COMPARISON OF TRANSESTRIFICATION EFFICIENCY USING ALKALINE AND ACID CATALYZERS

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Summary. The paper presents the results of research determining the efficiency of rapeseed oil transestrification using alkaline an acid catalyzers. Due to different properties of the applied catalyzers the transestrification was conducted under different conditions. When acid catalyzers were used molar ratios of ethanol to oil and the temperature at the beginning of transestrification process were much higher than for alkaline catalyzers. The highest degrees (> 94%) of rapeseed oil conversion into methyl esters, Biodiesel FAME, were obtained from the two-stage process through catalytic commixtures with the following alkaline catalysts: KOH and NaOH. Higher degrees of conversion were obtained for alkaline catalyzers. Applying as a catalyst acids H3PO4 and H2SO4 resulted in slightly lower results, the degree of conversion was 3% lower.

Key words: Biodiesel, transestrification, alkaline and acid catalyzers.

INTRODUCTION

Autonomous fuels may also be Biofuels type CVO (Clear Vegetable Oils) pure plant oils or Biodiesel. Since the physical and chemical characteristics of the oils are different from the DERV 3 characteristics, it is not expected that a wider use for feeding compression-ignition engines will be explored. One of the greatest differences is kinematic and dynamic viscosity and density, the following example illustrates the meaning: the kinematic viscosity of rapeseed oil at the temperature of 293K is about eighteen times greater than the DERVs viscosity. In order to exclude unfavorable characteristics of plant oils and animal fats, they are put through a transesterification process and changed into methyl or ethyl esters of higher fatty acids known as Biodiesel. The world’s best known biofuel is Biodiesel FAME (Fatty Acid Methyl Esters). Taking into account different climate and soil conditions biofuels of different origins are going to dominate on particular continents.

Furthermore, scientific research is also being carried out with biofuels, used during the transesterification process with different alcohols. Ethanol is very interesting as it can be produced out of plants, whereas methanol is usually produced chemically; therefore, Biodiesel produced with the use of ethanol would be 100% renewable fuel.

The process of transesterification of oils may be carried out in the thermal or catalytic form. In the catalytic method to produce methanol, homogeneous alkaline catalyts are used or acidic (i.e. hydroxide, alcohol, carbon or mineral acids), heterogeneous (i.e. amino acids, alkalide metal oxides,
Ionic resins or zeolites) as well as enzymatic. During the process of transesterification ionic alcohols are implemented quite often, the most common is sodium or potassium [Komers et al., 2001].

Currently there is a great effort to find permanent catalyzers that will be able to produce Biodiesel fuels. These types of substances are heterogeneous catalyzers, using i.e. guano as a catalyzer in the methanolyse process, utilizing the oil from soy beans at the temperature of 337K there was above a 90% reaction, meaning conversion level [Sercheli et al., 1999]. There has also been research carried out with zeolites (aluminosilicate) in transesterification. Firstly, materials of this type are quite interesting because of their spatial structure. The catalyst process may take place, contained or not. Secondly, another very positive attribute is in fact based on the “shape-selection” since we may be able to influence this part of the production of such materials, thus being beneficial from the biofuels perspective. One of the negative aspects could possibly be in the sealing of the channels with the adsorbtion substratum of the zeolites. In the research that was carried out utilizing the Y-zeolite activated with guano has proven to be effective in the transesterification of plant oils. Finally, other types of research that have taken place have been with the usage of metallic salts, for example: Ni, Cd, Fe and Cu in the transesterification of oils; proving their usefulness in the methanolyse process of oils [Peter et al., 2002].

AIM AND SCOPE OF RESEARCH

The aim of the research was to determine the influence of the type of catalyst on the degree of conversion that is in the change of oil into the esters of rapeseed oil – Biodiesel RME. Biofuels were produced in a cubature reactor type GW-10, constructed by the author, property of Malopolskie Centre of Renewable Energy Sources „BioEnergia” – Fig. 1.

![Process Flow Diagram – 2-stage FAME process](image)

Fig. 1. Process Flow Diagram – 2-stage FAME process
This appliance is the only one in Europe that is able to produce Biodiesel FAME within a full glycerin phase of two hours. For the methanolyse process methanol was applied. As the catalyst four different substances were used, two alkaline and two acidic. The alkaline catalysts were pure potassium hydroxide p.a. and pure sodium hydroxide, the acidic ones were phosphoric acid and vitriolic acid. The process was conducted in single and two step stages and the transesterification process began at the temperature of 330K. In the following example, the manner of conducting the transesterification process with the use of KOH as a catalyst is described. The processes of transesterification in which three other catalysts were used, were conducted in a similar manner.

**Transesterification process.** For rapeseed oil transesterification (methanlysis) methanol was applied. The catalyst in this chemical reaction was KOH (Potassium hydroxide pure p.a.). Transesterification was a two-stage process, both times between the temperature of 330-340K. First, the commixtion of methanol and the catalyst were prepared, then rapeseed oil was heated up to 330K, and the commixtion was added. Catalytic commixtion was prepared by blending methanol and potassium hydroxide. As a result of the initial chemical reaction of methanol and the catalyst, a transitional complex compound is obtained: potassium metanolan CH₃OK. The process took place in the reactor, it lasted for 50 minutes. The catalytic commixture was created by mixing together methanol and Potassium hydroxide pure p.a.

To obtain the high degree of conversion of oil into methyl esters, the methanolyse process was conducted with a 30% excess of methanol. During the first stage 85% of the mass of the commixture of alcohol and the catalyst was added into the oil. After the first stage the commixture was decanted and during the decantation phases glycerine and ester were at the stage of esterification. The ester phase is presented in the example of the main transesterification reaction diagram.

![Fig. 2. Diagram of rapeseed oil transesterification](image)

The methanolyse process of rapeseed oils with the use of basic, alkaline catalyzers is carried out in the following way: that on 1 mole of triacylglycerides there are added 4 moles of methanol. In effect there should be 3 moles of Rape Methyl Ester RME as well as 1 mole of glycerin and 1 mole of methanol. This theoretically would be achieved during a 100% reaction during transesterification of the conversion level of oils into methanol esters. Hence, per 1kg of rapeseed oil 0.13 kg of methanol and 8.5 grams of the catalyzer was gained. However, the transesterification process utilizing acids will take per 1 mole of oil 15 moles of methanol. Per 1 kg of rapeseed oil 0.56 kg of methanol and 20 grams of the catalyzer was gained.

After each transesterification the catalysts were neutralized. For example, methyl esters – Biodiesel RME for which catalyst was NaOH, were neutralized with 1% acetic acid CH₃COOH; 20ml of CH₃COOH solution was used for 100ml of Biodiesel. The soap that remains after the use of potassium hydroxide can be used as soil fertilizer.
The following description aims at outlining the effectiveness of the transesterification of methanol carried out in the presence of four different types of catalysts with given levels of the conversion of oils into RME. The conversion levels is the adequate degree of the reaction of the rapeseed oils (including all acids present in the oil) with the methanol esters. 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 low 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 (C_{14}) are up to the peak of the lignoceric acid methyl ester (C_{24}) and nervonic acid methyl ester (C_{24}). Based on the received marked information below are the formulas of the contents of “C” esters.

\[ C = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \]

where:
- \( \sum A \) – the entire surface peaks of methyl esters from C_{14} to C_{24},
- \( A_{EI} \) – surface peaks representing heptadecanoic acid methyl ester,
- \( C_{EI} \) – used concentrated dilution of heptadecanoic acid methyl ester; in milligrams per milliliter,
- \( V_{EI} \) – the 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

Table 1 compares the results of the obtained degrees of oil conversion into esters with the use of four catalysts and both single and two-stage transesterification. Degrees of conversion are represented in volume, which says how much of a percent of oil volume was changed into esters.

The experiments were carried out at 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 catalyzer did not exceed 2%.
Table 1. Results of the obtained degrees of oil conversion into esters – Biodiesel FAME

<table>
<thead>
<tr>
<th>The kind of catalyst</th>
<th>KOH</th>
<th>NaOH</th>
<th>H₃PO₄</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>The number of transesterification stages</td>
<td>Degree of conversion in %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single-stage process</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapeseed oil unrefined</td>
<td>91</td>
<td>92.5</td>
<td>86</td>
<td>84.5</td>
</tr>
<tr>
<td>Rapeseed oil refined</td>
<td>97</td>
<td>97.5</td>
<td>94</td>
<td>92</td>
</tr>
<tr>
<td>Two-stage process</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapeseed oil unrefined</td>
<td>94</td>
<td>95</td>
<td>94.5</td>
<td>93</td>
</tr>
<tr>
<td>Rapeseed oil refined</td>
<td>98.5</td>
<td>99</td>
<td>96</td>
<td>97</td>
</tr>
</tbody>
</table>

Table 1 indicates that the highest degrees of rapeseed oil conversion into methyl esters, Biodiesel FAME, were obtained from the two-stage process through catalytic comixtures with the following alkaline catalysts: KOH and NaOH. Potassium and sodium hydroxides are good and cheap catalysts. Their fault results from their hygroscopic characteristics; even vestigial traces of moisture cause catalyst deactivation [Darnoko, Cheryan, 2000].

Applying as a catalyst acids H₃PO₄ and H₂SO₄ resulted in slightly lower results, the degree of conversion was 3% lower. It may have been caused by low temperatures during the transesterification process. All the processes of transesterification (no matter which catalyst was used) started at the temperature of 310K. However, it was found that acid catalysts demand higher temperatures. To obtain a high degree of conversion, the process needs to be carried out at a temperature of 338K, which is the temperature of boiling methanol. Carrying out the process at such a temperature, with the use of a 1% catalyst and molar proportion of methanol to oil 30:1, the degree of conversion was 99.5% [Friedman et al., 1984]. Another important conclusion is that applying a two-stage transesterification gives better results. Esters obtained this way fulfill the European norms EN-14214 and EN-14114 – for the minimum amount of esters in biofuel type Biodiesel FAME. The norm assumes that calculating by the volume there must be at least 96.5% of esters in Biodiesel RME. The degree of conversion is influenced by many factors. Aside from the temperatures and the sort of catalyst the quality of the material is also of great importance. Research carried out earlier on unrefined oil with WKT – free fatty acids, indicated that the degree of conversion was lower. These results are confirmed by other researchers, in such a case it is advisable to increase the temperature of the process [Cvengros, Powazanec, 1996, Noureddini et al., 1998].

It is important to remember that the higher the quality of the biofuels, the greater engine performance, therefore high levels of methyl esters must be present and very low levels of mono-, di and triacylglycerides. The norm as outlined in EN 14124 states that in FAME there should be found minimally 96.5 % (m/m) of methanol esters. As we can very clearly observe in Table 1, in order to achieve the conversion levels of unrefined oils, while using any type of catalyst in the transesterification process, both single and two step processes are too low. Bringing us to the conclusion that using this type of FAME to fuel a high compression engine is not possible. In order to fulfill the requirements necessary to reach the required conversion levels of refined rapeseed oils it is necessary to implement an alkaline catalyzer. This type of FAME may be used to fuel high compression engines. When using acidic catalysts in the form of H₂SO₄ it was possible to achieve the quality of esters that fulfill the requirements outlined per EN 14214, only in the case of the refined oils in a two step transesterification process.
The research focused on the comparison of the effectiveness of different types of catalyzers during the methanolyse process of rapeseed oils. Methanol was used in the methanolyse process which allowed for the comparison of the achieved levels of conversion, the process had to be carried out starting at the same temperature level. As the experiments have illustrated, even though the process was carried out with excess levels of methanol, there was a lower level of conversion when comparing it to the alkaline catalyzers; this in turn has shown that the temperature of the methanolyse process in acidic catalyzers is too low. Such a conclusion is validated as well as confirmed; in the following research the temperatures were raised during the process and satisfactory results were reached. The reaction was above 96.5% (m/m) achieved with H$_2$SO$_4$ acid at the temperature of 354K, and when using H$_3$PO$_4$ at the temperature of 363K.

My research is directly specialized in the production of FAME for one’s own usage. Under special circumstances in certain European Union countries it is possible to produce biofuels for your own personal use. In Poland, in accordance with the regulations regarding biocomponents of biofuel fuels (Reg. Para. # 06.169.1199 passed September 25, 2006.), it has been possible since January 1, 2007 for farmers or other people who own more than 10 transportation vehicles. The only requirement to develop this sector is the detailed outline of an effective method in the methanolyse process implementing very simple technology; hence, my personal research on the subject.

REFERENCES


Europe standard EN-14214, EN 14114, EN 14103, EN ISO 3170, EN ISO 5508.


PORÓWNANIE SKUTECZNOŚCI TRASNESTRYFIKACJI PRZY UŻYCIU KATALIZATORÓW ZASADOWYCH I KWASOWYCH

Streszczenie. W referacie zaprezentowano wyniki badań określających skuteczność transestryfikacji oleju rzepakowego przy użyciu katalizatorów zasadowych oraz kwasowych. Ze względu na różne własności zastosowanych katalizatorów transestryfikację prowadzono przy innych warunkach. Stosując katalizatory kwasowe stosunki molowe metanolu do oleju oraz temperatura początku procesu transestryfikacji były znacznie większe niż dla katalizatorów zasadowych. Dla katalizatorów zasadowych uzyskano wyższe stopnie konwersji. Najwyższe stopnie konwersji (> 94%) oleju rzepakowego w estry metylowe – RME uzyskano przy dwustopniowym prowadzeniu procesu dla mieszanin katalitycznych z katalizatorami zasadowymi KOH i NaOH. Zastosowanie w roli katalizatora reakcji transestryfikacji kwasów H3PO4 i H2SO4 dało nieco gorszy wynik, a uzyskany stopień konwersji był niższy o około 3%.

Słowa kluczowe: Biodiesel, transestrifikacja, katalizatory zasadowe i kwasowe.