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Alkali catalysed transesterification of rapeseed oil

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The table of contents

Annotation

The subject of this thesis was a study of the preparation of ester with a low content of free fatty acids by alkali catalysed transesterification. The transesterification of rapeseed oil was carried out under homogeneous catalyst (batch reactor) and heterogeneous catalyst (fixed bed reactor). For the homogeneous catalysis (potassium hydroxide), the attention was paid to (i) the monitoring of transesterification by pH and conductivity, (ii) the preparation of esters with a low content of free fatty acids by two methods: one method is purifying the esters with a high content of free fatty acids by adding calcium hydroxide and second method is stopping of reaction by addition of inorganic acids, (iii) the detailed description of side product of transesterification (the glycerol phase), including ester losses after separation of the ester phase from the glycerol phase. Butanol as another alcohol, which is possible to use in transesterification of rapeseed oil, was used and the transesterification including the various types of stopping reaction and separation of products were described. The obtained data were statistically evaluated in programs STATISTICA and QC Expert.

In the case of the heterogeneous catalysis, the possibility of using mixed oxides in a fixed-bed reactor was studied. Two types of mixed oxides (Mg-Al and Mg-Fe) were used in the transesterification with methanol and obtained results were compared. Moreover, the long-term catalyst test (300 h) was carried out to study the stability of mixed oxides.

Keywords: Transesterification, alkali catalyst, free fatty acids, esters

The aim of the thesis

The aim is the description of various possibilities of preparation of esters with a low content of free fatty acids by alkali catalysed transesterification with alcohols (methanol and butanol). The studied preparation of esters with a low content of free fatty acids is important because the increasing content of free fatty acids in esters can cause corrosion of fuel system. Moreover, the free fatty acids can react with parts of the fuel system and formed soaps, which plug up filters in diesel engines. The free fatty acids are possible to eliminate by (i) their neutralisation from the ester phase or by (ii) precise addition of inorganic acids after the transesterification so that the soaps are not converted to free fatty acids. Both approaches for the preparation of ester with a low content of free fatty acids are described in detail and statistically evaluated. The ester losses occur during the transesterification of rapeseed oils and the separation of products, which significantly decreases the ester yield. Therefore, the attention is also paid to a detailed description and explanation of the causes of esters losses. The transesterification is carried out under homogeneous catalysts (potassium hydroxide) in a batch reactor and under heterogeneous catalyst (the mixed oxides Mg-Al and Mg-Fe) in a fixed-bed reactor

1. Introduction

The world's consumption of fuels and the demand for alternative fuels has increased in the last few years. Many research groups looking for a new kind of renewable fuel, which could replace fossil fuels. Non-renewable resources including fossil fuels (coal, oil, natural gas, etc.) are found in limited reserves and can be depleted, unlike renewable resources which cannot be depleted [1]. Renewable energy belongs to the natural resources that can naturally recover in a human time scale. They provide several key objectives: (i) security of energy supply, (ii) the reduction of greenhouse gases, (iii) the reduction of energy price, (iv) the possibility of new jobs and general economic growth [2]. Primarily, these are resources of energy gained from thermonuclear hydrogen combustion within the Sun. In their drawing can theoretically continue for other millions of years – until the Sun shines. This kind of energy can be obtained from sunlight, wind and hydropower. In recent years, biofuels (belong into the renewable resources) gain more attention of the public and scientific community, which is due to rising oil prices, the need to increase energy security, concern over greenhouse gases from fossil fuels and equally important is the support of renewable fuel by government subsidies. The European Union determined that the percentage of biofuel in fuels will be 10% in 2020. Therefore biofuels also gain more attention from the public and scientific community in recent years [3].

The biofuels are sorting according to the raw materials used for their preparation to the first, second and third generation. The first generation biofuels (produced from food crops) has a limited ability to replace fossil oil. Biofuels include bioethanol (produced from sugar cane, corn, etc.) and methyl esters of fatty acids (produced from palm oil, soybean oil, rapeseed oil, etc.). Bioethanol is preferred in the USA and Brazil and in Europe is biodiesel primarily used. The second generation biofuels is produced from non–edible biomass (such as forest biomass, agricultural waste, fast-growing grasses and wood. The fuels are synthesized by Fisher-Tropsch reaction. The second generation biofuels has great potential to replace fossil fuels, but the main disadvantage is the complexity of the technological process of biofuels preparation than the preparation of biofuels from food crops [4]. The third generation biofuels is using microorganisms such as algae and cyanobacteria [5].

2. Biodiesel and transesterification

Biodiesel – the mixture of methyl esters of higher fatty acids (most often oleic, linoleic, linolenic, palmitic and stearic) is an alternative fuel for combustion engines. Biodiesel belongs to the renewable resources of energy and can be used in existing diesel engines without any modification [4]. The carbon balance of pure biodiesel is zero because carbon dioxide formed by combustion is removed from the atmosphere by the photosynthesis of plants and converted back into oil. Therefore it is a sustainability resource of energy [6]. Biodiesel is a nontoxic ecological fuel, which does not contain sulphur or aromatic hydrocarbons and it is also biodegradable. Its biodegradability in water is significantly better than diesel [6]. It can be prepared from vegetable oils, animal fats, microalgae or waste cooking oils as a source of triacylglycerols by a mostly catalysed reaction called transesterification [7]. Transesterification is a reaction between triacylglycerol and lower alcohol (the most often methanol, but it can be used other alcohols such as ethanol. butanol, etc.) to form esters of higher fatty acids (biodiesel) and glycerol (Figure 1). Biodiesel has to conform with the European standard (EN 14214), which define its properties and chemical composition such as density and viscosity, the content of free fatty acids, which is determined by the acid number, the content of sodium or potassium ions, water content, glycerides content, etc. [8]. The transesterification has to be catalysed under mild reaction conditions, but it is also possible without catalyst at higher temperature and pressure [9]. The homogenous alkali catalyst, mostly KOH, NaOH and CH_3ONa, is the most frequently used in industry because of its low cost, high efficiency and easy availability, but the catalyst is not possible to reuse. Moreover, it reacts with triacylglycerol and free fatty acids (FFAs) to form soaps by the reaction saponification, which decreases the yield of esters, make separation difficult and also consumes the catalyst [10]. Other types of homogenous catalyst are strong acids, such as concentrated inorganic acids (HCl, H_2SO_4) and sulfonic acid. These types of catalyst are usually used for the transesterification of oils with a higher content of FFAs and water, but they are less active (require longer reaction time and higher temperature than alkaline ones) and more corrosive [11, 12]. Other types of catalyst that are suitable for the transesterification are heterogeneous.

Heterogeneous catalyst can solve the problems with the separation of catalysts and their reusability and are consider as more environmental friendly due to decreasing of using water during production and separation process in compare with a homogeneous catalyst [13]. Moreover, glycerol is an easy recovery from the reaction mixture [14]. Heterogeneous catalyst can be also used for the preparation biodiesel from oils with a high content of FFAs [15].

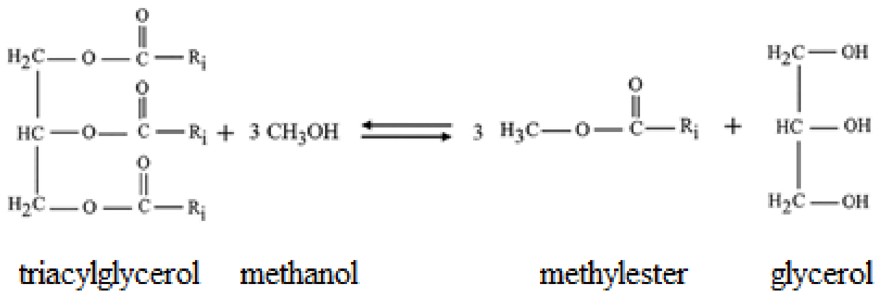

Figure 1 *Simplified scheme of transesterification*

3. Homogeneous catalysis

3.1 Transesterification and neutralisation of catalyst

The strong hydroxides are usually used as alkaline homogeneous catalysts. The reaction particle, which catalysed transesterification, is alcoholate of corresponding metal formed by dissolving of strong hydroxide in alcohol. In this thesis, KOH was exclusively used and the methoxide ions are formed from methanol and KOH (1) [16].

$$\mathrm{CH_3OH} + \mathrm{K^+OH^-} \leftrightarrows \mathrm{CH_3O^-K^+} + \mathrm{H_2O} \qquad (1)$$

It is an equilibrium reaction and therefore it is suitable to use feedstock with lowest possible water content since the presence of water shifts the equilibrium towards to the alcohol and hydroxide which leads to a side reaction (saponification). The saponification is an undesirable reaction, which (i) consumes the catalyst, (ii) decreases the yield of esters and (iii) makes difficult the separation of the ester phase (EP) from the glycerol phase (GP) [17].

As equation 1 shown, the methoxide ions and hydroxide ions are formed, therefore the course of transesterification was monitored by pH and conductivity. The measuring of pH during the transesterification process is complicated by the fact that this reaction is carried out in a non-aqueous environment and therefore the special electrode designed for the non-aqueous titration is necessary to use. The pH and specific conductivity were monitored during the transesterification reaction (Figure 2).

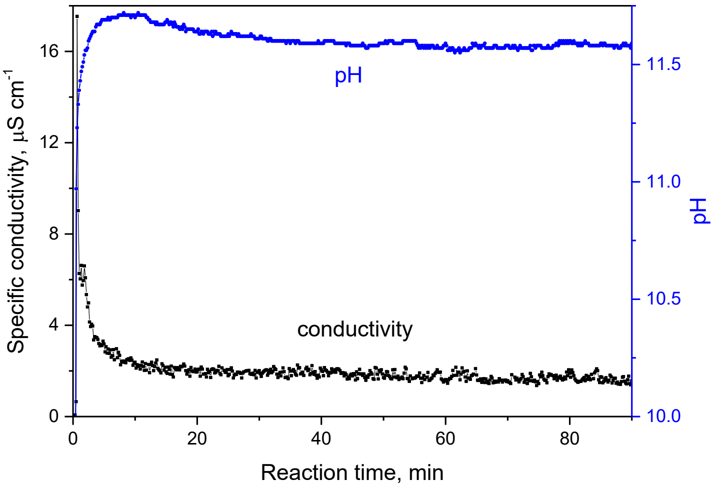

Figure 2 *The dependence of pH value and conductivity during the transesterification*

At the beginning of the reaction, the pH value is stabilised at a relatively constant (pH value is approximately 12) because hydroxide ions are formed by dissociation in the reaction mixture. During the reaction, pH value gradually decreased because the side reaction (saponification) consumed the OH- ions and formed undissociated soaps. Unlike pH value, the conductivity firstly sharply increased (near to value 16 µS cm^{-1}) after addition of methanolate into the oil and almost immediately decreased to a constant value (approximately 2 µS cm^{-1}) and subsequently decreases very slowly similar as the pH value. Thus, the ions are not almost present during the reaction. However, methoxide and hydroxide ions, as well as soaps, were determined (by titration) in the reaction mixture. This can be explained by the existence of micelles that surround the ions immediately at the start of the reaction and ions cannot be detected by the conductivity and are likely cannot take part in the reaction [18].

Transesterification is a reversible reaction, therefore it has to be stopped before alcohol is removed because during the process of removal unreacted alcohol a reverse reaction to the reaction intermediates (monoacylglycerol, diacylglycerol and triacylglycerol are formed from esters and glycerol) can take place [19]. Two approaches for reaction stopping are described: (i) the separation of the EP from the GP where the catalyst remains. The EP is usually known as crude biodiesel, which contains many impurities such as the remainder acylglycerols, glycerol, the FFAs, methanol vegetable dyes, soaps and salts. The GP is usually low quality because of also contains many impurities such as water, soaps and remaining catalyst. Both phases have to be purified, i.e. a further technological treatment is necessary, which increases the energy consumption of biodiesel production. This way of stopped is usually used in the industry [20].

Another possibility is to stop the reaction by neutralisation of the catalyst by acid addition to the whole reaction mixture. It is possible to use weak acid such as gaseous carbon dioxide, which cannot convert soaps into the FFAs and so the acid number of the EP stays zero. If inorganic acid is added into the reaction mixture until pH falls to 2-3, then the fatty acids are formed from soaps and the acid number is above the standard. It is possible to remove the FFAs from biodiesel by reaction with $Ca(OH)_2$. If the acid is added accurately, only the catalyst is neutralised, so the FFAs are not formed from soaps and the acid number remains almost zero.

The reaction was stopped by neutralisation of the catalyst by acid addition into the reaction mixture, especially inorganic acid. If inorganic acid was added until pH value fell to down 2-3, then the formed biodiesel conformed with the standard, expect the FFAs content. The FFAs content (determined as the acid number) was higher than allows the standard because inorganic acid converted soap into the FFAs, which increased the acid number of biodiesel. The increased FFAs content is undesirable because the FFAs can cause corrosion of the fuel system. The FFAs from the EP can be removed by neutralisation by calcium hydroxide addition into the reaction mixture after transesterification and separation of the EP from the GP. The calcium hydroxide was used because the calcium soaps are insoluble in the EP, unlike potassium soaps. The formed calcium soaps can be removed from the EP by the centrifugation. The $Ca(OH)_2$ is poorly soluble in the EP, therefore the water was added to improve the solubility of the $Ca(OH)_2$. It was found, that the addition of a small amount of water into the EP significantly improve the solubility of $Ca(OH)_2$ and dissociation into ions (calcium cations). The ions are necessary for removing of the FFAs from the EP. Based on preliminary experiments, the reaction conditions (independent variables) and their upper and bottom limit were chosen that influenced important properties of the ester phase (dependent variables). As independent variables were chosen: the acid number of input ester phase – $\mathrm{a}n_{in}$ $(\mathrm{mg\ \ KOH\,g^{-1}})$, molar ratio of calcium to the FFAs – MR $(-)$, addition of water – V_w $(\mathrm{\mu l})$, reaction time – t (h), stirring speed – f (rpm) and reaction temperature – T $(\mathrm{°C})$, which influenced the dependent variable: acid number of output ester phase – $\mathrm{a}n_{out}$ $(\mathrm{mg\ \ KOH\,g^{-1}})$, calcium ions content – $\mathrm{Ca^{2+}}$ $(\mathrm{mg\,kg^{-1}})$ and water in the EP – w_{H_2O} (ppm). The experiments were planned according to the Placket-Burman designs and linear models were used to describe the relationship between the dependent and independent variables and obtained data was statistically evaluated. The final equations were found for dependent variables: an_{out} (2), Ca^{2+} (3) and w_{H_2O} (4) and optimal conditions were calculated from these equations. The optimal conditions were found the following: the molar ratio of calcium soaps to the FFAs of 3.33:1, the water addition of 0.14 wt% and the reaction time of 3 h. The predicted (calculated) and experiments values of dependent variables were compared. It was found a good correlation between predicted and measured values for output acid number and calcium content, which were very similar to the predicted value. The water content was higher than the predicted value and was not conformed with the standard.

$$\begin{gathered} an_{out} = 1.64 + 0.57\ an_{in} - 0.19\ t \\ (R^2 = 0.885) \end{gathered} \tag{2}$$

$$\begin{gathered} Ca^{2+} = 46.4 - 20.4\ an_{in} - 10.3\ V_w + 19.7\ t + 32.5\ T \\ (R^2 = 0.829) \end{gathered} \tag{3}$$

$$\begin{gathered} w_{H_2O} = 605.7 + 149.1\ MR + 105.1\ V_w - 76.6\ f - 109.6 - 124\ T \\ (R^2 = 0.919) \end{gathered} \tag{4}$$

The precise addition of inorganic acids so only the methoxide ions were neutralised and soaps were not converted to the FFAs. The new method of acceleration and simplification of the whole process biodiesel production was introduced. The effect of varying amount of concentrated hydrochloric acid (the amount of acid was related to the reaction mixture) on the acid number and potassium content of the EP was studied a detailed described (Figure 3). Initially, the potassium content and the acid number of the EP were relatively constant up to about 0.25 wt% HCl (because chloride ions and methanol were formed from the potassium hydroxide and methanol). Further addition of hydrochloric acid caused an increase of the acid number because the soaps were converted into FFAs. The dependence of acid number was expected, unlike the dependence of potassium content. The potassium content in the EP increased sharply from 0.25 to 0.35 wt% HCl and then decreased to almost zero. This finding was explained, by the fact that the FFAs caused dissociation of potassium soaps and when all soaps were converted to the FFAs, the potassium content decreased almost zero (because formed KCl as a polar substance passed into the GP). This finding was confirmed by an independent experiment.

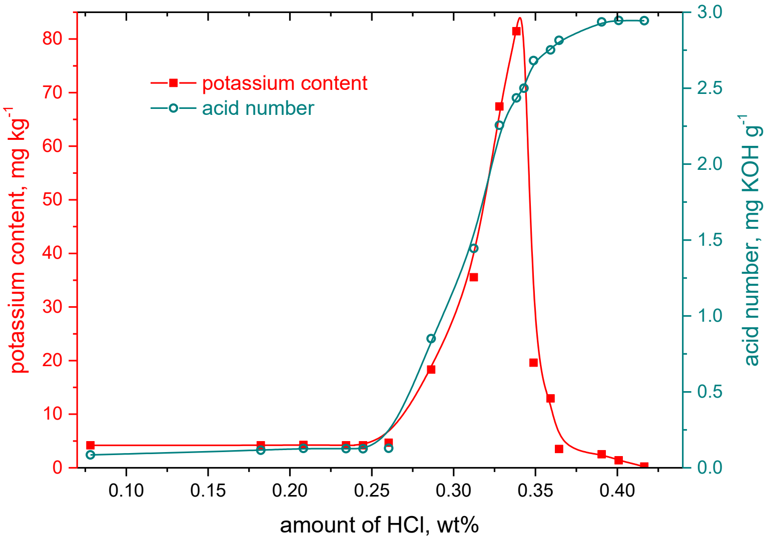

Figure 3 *The relationship between potassium content and acid number in the EP on the amount of added hydrochloric acid*

Different pH dependence on the amount of acid during the addition of acids to the reaction mixture was found for HCl and H_3PO_4. Hydrochloric acid had one inflexion point unlike phosphoric acid, at which the pH gradually decreased (consecutive changes in the formation of phosphoric acid derivatives). Therefore, the exact amount of methoxide ions in the reaction mixture was determined by titration of HCl.

Experiments for both acids (HCl and H_3PO_4) were repeated ten times and important properties of the EP and GP were determined. For each property, the mean values and the standard deviation of measurement were calculated by Horn's procedure for a small selection (according to [21]). The emphasis was placed on the acid number and the potassium content of the EP, which were influenced by the amount of acid added when methoxide ions were neutralised. The best results were obtained by using concentrated phosphoric acid when the prepared methyl ester conformed with the EN 14214. The separation of the EP from the GP took approximately 5 hours (for stopping the reaction by CO_2 separation took more than 24 hours) and separation could be accelerated by centrifugation, which took only 5 minutes and obtained methyl ester conformed with the EN 14214. This approach significantly simplifies the process of methyl esters (biodiesel) production and improves economic and environmental balance of the total biodiesel production, because (i) eliminates purification steps (such as wet and dry washing) (ii) biodiesel conforms with the norm including water content and therefore no drying process is needed (iii) the glycerol content in the GP is relatively high in comparison with stopping reaction by CO_2 addition.

3.2 Methyl esters losses in the glycerol phase

The focus was also paid to side product of transesterification – the glycerol phase because the studying of the GP is mainly omitted in other works. Therefore, the detailed description and understanding of the GP composition, especially the ester content are important for (i) the explanation the causes of ester losses (increasing ester yield) (ii) easier further treatment and usage of the GP. The GP usually contains 30-60 wt% of glycerol and further matter such as soaps, water, salts, alcohol, remaining catalyst and also esters [22]. The exact composition of the GP generally depends on the transesterification process used and the method of separation and purification of the obtained esters.

Three types of transesterification stopping by neutralisation of the catalyst by (i) gaseous carbon dioxide, (ii) gaseous carbon dioxide with water added to accelerate the separation (iii) precisely addition of phosphoric acid were used. Moreover, the methyl ester distribution of free fatty acids was also studied because vegetable oil is composed of several types of fatty acids. In the case of used rapeseed oil, the following fatty acids are mainly represented: oleic, linoleic, linolenic and palmitic acids. It was found, that the ester losses for transesterification with methanol were in the range of 6-8 wt%, which complied with previous papers [23]. The ester losses were almost similar for various type of transesterification stopping, expect to stop of reaction by gaseous CO_2 with the addition of water, which was approximately 15% higher than stopping by CO_2 without water. The reason was that water increased the solubility of the esters in the GP.

The different distributions of methyl esters of fatty acids in the GP for three types of stopping transesterification (CO_2, CO_2 with water and H_3PO_4) and input oil were found. The most different distribution of methyl esters of the FFAs in the GP was found for the stopping by H_3PO_4 and therefore it was chosen for detailed analysis. Four independent variables (reaction time – t (min), the molar ratio of methanol to oil – MR $(-)$, catalyst amount – P $(\mathrm{wt\%})$ and reaction temperature – T $°\mathrm{C})$) were chosen which influenced dependent variables (focused on the GP, i.e. glycerol content – w_G (wt%), ester content – w_E(wt%), soaps – w_{soaps} (wt%), salts – w_{salts}(wt%) and water – w_{water}(wt%). The factorial designed experiments were carried out to plan experiments. Main attention was focused on the influence of ester losses by changes independent variables and the relationship between dependent (GP properties) and independent variable (reaction conditions) was described. The chosen properties of the GP properties were statistically evaluated by the linear model, which described the relationship between variables. The equations for the important properties of the GP were obtained. The obtained equations confirmed that the increasing temperature and catalyst amount supported the side reaction – saponification and form polar soaps that remain in the polar GP. Moreover, the soaps content decreases with higher molar ratio methanol to oil because the higher molar ratio shifts the reaction towards the main products (Figure 1).

However, the main attention was paid to describe the methyl ester losses in the GP, i.e. methyl esters content in the GP. The relationship between the esters content and reaction conditions were evaluated by the linear model (5) and also by the non-linear model (quadratic model) (6), which had higher regression coefficient and described the relation more detailed.

$$\begin{gathered} w_E = 12.22 - 7.58\,MR + 2.54P + 2.79\,T \\ (R^2 = 0.92) \end{gathered} \tag{5}$$

$$\begin{gathered} w_E = -4.86 + 5.51\,P + 3.13\,T + 9.28\,(MR)^2 - 4.59\,(MR) - 2.37\,(MR)T \\ (R^2 = 0.99) \end{gathered} \tag{6}$$

The principal component analysis was evaluated for important properties of the GP (dependent variables) and also for the distribution of methyl esters according to higher fatty acids (Figure 4). The principle weight plot (CWP) for dependent variables confirmed results obtained from linear regression as well as quadratic model (i.e. soaps and methyl ester content had a very strong positive correlation).

The distribution of methyl esters according to higher fatty acids in the GP was also evaluated by the CWP for each run of factorial designed. It was not found any significant relationship between methyl esters distribution and reaction conditions. Thus, the correlation for dependent variables was studied by the CWP and it was found a strong positive correlation between methyl esters of oleic acid and linolenic acid and methyl esters of palmitic acid and esters content in the GP. It means that the GP contained increasing content of methyl esters of palmitic acid than the esters content in the GP is also increased.

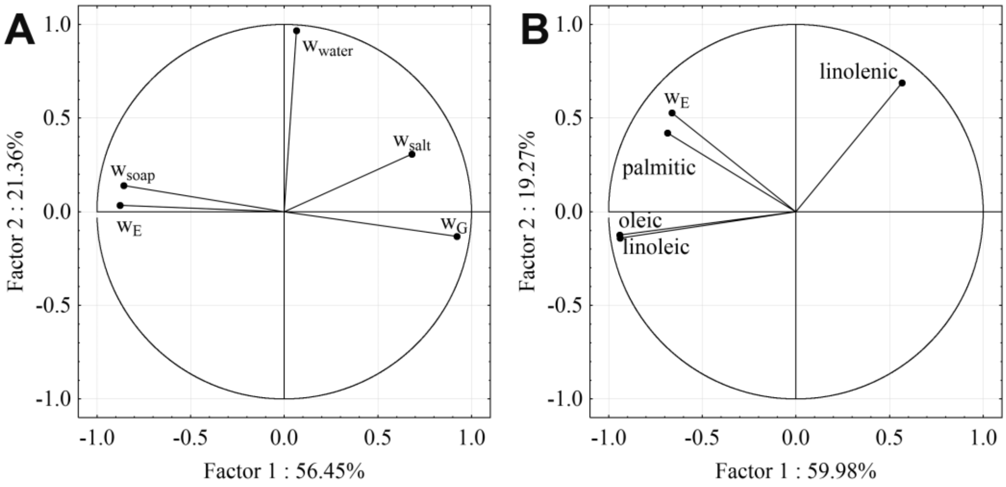

Figure 4 *The CWP for (A) properties of the GP and for (B) methyl esters of higher fatty acids*

3.3 Using of butanol in transesterification

Various alcohols can be used in transesterification, the previous part of work was focused on using methanol and another part is focused on using butanol as a reactant. Butanol has some advantageous properties compared to methanol, such as it is hydrophobic, less corrosive, it has a higher boiling point, it is miscible with oil and butyl ester has higher caloric value than methyl esters.

The butyl esters were prepared by the transesterification of rapeseed oil catalysed by potassium hydroxide. The reaction was stopped by neutralisation of the catalyst by CO_2 and also inorganic acids added into the whole reaction mixture. Moreover, the separation was carried out with addition or without the addition of water, and both methods were compared. Six independent variables (molar ratio of butanol to oil, catalyst amount, reaction temperature and time and method of oil addition) were chosen because these variables influenced the chemical reaction and also separation (separation method). The experiments were planned according to the Placket-Burman designed. The relationship between dependent and independent variables was described for transesterification and separation was also studied. The content of acylglycerols in the reaction mixture was determined after reaction without separation. The reaction was homogeneous (mixture not separated) for molar ratio butanol to oil 6:1 and increases acylglycerols content. The obtained results corresponded with the previous finding, i.e. increasing molar ratio of butanol shifts reaction towards product and increasing catalyst amount and temperature supported saponification. The transesterification was stopped by neutralisation of the catalyst by (i) inorganic acid addition (phosphoric acid, hydrochloric acid and sulphuric acid) into the reaction mixture until the pH fell to 2-3 and soaps were converted into the FFAs (i.e. the acid number was increased), (ii) weak acid gaseous CO_2 addition into the reaction mixture (with water or without water addition). The advantages of using an inorganic acid were: the separation took only minutes, the content of potassium ions and free glycerol in the EP were almost zero. The disadvantage is that inorganic acid converted soaps into the FFAs (i.e. the acid number is increased). Conversely, when gaseous CO_2 was used, the acid number was almost zero, but the content of potassium and free glycerol were increased and separation took more than 24 hours. The separation was improved by water addition and the content of potassium and free glycerol were significantly decreased and separation was accelerated.

The relationship between butanol content and the flashpoint was described. Moreover, the important physical-chemical properties of butyl ester were compared with methyl ester and diesel from crude oil. It was found, that butyl ester had a higher kinematic viscosity than methyl esters and diesel. The butyl esters had a caloric value of approximately about 7.5% higher than methyl ester which was similar or slightly lower than diesel, according to the different paper sources of value for diesel. Unlike density and viscosity, the caloric value is not given by the standard a probably it depends on the type of esters and diesel.

4. Heterogeneous catalysis

The problems associated with homogeneous catalyst are (i) difficult separation from the reaction mixture, (ii) reusability not possible, (iii) producing a large amount of wastewater. All these problems can be solved by using heterogeneous catalysts, which are considered more environmentally friendly. The heterogeneous catalysts can be easily separated from the reaction mixture by filtration (in a batch reactor) and they are possible to reuse, which could facilitate biodiesel production in a continuous process (the catalyst is fixed in the bed).

In transesterification of rapeseed oil the mixed metal oxides were used. Mixed metal oxides were prepared from hydrotalcite-like precursors by thermal pre-treatment – calcination. The hydrotalcites are ionic clays having a layered structure with a general formula $[M_{1-x}^{II} M_x^{III} (OH)_2^{x+}](A_{x/n}^{n-}) \cdot m\, H_2O$, where M represents bivalent (Mg, Ca, Zn, etc.) or trivalent metallic cations (Al and Fe), x is the stoichiometric coefficient of M^{3+}, A^{n-} is anion (such as nitrate, chloride, etc.) and m is the number of molecules water. The structure is derived from brucite, which is magnesium hydroxide $Mg(OH)_2$, but part of the magnesium cations are replaced by another cation (e.g. Ca, Al, Fe). By this substitution, the cation-containing layer obtains a positive charge, and keep the electroneutrality, this charge is compensated by the negative charge of anions in the anionic layer. The anionic layer is located between two positively charged cationic layers and also water is bounded in it. The mixed oxide is then formed by the thermal pre-treatment (calcination) of hydrotalcites, during this process water is removed and the layered structure is destroyed [24].

The transesterification by mixed oxides are usually carried out in a batch reactor, but in this work was carried out in continuous reactor catalysed by mixed metal oxides Mg-Al and Mg-Fe. The Mg-Al and Mg-Fe mixed oxides were tested in fixed-bed reactor Parr (length: 820 mm, insert diameter: 9.4 mm) with a 4871 process controller. The transesterification was studied at different reaction temperature and weight hour space velocity (WHSVs), which is defined as the ratio of the rapeseed oil mass rate to the catalyst amount. Moreover, both catalysts were tested in a long-term catalyst test, which took 300 hours (i.e. 12.5 days), including the stability of the catalysts. The mixed metal oxides (Mg-Al and Mg-Fe) were prepared by the co-precipitation method at constant pH (for Mg-Al 9.5 and Mg-Fe 10) from a cation solution (from nitrate of Mg, Al and Fe) at the temperature of 60°C for Mg-Al and room temperature for Mg-Fe. The obtained catalysts were characterised by various methods (XRD, TGA, XRF, etc.). The catalysts structure were confirmed by the XRD analysis when typical diffraction lines were observed for hydrotalcites and also for mixed oxides and crystal size of the MgO was calculated. The Mg-Fe mixed oxides had the higher specific surface area and the crystal size than Mg-Al mixed oxides, but Mg-Al mixed oxides had the total concentration of basic sites (determined by temperature-programmed desorption of CO_2) two times higher than Mg-Fe mixed oxides.

The catalysts activity were tested at a constant molar ratio of methanol to oil 24:1 and the influencing of catalysts activity by temperature and WHSVs were studied. Each temperature and WHSVs were tested for 32 hours. The WHSVs values of 1, 2 and 3 h^{-1} were tested at constant temperature 110 °C and the WHSVs value 1 h^{-1} was repeated at the end to verify catalyst stability. The ester yield and triacylglycerol conversion (both were determined for samples taken every 4 hours) decreased with increasing WHSVs (it means decreasing contact time). The Mg-Al mixed oxide was achieved higher esters yield and triglyceride conversion are compared with the Mg-Fe mixed oxides, which correspond with a higher concentration of the basic sites. Three temperatures 115, 150 and 200 °C were tested at a constant WHSV 1 h^{-1} and temperature 115 °C was repeated at the end to verify catalyst stability. The triacylglycerol conversion and also ester yield increased with increasing temperature for both mixed oxides catalysts. The Mg-Al had almost twice higher concentration of the basic sites than Mg-Fe, therefore it had higher catalytic activity at temperatures 115 and 150 °C (higher yield and triacylglycerol conversion). Both catalysts had almost the same catalytic activity at highest temperature 200 °C because the reaction rate was high (according to the Arrhenius equations) at this temperature. The lifetime of both catalysts in transesterification reaction was tested in the long-term catalyst, which takes 300 hours and samples were taken every 6 hours and the ester yield and triacylglycerol were determined for each sample. The long-term catalysts test were carried out at a constant temperature 150 °C and WHSV 1 h^{-1} (Figure 5). It was confirmed, that both mixed metal oxides were stable during the tests because the activity of the catalyst only slightly decreased for both catalysts. The Mg-Fe mixed oxide had the lower catalyst activity because it had the smaller amount of the basic sites. Moreover, the total leaching of the catalyst was determined for all experiments and was found as insignificant.

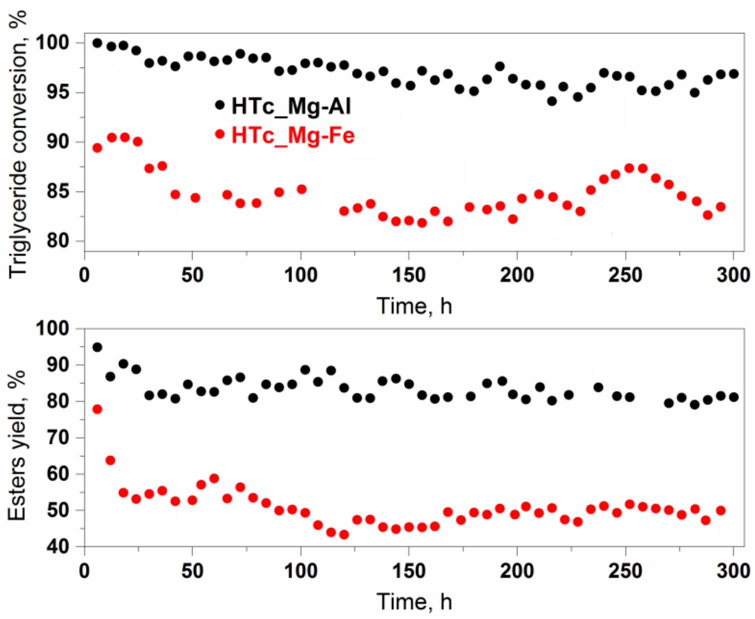

Figure 5 *The long-term catalyst of Mg-Al and Mg-Fe mixed oxides*

5. Conclusions

The dissertation thesis was focused on the transesterification of rapeseed oils with alcohols (methanol and butanol) catalysed by alkaline catalysts – homogenous (potassium hydroxide) and heterogeneous (mixed oxides Mg-Al and Mg-Fe). Obtained data presented in this thesis can be summarised as follows:

- The methyl esters with a low content of free fatty acids were prepared by stopping the reaction by neutralisation of the catalyst by the addition of inorganic acid. Two methods of neutralisation catalyst by inorganic acid were used:
  - The inorganic acids were added until pH value felt to 2-3, which means that soaps were converted into free fatty acids. The advantages of this method are a relatively fast separation of the ester phase from the glycerol phase and the ester phase does not contain potassium ions and free glycerol. The disadvantage is the formation of free fatty acids from soaps, which had to be removed from the ester phase by neutralisation of free fatty acid by calcium hydroxide.
  - Inorganic acids were added precisely so that the only catalyst was neutralised, and free fatty acids were not formed. Obtained ester phase was conformed with the European standard for biodiesel (EN 14214) without other purification processes.
- The glycerol phase (side product of transesterification) was thoroughly described. The focus was mainly on methyl ester losses after the different methods of stopping reaction (by weak acid gaseous carbon dioxide or inorganic acid). Moreover, the distribution of esters according to higher fatty acids (such as linolenic, linoleic, oleic a palmitic) was determined for all methods of stopping the reaction. The description and understanding of methyl esters content in the glycerol phase during the preparation of biodiesel can enable to minimize their losses and make the biodiesel preparation more ecological and economically friendly.
- The ester was prepared by using butanol as a reactant with potassium hydroxide as a catalyst. The butyl ester preparation and separation of the reaction product after the reaction were described.

  Transesterification of rapeseed oil with methanol was carried out in a fixed-bed reactor catalysed by mixed oxides Mg-Al and Mg-Fe as a catalyst. The stability of the catalyst was described by a long-term catalyst test.

6. References

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