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TRANSESTERIFICATION OF TRIACYLGLYCEROLS OVER CALCIUM OXIDE AS HETEROGENEOUS CATALYST

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Abstract

The use of a heterogeneous catalyst for transesterification of triacylglycerols (TAG) to methyl esters of fatty acids (FAME) by methanol enables its simple isolation from the reaction mixture and yields glycerol (G) of a good quality. Calcium oxide appears to be a promising heterogeneous catalyst. The paper presents the results of transesterification obtained from two samples containing CaO from two different producers. The first tested CaO exhibits high catalytic activity with high conversion > 97 % of TAG to FAME, while the second tested CaO exhibits low conversion of only 20 %. In the case of catalytic active CaO is the content of G in the polar phase higher than 97 %, but low fraction of calcium soaps remains in the ester phase. X-ray diffraction analysis, IR spectra and determination of specific surfaces and of the pore distribution pointed to differences of both tested CaO.

Keywords: fatty acid methyl esters; transesterification; CaO; heterogeneous catalyst.

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1. Introduction

Methyl esters of higher fatty acids (FAME) are applied as non-toxic fuel for diesel engines. They are prepared from natural triacylglycerols (TAG) of vegetable oils and animal fats by alkali catalysed transesterification with methanol. The FAME are miscible with fossil fuel in any ratio and have similar properties. Comparing to the fossil fuel, the FAME have several advantages. They can be obtained from renewable sources, CO_2 production during combustion is roughly the same, composition of emissions is more favorable with minimum of polyaromatic hydrocarbons and solid particles, they are fully biodegradable, have higher cetane number, good lubrication ability and other advantages. On the other hand their disadvantages include limited resources, high price due to high input and operational costs, problematic low-temperature properties exhibited especially in climatically more demanding areas, possibly higher NO_x emissions formed in engine at higher combustion temperatures, and degradation of the engine oil during engine operation.

The FAME are prepared by relatively simple transesterification reaction, usually in two steps with high conversion of TAG to FAME over 98 % and with the FAME recovery over 96 % in the presence of homogeneous alkaline catalysts – hydroxides or K or Na alkoxides – in slight excess of methanol (MeOH). High conversion of TAG to FAME is subjected by low acid value (AV) of the initial TAG below 2.0 mg KOH/g, as well as by low content of water (below 0.1 wt %) in the reaction mixture. At temperatures 60 to 64°C the reaction is finished approximately after 3 hours. During the reaction glycerol (G) is evolved in both reaction stages in the form of so called G-phase, which creates a separate liquid phase, which shifts the equilibrium in the reaction mixture towards the formation of FAME. Raw FAME are refined by removal of unreacted MeOH, cooling, filtration or centrifugation of precipitated solid components, washing with water for removing of alkali residua and G, centrifugation after washing and drying of the final product, which then by its parameters meets the standard EN 14 214.

Valuable by-product from FAME production is G, whose theoretical fraction is approximately 10 wt % with respect to the initial TAG. In reality the fraction of the G-phase is approximately 15 to 17 wt %. Along with G the G-phase contains also alkaline catalyst in the form of alkalis and soaps, unreacted MeOH, trapped FAME and moisture.

Along with economical and ecological disadvantages of homogeneous catalysts in the production of FAME the literature mentions, along with impossibility of catalyst regeneration, also complicated and costly final treatment of FAME. High amount of washing water is mentioned. In fact volume of washing water does not have to be large, and in optimally directed reaction a one-stage washing process with water consumption of 0.5 to 2.0 wt % with respect to FAME is sufficient. More complicated situation is in the case of the G-phase and refinement of raw G, which is difficult. In conventional technology the G-phase is decomposed with mineral acid (H_2SO_4, H_3PO_4, HCl) to so called organic layer, which contains free fatty acids (FFA), FAME, MeOH, acylglycerol residues (AG) and organic pigments. Evaporation of MeOH from G-phase before its decomposition is possible although difficult due to intensive foaming and high melting temperature of distillation residue. It is therefore easier to remove MeOH from the organic layer. The lower polar layer, after decomposition of the G-phase by mineral acid, so called G-layer, contains G, MeOH, water from the acid used for decomposition, and also K or Na inorganic salts of the respective acid. According to circumstances part of the salts forms the third phase at the bottom of the vessel. After evaporation of MeOH raw G contains 78 – 82 % of G, 6 – 8 % of salts and approximately 10 % of water. By further evaporation of water in a vacuum film evaporator the content of G over 90 wt% can be achieved. Removing of water from raw G leads to further crystallization of salts and their sedimentation is induced. However, the viscosity of raw G is relatively high and filtration becomes difficult. Raw G is completely refined by distillation in film evaporator at the pressure of 2 kPa with recovery lower than approximately 90 % with respect to the present salts. The refinement of G was discussed in paper [1]. Final purification of G is performed by adsorption on active coal. Ion-exchange chromatography is also applied for operational refinement of G [2]. The G is valuable product and a raw material for more than 1800 products [3]. The rapid increase of the production of FAME caused that the offer on world market exceeded significantly demand and the prices of G decreased rapidly. At present remarkable fluctuations of the prices of G prices on the market are registered, especially of its qualitatively lower commodities [4].

At high production costs related to production of FAME one of the possibilities for improving the economical parameters is the use of G as a by-product. Along with low price sufficient quality is prerequisite, which cannot be guaranteed by the technology of homogeneous alkaline transesterification. Massive research efforts today are therefore focused on technologies utilising heterogeneous catalysts, which should make the final treatment of both key products (FAME and G) significantly simpler. The heterogeneous catalyst is not lost, and from the reaction mixture is removed by filtration. Time consuming washing treatment can be omitted. Moreover, catalyst removed by filtration can be re-used unlike the homogeneous catalysis. Alkaline zeolites [5], oxides of alkaline metals and alkaline earths [6,7], carbonates of alkaline metals and alkaline earths [8], guanidines on carriers [9,10], alkaline hydrotalcites [11,12] etc. were tested as heterogeneous alkaline catalysts. In fact, none of these catalysts was able to replace the homogeneous alkaline catalysts such as oxides, hydroxides, or metoxides of Na and K. The only exception is the ESTERFIP-H® process. The first commercial Esterfip-H unit with a capacity of 50 000 tpy was put on-stream in March 2006 by Diester Industrie in Sète, France. A second plant was completed in May 2007 at Perstorp's Stenungsund, Sweden, chemical complex. Six more Esterfip-H plants are at various project stages around the world for a cumulative capacity of 1.3 million tpy. In September 2007, Esterfip-H™ technology awarded a turnkey construction contract to build a 250,000 metric tons per year biodiesel plant in Kuantan Port, Malaysia [24]. This unit is planned to run on palm oil. The heterogeneous catalyst is a mixed oxide of two metals (Zn and Al) coated on γ-alumina. The conversion of TAG to FAME is over 99 %, recovery of FAME close to 100 %, and predicted lifetime of the catalyst several years. The G as a by-product is obtained with a purity over 98 %. Such quality of G improves the economic parameters of the FAME production [13, 14].

The review and evaluation of published results suggest a large chance of calcium oxide CaO for successful application as a heterogeneous catalyst. At present there exists no published reference, which would indicate better heterogeneous catalyst for transesterification of TAG to FAME than CaO.

Kouzu et al. [15] compared the conversion of TAG to FAME with CaO, $Ca(OH)_2$ and $CaCO_3$. After one hour in one stage reaction the conversion of TAG (edible soybean oil) with CaO, $Ca(OH)_2$ and $CaCO_3$ was 93 %, 12 % and 0 % respectively. At the same time, under comparable conditions, (65°C, the molar ratio of oil:MeOH = 1:12, i.e. the ratio acyls:MeOH = 1:4) the conversion of TAG to FAME with alkaline homogeneous catalyst KOH was practically complete. The fraction of CaO with respect to the initial oil was 0.85 %. High conversion, over 99 % was achieved for CaO after 2 hours and for $Ca(OH)_2$ after 4 hours. CaO was prepared from $CaCO_3$ by calcination at 900 C in flowing helium. Edible soybean oil used for the experiments had the acid value below 0.1 mg KOH/g and the content of water 0.01 wt %. The experiments were carried out also with used fritting oil (UFO) with the AV 5.1 mg KOH/g, with water content 0.05 % and with 18.7 wt % of polar compounds. The FFA destroy the CaO catalyst, form calcium soaps, which are oleophilic and soluble in FAME. This is reflected both by weight loss of recuperated CaO (up to 80 %), and by the content of Ca in the FAME, which increased from 187 ppm in neutral soybean oil to 3065 ppm for UFO with the AV 5.1 mg KOH/g. Despite this the conversion of TAG to FAME was not degraded and also in this case the conversion after 2 hours was around 99 %. The influence of humidity and polar compounds on the conversion was substantially smaller. Since Ca soaps form organosol with the FAME, the catalyst need to be protected by reducing the acidity of oil before transesterification e.g. by preliminary esterification with MeOH. The authors [15] do not address the problem of final treatment of FAME. The proposed reaction scheme of CaO-catalyzed transesterification was as follows: In the first step a proton from MeOH is trapped on the basic centre of the solid catalyst and forms a metoxide anion. This attacks a carbonyl carbon in a TAG molecule, which yields alkoxy-carbonyl transient product. The product cleaves into two molecules – FAME and diacylglycerol anion, which traps the proton from the catalyst surface and the process is repeated.

The same authors in their next paper [16] presented a modified function of the heterogeneous catalyst CaO. CaO forms with G, created as a by-product, calcium diglyceroxide, which, according to authors, is the true basal transesterification catalyst. The absence of expected calcium metoxide was confirmed by spectral methods. The recycled catalyst already after the first cycle is therefore the modified CaO. Although the recycled catalyst is not as active as the fresh CaO, it nevertheless ensures equally high conversion of TAG to FAME and is more tolerant against deactivation effect of air (humidity, CO_2).

The reference [17] describes activation of CaO before its application in the reaction. The activation is based on mixing the MeOH with the catalyst (0.1 g CaO + 3.9 g MeOH) and stirring the mixture for 1.5 hours at room temperature. Then the rapeseed oil (15 g) is added and heated to 60 °C and left to react for several hours. CaO was not treated before its use. The difference in catalytic activity of activated and non-activated CaO was significant. However, the achieved conversions were relatively low and in the optimal case varied around 87 %. Lower conversion e.g. in comparison to the results in [15] was probably linked to lower weight ratio MeOH:oil = 2.34, while in [15] it was 3.84. The content of the catalyst in the paper [17] and [15] was approximately 0.65 % and 0.87 %, respectively.

Xuejun Liu et al. [25] recommend the adjustment of reaction conditions so that the ratio MeOH:oil is 12:1 mol, the content of the CaO catalyst 8 wt %, temperature 65 °C, addition of water to MeOH 2.03 % with respect to oil. FAME recovery after 3 hours was 95 %. The catalyst preserved high activity even after 20 cycles.

Granados et al. [20] emphasise the preparation and activation of CaO. From their study of the influence of water and CO_2 when the catalyst is in contact with air, from the study of stability of the catalyst during its recycling, and from the study of heterogeneously catalysed reaction, they concluded that in the presence of air CaO is being rapidly hydrated and carbonized. Several minutes are sufficient for chemisorption of significant amounts of water and CO_2. The main de-activator is CO_2 while the effect of water is less significant. The temperature exceeding 700°C is required for re-activation. The catalyst can be used in several cycles without notable decrease of the catalytic activity. The catalytic activity is the result of homogeneous and heterogeneous processes. Part of the reaction takes place on alkaline centers at the catalyst surface, part in the dissolved form of CaO in MeOH.

The aim of the present paper is to verify some published data and to evaluate possibilities of the use of CaO as a heterogeneous alkaline catalyst in transesterification of TAG to FAME.

2. Experimental

2.1 Catalyst treatment

In the study of the reaction activity of calcium oxide in the process of transesterification we used two CaO samples in the form of fine powders: CaO, purum from Lachema Brno (Czech Republic) and CaO purissimum from Riedel-de Haen, Seelze (Germany) with a content of CaO over 96 %. The catalysts were activated before transesterification. The catalysts were dried for 24 h at 105°C. This way treated CaO was calcinated. The CaO catalysts from Riedel-de Haen are labeled *A* and *B*, the catalysts from Lachema are labeled *C* and *D*. The catalyst *A* was calcinated at 550°C with the heating rate 300°C/h for 5 hours. The catalysts *B* and *C* were calcinated at 700°C for 5 hours. The catalyst *D* was not activated, but together with the catalyst *C* was dried under conditions given above. Calcinated as well as dried catalysts were stored in desiccator to prevent hydration of catalysts with H_2O and carbonization with CO_2.

2.2 Reactants

Untreated edible rapeseed oil RACIOL (Palma Tumys Bratislava, SK) was used for the measurements. Its AV was 0.12 mg KOH/g. Pure MeOH was delivered by the company Mikrochem Pezinok, Slovak Republic.

2.3 Transesterification procedures

The tests of transesterification of rapeseed oil with MeOH in the presence of heterogeneous catalyst were carried in the batch reactor with overall volume of 250 mL and outer casing for heating medium equipped with massive magnetic blender with PTFE coating to assure efficient homogenisation of reactants and the catalyst.

At first the calculated amount of MeOH was poured into the reactor. Then the CaO catalyst was added with the ratio of 2 to 8 wt % with respect to vegetable oil. In selected measurements the water with the ratio of 0.5 up to 2 wt % with respect to vegetable oil was added to the mixture of MeOH/CaO and the formed reaction mixture was mixed for 10 minutes. Some experiments were carried out without the addition of water. Then the rapeseed oil (100 g) was added and temperature of the reaction mixture was set between 64 and 65 °C. Transesterification proceeded under the reflux of methanol under continuous stirring of the reaction mixture for 4 hours. After this period of time free MeOH was removed from the reaction mixture on vacuum rotor evaporator and obtained product was filtrated through paper filter. Filtrate was left in separating funnel to separate ester and glycerol phases.

2.4 Analytical methods

Conversion of acylglycerols on FAME was determined according to method published in [23]. Method is based on comparison of spectrum areas of FAME in a sample before and after treatment of the sample with effective transesterification reagent. The analyses were performed on gas chromatograph Chrompack CP 9000 with flame-ionization detector and with 1.8 m glass filling column with inner diameter 0.3 cm. 10 % SE 30 on Chromatone NAW DMCS with a grain size 0.125 – 0.16 mm was used as a stationary phase. Samples were analyzed isothermally at 250 °C. Injector temperature was 240°C and temperature of the flame-ionization detector was 270 °C. Nitrogen with the flow 30 $cm^3 min^{-1}$ was selected as carrier gas.

Glycerol present in the G-phase was determined by GLC using the method of direct calibration on a gas chromatograph Chrompack CP 9000 with flame-ionisation detector and with 0.60 m glass filling column with inner diameter of 0.3 cm, and the stationery phase. Samples were analyzed isothermally at 250°C. Injector temperature was 230°C and temperature of the flame-ionization detector was 250°C. Nitrogen with the flow of 30 $cm^3 min^{-1}$ was selected as the carrier gas.

2.5 Characterization of catalysts

Some physical and chemical parameters of the used catalysts were examined by means of X-ray diffraction (XRD), IR spectroscopy and by textural characterization.

Powder X-ray diffraction patterns were recorded on a Bragg-Brentano focusing diffractometer Philips PW 1730/1050 using $Cu_{K\alpha}$ radiation (k = 0.154 nm) at 40 kV and 35 mA range of 2Θ 3° - 71° (step size 0,02°).

IR spectrum of the used CaO were measured on a FTIR Excalibur FTS 3000 MX from the company Digilab, USA, in the range of 4000 to 400 cm^{-1} and the number of scans 36. The used method: transmission, KBr tablets of 0.25 g KBr + 5 % of sample, pressed at 700 MPa. Alternative IR spectrum was obtained by DRIFT technique (diffusion reflection from powder).

Surface characteristics of the used catalysts based on physical adsorption of nitrogen at the temperature of liquid nitrogen, where standard isotherms BET were determined, were carried out using the equipment Micromeritics ASAP2400. Before the measurement the samples were activated at the temperature 350°C and the pressure of 2 Pa for about 12 hours.

3. Results and discussion

3.1. Transesterification

Table 1 summarizes the conditions of transesterification experiments of refined rapeseed oil with MeOH in the presence of CaO catalyst and measured conversions of AG to FAME.

Tab. 1 Reaction conditions and AG conversion to FAME

sample	molar ratio TAG:MeOH	CaO	kat. wt %.	H_2O wt %	conversion, %
1	1:6	*A*	8	2	98.8/51.0*
2	1:12	*A*	8	2	98.9/68.9*
3	1:6	*B*	8	2	-/56.1*
4	1:6	*B*	8	0	97.0
5	1:6	*B*	2	0.5	96.3
6	1:6	*B*	2	0	96.9
7	1:6	*B*	2	0	98.8
8	1:6	*B*	1	0	96.0
9	1:6	*C*	2	0	18.6
10	1:6	*D*	2	0	9,7

**conversion determined after final treatment*

The experimental results indicate that the use of CaO, as a heterogeneous basic catalyst after appropriate treatment, together with high quality of reactants, enables to reach high conversion of TAG to FAME in a one-stage operation, at the level meeting the requirements of the EN 14 214 standard. The analysis of prepared FAME carried out with the use of our developed TLC method showed that also the contents of MAG, DAG and TAG are in optimal cases lower than the maximum values allowed by the standard.

High activity of CaO can be simply achieved by calcination at 700°C and by ensuring the usual storage conditions (desiccator). Complicated operations related to preparation of mixed oxides, metoxide as well as the manipulation with CaO after activation are not necessary.

The advantage of CaO catalyst activation with water – partial conversion of CaO to $Ca(OH)_2$ published in [19] - was not confirmed. For experiments with CaO (Riedel-de-Haen), measurements 1 and 3, with addition of water, high conversions over 96 % were determined, with the content of FAME around 70 %. Organosol was formed in FAME prepared in these measurements. The products were viscous even gelatinous and showed alkali reaction on the indicator tape. This fact is due to the presence of significant amount of calcium in FAME. Organosol, as the result of the presence of calcium soaps of fatty acids binds in its structure except of FAME probably also part of G, part of MeOH and other components of the reaction mixture. The result is low content of FAME in ester layer, despite of high determined conversion. After washing with water with addition of mineral acid the organosol is probably disrupted. Surprising is low conversion between 50 and 70 % determined after this operation, which can be related to hydrolysis of FAME. In further measurements, water was not used for anticipated, and in [19] recommended activation. Subsequently, the conversions were high, and did not change after washing with acidified water. The formation of organosol was thus limited, but not completely excluded. The presence of calcium salts (in fact calcium soaps) is indicated also by highly stable emulsion of milky character, which is formed after addition of water to FAME from reaction, but also to FAME after insufficient treatment with acidified water. Bubbling of FAME with CO_2 with the aim to bind the present Ca in the form of carbonate was not successful; carbonic acid is probably not sufficiently strong. The test of catalytic activity after transesterification with CaO Lachema (measurements 9 and 10 in Table 1) under the same conditions as the test with CaO Riedel de Haen were not successful, achieved conversions were not sufficient, and did not increase even after prolonged reaction times. The reaction mixture was in this case cloudy, and viscous from the present organosol. In the following discussion we will therefore take into consideration only the measurements with CaO Riedel de Haen.

The fraction of CaO in the reaction mixture is sufficient at the level of 1 to 2 wt. % with respect to oil, higher concentrations lead to increased formation of organosol, especially in combination with water.

Surprisingly, the G-phase does not contain any significant amount of Ca. The content of G in measurement 6 was determined to be 97.8 % with relative error approximately ± 1 %. Sufficiently efficient qualitative test on the presence of Ca with water solution of H_2SO_4 (haze from $CaSO_4$) was negative. Calcium soaps are probably concentrated in the ester phase. While final treatment of G is not required, final treatment of FAME is necessary.

The fraction of G obtained as separate phase is smaller than theoretical, it ranges between 7 and 9 % in comparison to the theoretical value 10 %. This can be related either to loss of G on hydrophilic polar surfaces of glass apparatus, or with certain fraction of G bound in organosol in FAME, and also with the fraction of G bound to the surface of the catalyst in the form of diglyceroxide. This fraction should not increase during repeated use of the catalyst. The tests of the catalyst lifetime were not performed.

3.2 Spectral and structural characterization of catalysts

From the course of standard isotherms of nitrogen adsorption (Fig. 1) we determined specific surfaces S_{BET} at the relative pressure p/p_o in the interval 0.05 to 0.30 and the total volume of adsorbed nitrogen $V_{0.98}$ at the relative pressure p/p_o = 0.98. The results are shown in Table 2. Fig. 2 shows the size and distribution of pores for both tested catalysts.

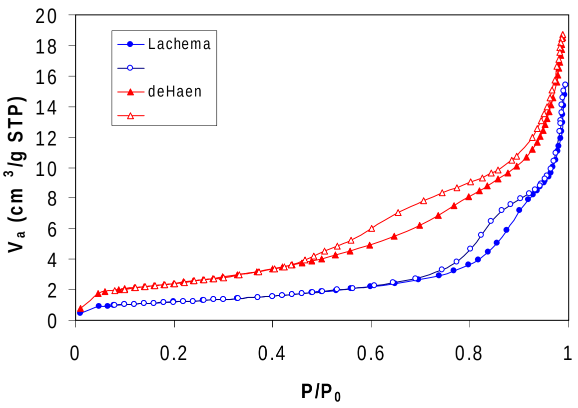

Fig. 1 BET isoterms for tested CaO catalysts

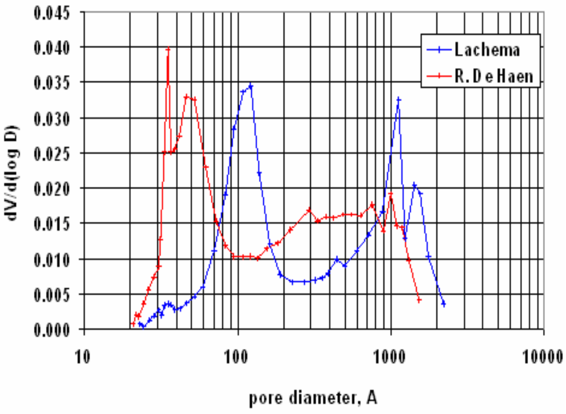

Fig. 2 Pore size distribution for tested CaO catalysts

Tab. 2 Specific surface and total volume of adsorbed nitrogen for tested catalysts

Sample	S_{BET}, m^2 g^{-1}	$V_{0.98}$, cm^3 g^{-1}
CaO Riedel-de Haen	8.8	0.027
CaO Lachema	4.3	0.021

The CaO Riedel de Haen exhibits higher specific surface, approximately twice as high as the CaO Lachema. The hysteresis curves on adsorption-desorption isotherms indicate the presence of mesopores. In the CaO Riedel de Haen their diameter is between 2 and 50 nm, the mean diameter is about 5 nm. In the CaO Lachema the pores are larger, with the diameter around 12 nm, maximum value around 120 nm, and their number is higher. More active transesterification catalyst has therefore higher specific surface, and smaller pores, but the difference in specific surface is not significant.

IR spectra of tested CaO-based catalysts in Fig. 3 reflect the existing differences between the two materials. Different is the shape of the band around 1500 cm^{-1}, and also the band around 3600 cm^{-1}, which is characteristic for water (moisture). In catalytically more active CaO Riedel de Haen the band is more intensive than in less active CaO Lachema. Literature quotes partial activation of CaO with water as a successful operation enhancing catalytic activity of CaO [19].

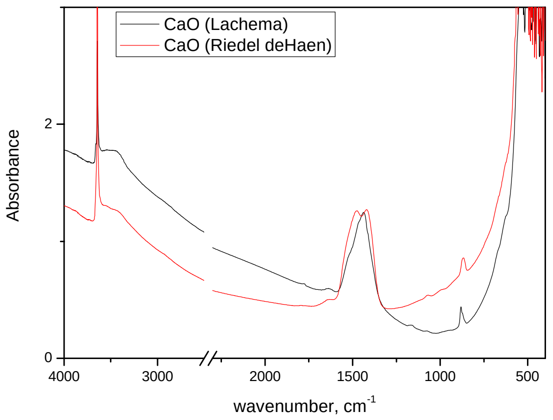

Fig. 3 IR spectrum of tested samples CaO (KBr technique)

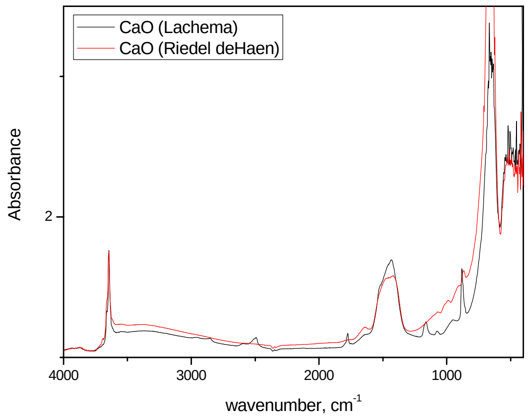

Fig. 4 IR spectrum of tested samples CaO (DRIFT technique)

Also in the IR spectra on Fig. 4 obtained by the DRIFT techniques with diffusion reflection from powder it is obvious that the band for moisture around 3600 cm^{-1} is more intensive for the CaO Riedel de Haen. Also the structure of the band around 1500 cm^{-1} is slightly different. In this type of spectrum, also the area 1800 – 1000 cm^{-1} is richer in bands in the CaO Lachema.

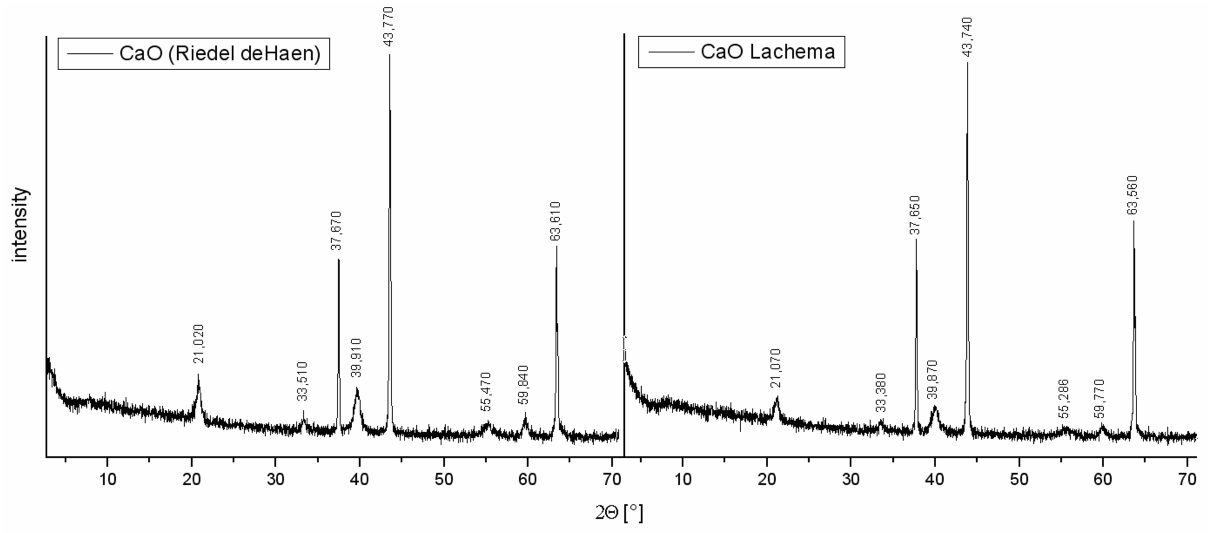

Fig. 5 XRD spectrum of tested samples CaO

Fig. 5 shows the X-ray spectra obtained by the powder diffraction method. Three pronounced peaks (in the 2Θ values) 37.6 °, 43.7 ° and 63.6 ° belong to CaO crystals, and the peaks at the 2Θ values 21,0 °; 33,4 °; 39,9 °; 55,3 ° a 59,8 ° are characteristic for $Ca(OH)_2$. The presence of $CaCO_3$ was not detected due to low sensitivity of the equipment; the content of carbonate in CaO specimens can range around 1 %, which probably does not represent significant change of the properties of the catalyst, or its deactivation. The results of X-ray spectroscopy confirm the qualitative data acquired by IR spectroscopy.

Both samples for measurement were prepared in the same way, which in the maximum possible extent prevented contamination with air moisture and CO_2. From the quantitative point of view the peaks attributed to $Ca(OH)_2$ in the CaO Riedel de Haen catalyst are more intensive then in the catalyst CaO Lachema. Approximate composition of both tested CaO samples was obtained by semiquantitative analysis. In the first case the Riedel de Haen catalyst contained 84.6 % of CaO and 15.4 % of $Ca(OH)_2$. For the catalyst Lachema the composition was determined to be 90.9 % of CaO and 9.1 % of $Ca(OH)_2$.

It is possible that the reported differences are the reason of various catalytic activity of tested CaO, but this cannot be said with absolute confidence.

4. Conclusions

Properly treated calcium oxide with specific surface structure can be successfully used as a heterogeneous catalyst for transesterification of triacylglycerols to methyl esters. Its activation is relatively simple, it is accessible from the point of view of prices, ecologically clean, and efficient also at low concentration. The reaction proceeds with small excess of MeOH at the temperature of about 65°C in one-stage process for 4 hours. The fraction of glycerol in polar phase from transesterification is high, around 97 %. However, the ester phase as raw FAME requires final treatment with separation of small amount of calcium soaps.

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