mutual proportions of three fatty acids in the structure, i.e. oleate acid $C_{17}H_{33}COOH$, linoleic acid $C_{17}H_{31}COOH$ and linoleic acid $C_{17}H_{31}COOH$ [Wcisło 2009, Zang *et al.*, 2003]. Research has shown that the higher the content of oleate acid in plant oils, the better the quality of the obtained biofuels FAME. [Jakóbiec 2006, Wcisło 2004, 2007].

Physico-chemical properties of FAME (Fatty Acid Methyl Esters) depend also on the quality of the raw material used, initial preparatory processes, e.g. refining, effectiveness of transesterification process and thorough purification of the final product from the remaining glycerine, soaps, catalyser and alcohol [Jakóbiec *et al.*, 2005, Piazza *et al.*, 2001].

It is most important that free fatty acid contents (FFA) should not exceed the value of 0.55 - 3% v/v, because a higher amount necessitates the use of a bigger amount of catalyser, thus worsening FAME quality due to higher amount of glycerine fraction remaining in the esters. Also, the quantity of water remaining in the oil should be limited so that it would not exceed 500mg/kg [PN-EN 14214]. Too much water in esters may be the reason for soap forming during transesterification process leading to engine corrosion [Bocheński 2003]. Also, leaving even a small amount of glycerine fraction in esters would lead to an increase in particularly dynamic viscosity, which

in turn would worsen the fuel liquidity and negatively affect the injection process and spray in the engine [Atadashi *et al.*, 2010, Wcisło 2009, 2009].

Currently, a greater attention has been put to seeking cheap raw materials for biofuel production. Used oils and fats obtained as a post-frying product in gastronomy are gaining growing popularity. The units particularly interested in the use of this type of raw materials for fuel production are small enterprises producing biofuels, including agri-refineries. The factories of this type in the first place produce biofuels for their own vehicles equipped with auto-ignition engines.

AIM AND SCOPE OF RESEARCH

The research aimed at the determination of the effectiveness of transesterification of used oils and fats. The raw materials used for the experiments were: palm oil, rapeseed oil, sunflower oil and animal fat. Pure potassium hydroxide p.a. was used as the catalyser and methanol was used for methanolysis. The process was conducted in single and two step stages and the transesterification process began at the temperature of 310K. Biofuels were produced in a cubature reactor type GW-10, constructed by the author, property of Małopolskie Centre of Renewable Energy Sources „BioEnergy”

The process of transesterification of oils and fats occurs in three stages, where first triglycerides are transformed into di- and then to monoglycerides leading to the final glycerol – trihydric alcohol. At each stage of the transesterification process one mol of ester and one mol of alcohol form. Transesterification relies on the reaction of triacylglycerols (TAG) with alcohol, usually methanol [Komers *et al.*, 2001, Boocok *et al.*, 1999]. Transesterification process of a typical triglycerol for the rapeseed oil has been presented in Figure 1.

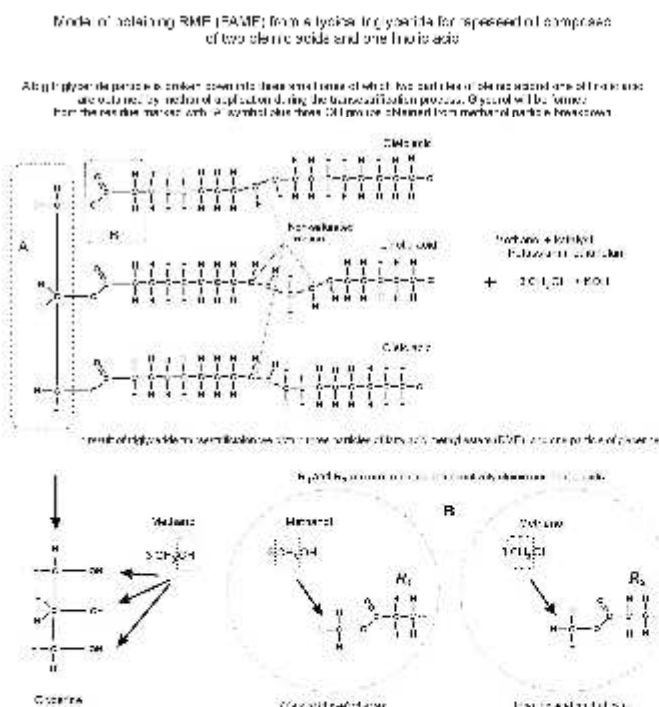


Fig. 1. Diagram of rapeseed oil transesterification

In result of one oil particle transestrification we obtain three ester particles and one glycerine particle [Wcislo 2009].

Methanol was used for the transestrification (methanolysis) of the rapeseed oil, whereas potassium hydroxide was applied as the catalyser. The transestrification was conducted in two stages.

The procedure comprised first preparation of a methyl alcohol mixture with the catalyser. The rapeseed oil was heated to the temperature of 330K and the mixture of alcohol and catalyser was added to it. The process in the reactor was being conducted for 50 minutes. The catalyser mixture was prepared by mixing methanol with potassium hydroxide. As a result of the initial reaction of methanol and catalyser a transitory complex is obtained - potassium alcoholan (methanolan) CH_3OK .

In order to obtain a high degree of the oil conversion into methyl esters the process of methanolysis was conducted at the 30% excess of methanol. However, at the first stage only 85% of the alcohol mixture with catalyser mass was added to the oil. After the first stage the mixture was subjected to decantation during which ester phase was separated from the glycerine phase. Subsequently the ester part was used for the second degree of estrification.

The process of rapeseed oil methanolysis using alkaline catalysers involved adding 4 mol of methanol per 1 mol of oil (triglycerols). The expected result was obtaining 3 mol of fatty acid methyl esters, 1mol of glycerine and 1mol of methanol. Such situation would be possible if 100 percent conversion of the oil into methyl esters could be achieved in the reaction. There were 0.13kg of methanol and 8.5g catalyser per 1kg of rapeseed oil.

Catalysers were neutralized each time after the transestrification was completed. For instance, methyl esters - RME Biodiesel, for which NaOH was used as the catalyser, was acidified with 1% acetic acid CH_3COOH . 20ml of CH_3COOH per 100ml of Biodiesel was used. Soaps formed after the application of potassium hydroxide may be successfully used as agricultural fertilizer.

The degree of the oil conversion into esters (Biodiesel) was determined in order to assess the effectiveness of transestrification by methanol conducted in the presence of KOH catalyser.

The conversion levels is the degree of the reaction of the rapeseed oils (including all acids present in the oil) in the methanol esters in adequate. In order to determine the conversion levels it was necessary to appoint the Mount of mono-, di- i triacylglycerides as well as the methanol ester fatty acids of the rapeseed oil. All tests were carried out in accordance with all of the required standards for plant fuels EN 14214. In accordance with the aforementioned norms the contents of the methanol ester fatty acids should have the final results of no less than 96.5 % (m/m); however the contents of monoacylglycerides is maximum 0.8 % (m/m); diacylglycerides 0.2% (m/m). It is of utmost importance that the contents of the mono-, di- i triacylglycerides are as small as possible, because the above-mentioned glycerides do not necessarily burn completely in a high compression ignition engine fuel chamber, causing the walls of the fuel chamber and the pistons to be covered with a carbon deposit (hard carbon), which causes scratches on the smooth surface of the cylinders and rings, in turn wearing out the engine at a faster rate.

All of the hand taken samples were in accordance with all of the procedures that have been outlined by the norms in the EN ISO 3170. The contents of the methanol esters' fatty acids in rapeseed oil (FAME) are defined in accordance with EN 14103. The determined contents of methanol esters in rapeseed oils was in accordance with EN ISO 5508 using the internal form (heptadecanoic acid methyl ester). The gas chromatography research was carried out by the company THERMO Scientific, type GC Ultra. The integration of chromatography was established to be such that the peaks from the myristic acid methyl ester ($\text{C}_{14:0}$), were up to the peak of the lignoceric acid methyl ester ($\text{C}_{24:0}$) and nervonic acid methyl ester ($\text{C}_{24:1}$). Based on the received marked information below are the formulas of the contents of "C" esters.

$$C = \frac{(\sum A) - A_{E1}}{A_{E1}} \times \frac{C_{E1} \times V_{E1}}{m} \times 100\%,$$

where:

$\sum A$ - the entire surface peaks of methyl esters from C_{14} to $C_{24:P}$

A_{E1} - surface peaks representing heptadecanoic acid methyl ester,

C_{E1} - used concentrated dilution of heptadecanoic acid methyl ester; in milligrams per milliliter,

V_{E1} - volume of the used dilution of heptadecanoic acid methyl ester, in milliliters,

m - mass of the sample, in milligrams.

Esters were produced in the reactor designed and built by the author of this article. This appliance, as the only one in Europe, is able to produce Biodiesel RME with a full glycerin phase of two hours.

RESULTS AND DISCUSSION

The results of tests determining the effectiveness of used plant oils and animal fat transesterification at one and two stage process were compiled in Table 1. The molar ratio of methanol to oil during transesterification was 4:1. The changing parameter was the amount of reaction catalyser KOH, which was respectively 0.6, 1 and 1.4% of the oil or fat mass.

The experiments were carried out for three different times. In each case, the transesterification process was monitored with the utmost care down to the finest detail. The results given in table 1 are the average quantities of the marked conversion levels. The maximum difference that was achieved of the conversion levels in each catalyser did not exceed 2%.

Table 1. The effect of catalyser on the degree of oils and fats conversion into FAME esters

Kind of raw material.	Amount % [m/m] of catalyser in relation to oil.	Single-stage process	Two-stage process
sunflower oil	0,6	77	89
	1	78	91
	1,4	73	86
rape oil	0,6	80	91
	1	81	93
	1,4	75	89
palm oil	0,6	79	90
	1	80	89
	1,4	74	83
animal fat	0,6	73	83
	1	74	84
	1,4	69	79

For better illustration of results presented in the table above, they were also shown in Figures 2 and 3. Figure 2 presents the results of tests determining the effectiveness of transesterification after the first stage of the process. It should be remembered that at the first stage only 85% (v/v) of the reaction substrates were used. Subsequently, glycerine fraction was separated by means of decantation

after methanolysis and the remaining amount of esters was subjected to the transesterification process for the second time with the use of the remaining 15% (v/v) amount of the substrates. Determined conversion degrees after the two stages were presented graphically in Figure 3.

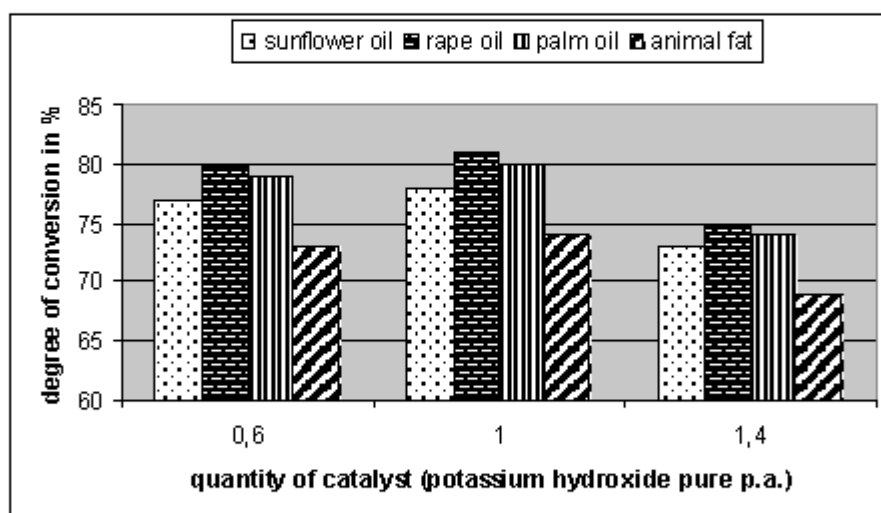


Fig. 2. Conversion degrees obtained after the first stage of transesterification process

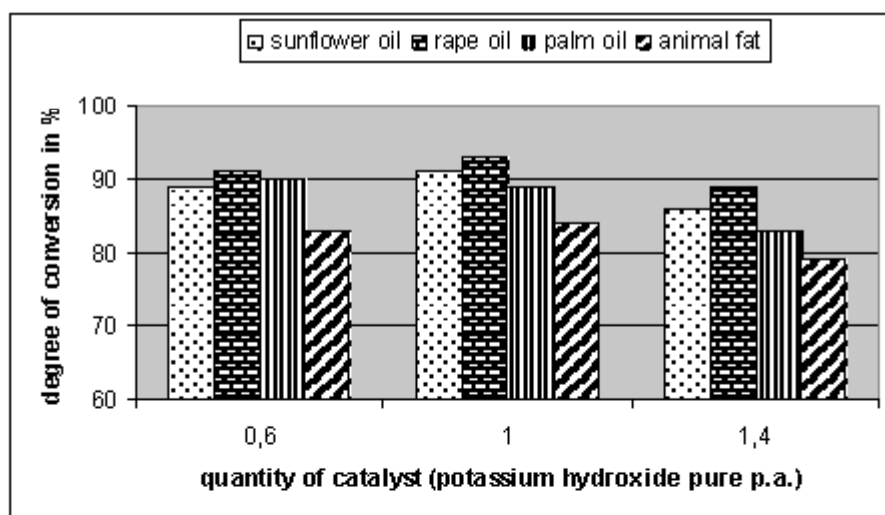


Fig. 3. Conversion degrees obtained after the second, final stage of transesterification process

CONCLUSIONS

- Potassium hydroxide proved an efficient catalyser for methanol, used oils and fat in the transestrification process. Methanol was applied for methanolysis in a molar ratio to oil 4:1. The efficiency of transestrification after the first and second stages of the process was determined using various amounts of KOH catalyser. It turned out that the degree of used oil and animal fat conversion depends on the quantity of applied catalyser. The amount of catalyser used was from 0.6 to 1.4 m/m of oil or animal fat.
- The transestrification process was conducted in two stages. Depending on the raw material after the first stage of transestrification between 69 and 81% (v/v) conversion degree was obtained, i.e. transformation of oils and fats into fatty acid methyl esters (FAME). The highest degree of transformation was achieved for rapeseed oil, whereas the lowest for animal fat. It demonstrates that over 17% more of crude FAME biofuel was obtained from the rapeseed oil than in result of animal fat methanolysis.
- Application of the second stage of transestrification allowed reaching a considerable improvement of the efficiency of the transestrification process. After the second, final stage the highest conversion degree was obtained, 93%v/v for the rapeseed oil, while the lowest, like after the first stage, was obtained for animal fat - 79% (v/v).
- It is noticeable that the highest degree of transformation was achieved using 1% m/m of the catalyser in relation to the initial raw materials. Decreasing, even by 40% the catalyser's amount led to a slightly worse effectiveness of the transestrification. This proves the key role of the reactor in biofuel production. Properly constructed, it allows to use a considerably smaller amount of catalyser for transestrification of oils and animal fat.
- A 40% decrease in the catalyser amount produces a result opposite to the intended one because in such situation considerably less of FAME esters were produced than at the other applied amounts of the catalyser.

The research demonstrated that in small agricultural refineries it is possible to obtain satisfactory amounts of biofuels from the post-frying raw materials. However, the obtained esters do not meet the quality requirements as stated by the standard EN-14214 for plant biofuels, because of the minimum allowed amount of esters in FAME (96.5% m/m). Therefore, to improve the efficiency of biofuels production from used oils, this raw material should be first adequately prepared, i.e. the excess of water should be evaporated and free fatty acids neutralized. Technologies used by farmers in Poland usually do not allow obtaining an adequate amount of biofuels of required quality, therefore greatly excessive quantities of methanol and catalyser are used. In such situations one should remember about the fuel neutralization, to the pH value 7-8. Otherwise methanol contained in esters, being a strong base, would cause a corrosion of metal elements of the injection apparatus and destroy other elements including all types of sealing, which may finally immobilize the engine.

Information and promotional campaign would be necessary to improve the awareness of the principle of good quality biofuels manufacturing. Better awareness concerning the principles of biofuel production would contribute to the development of a market for biofuels produced in small refineries or agri-refineries [Bozbas 2003, Rogulska *et al.*, 2006, Janaun *et al.*, 2010].

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WYKORZYSTANIE ZUŻYTYCH OLEJÓW I TŁUSZCZU DO PRODUKCJI BIOPALIW TYPU FAME

Streszczenie. Celem badań było określenie skuteczności transestryfikacji zużytych olejów i tłuszczów. Jako surowców użyto zużytych olejów: palmowego (fityna), rzepakowego, słonecznikowego oraz tłuszczu zwierzęcego. Jako katalizator zastosowano wodorotlenek potasu. Do metanolizy zastosowano alkohol metylowy. Proces prowadzono jedno i dwustopniowo. W zależności od rodzaju surowca po pierwszym etapie prowadzenia procesu transestryfikacji uzyskano od 69 do 81% (w/v) stopień konwersji, czyli przereagowania olejów i tłuszczu w FAME. Zastosowanie drugiego etapu transestryfikacji pozwoliło na znaczną poprawę efektywności prowadzenia procesu transestryfikacji.

Słowa kluczowe: biodiesel, transestryfikacja, katalizatory zasadowe i kwasowe