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# SOLID BASE-CATALYSED TRANSESTERIFICATION OF SUNFLOWER OIL. AN ESSENTIAL OXIDATION STATE/COMPOSITION OF CaO-BASED CATALYST AND OPTIMISATION OF SELECTED PROCESS PARAMETERS

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## ABSTRACT

Substantial relationships between the structural features of the solid base CaO catalyst (meso/macropores system, the essential composition – bare CaO crystal phase characterised with limited dimensions and total basicity of basic active sites near or onto $Ca^{2+}$ cations) and its catalytic efficiency in sunflower oil methanolysis have been found. The optimisation of the selected process parameters has shown that the optimum reaction temperature would be 60°C (fatty acid methyl esters yield 88% after 5.5 h of time-on-stream), and the optimum reaction pressure 15 bars (fatty acid methyl esters yield 91.5% after 5.5 h at 80°C) based on the obtained experimental data. A mathematical regression model is developed in order to optimise simultaneously numerous parameters (temperature, pressure, time-on-stream) that all together affect the biodiesel yield. This regression analysis may be used to improve the biofuel production process and reduce the production costs.

*Keywords*: an essential oxidation state, CaO as a solid base catalyst, mathematical model, transesterification of sunflower oil, optimisation of process parameters.

## AIMS AND BACKGROUND

Biodiesel is promising alternative for the fossil-fuel derived diesel due to its comparable engine performances. Namely, biodiesel usage results with similar energy content/power, an absence for additional modifications of engine unit(s), acceptable

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cetane index and ultra-low sulphur emissions[1,2]. Moreover, the use of biodiesel may positively affect environmental protection by reducing green gas emissions because bio-feedstock usually contains low level of sulphur and nitrogen, and additionally no compounds/precursors related to $CO_2$ generation in combustion process[2–4]. In addition, biodiesel derived from renewable feedstock can be suitable substitution for regular diesel fuel in actual circumstances of limited fossil resources.

Usually, biodiesel is produced over transesterification of vegetable oils or animal fats with methanol into a mixture of fatty acid methyl esters (FAME) (Refs 3–6). The reaction can be catalysed using both homogeneous (base or acid)[7–9], and heterogeneous (base, acid and enzymatic) catalysts[3,5,6,10,11]. Homogeneously catalysed transesterification reaction is much faster and provides high FAME yields. However, the homogeneous catalysts separation and purification is highly cost and difficult procedure[3,5,12]. The separation and purification of homogeneous catalysts by washing procedure additionally discharges a large amount of wastewaters[13].

On the other side, heterogeneous catalysts provide advantages from both economic and environmental standpoints. The use of these catalysts can diminish process cost due to cheaper steps of separation from the liquid mixture, heterogeneous catalysts exhibit long life-time and can be reused without regeneration. They are similarly environmentally benign[14]. Because of those numerous advantages, heterogeneous catalysts have attracted wide scientific attention. The extensive reports of solid base catalysts have been presented and used in transesterification[14]. Among them, calcium oxide has been extensively investigated due to its high basicity, availability, and low cost[5,7,10].

Different researches were conveyed over CaO as heterogeneous catalyst dealt with physicochemical properties of the catalyst[5,7,15], different calcination temperatures as activation procedures performed over CaO-based precursors[2–15], and various process parameters affected final catalytic performances[3,5].

Vujicic et al.[5] have investigated the influence of different process parameters (ex. reaction temperature, pressure) in the biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst. They have registered the highest FAME yield of 91% at 80°C after 5.5 h of reaction run, and almost the same yield for the reaction proceeded at 100°C less than half time of the previous reaction run. Some authors have researched solid acid catalysts that catalysed simultaneously esterification and transesterification reactions[16,17]. They have found that high reaction temperatures (180–260°C) and higher pressures (250 psig) were needed to achieve acceptable conversion of reactants to biodiesel[16,17]. On the other side, solid base catalysts showed higher catalytic activity for transesterification than solid acids[3,18,19].

There was developed the response surface methodology (RSM) as mathematical model for the optimisation of the process parameters in transesterification of different oils[20,21]. Namely, Velickovic et al.[21] have investigated the effect of temperature, ethanol-to-oil molar ratio and catalyst loading on the fatty acid ethyl esters (FAEE) yield in sunflower oil ethanolysis. A second-order polynomial equation is developed to relate the FAEE purity and the operation variables. The authors proved that RSM is suitable method for optimisation of operation conditions to maximise the FAEE purity.

Santos et al.[20] reported that RSM is adequate for simultaneously evaluation of all selected factors that could influence the yield of the soybean oil in base-catalysed transesterification maximising the yield and reducing the process/technology costs.

To the best of our knowledge, there is no total report on essential oxidation state/composition of CaO-based catalyst in transesterification of selected oils, and no detailed data on the developed mathematical model for the optimisation of chosen process parameters (ex. reaction pressure, calcination temperature) in biodiesel synthesis. This paper deals with judgement on the optimum composition of CaO in sunflower oil methanolysis, and mathematical regression model for the optimisation of selected process parameters.

## EXPERIMENTAL

*Materials and catalyst preparation*. The catalyst precursor was calcium oxide of technical grade (Aldrich Co.). The precursor powder was calcined at selected temperatures, 750 and 900°C, for 3.5 h under dynamic conditions in nitrogen flow of 25 $cm^3$/min. After activation thermal treatment, the calcium oxide based powder was pressed into pellets, and sieved to obtain fraction 1.0–1.5 mm in size. This catalyst fraction was optimised to avoid potential external diffusion restrictions in the batch reactor, and/or internal diffusions limitations within the catalyst dosage/layer. Catalysts are denoted: CaO-*T* where *T* presents the calcination temperature.

HPLC grade methanol (Aldrich Co.) was used in the test reaction of solid base-catalysed methanolysis of sunflower oil (domestic producer, Dijamant Co.). The sunflower oil is typical oilseed plant in the region. The essential physicochemical properties (ex. cetane index, low temperature features, sulphur content, water content, heating value) of the feedstock and the obtained alternative biofuel (biodiesel) were determined by the EU established standardised methods: EN 14104 : 2003, EN ISO 5165 : 1998, EN 116; SRPS EN ISO 2719, ASTM D 5453, SRPS ISO 12937, and ASTM D5865-07.

*Catalyst characterisation*. Textural characteristics (specific surface area, average pore diameter, pore volume and pore size distribution) of activated CaO catalysts were investigated by means of low temperature nitrogen adsorption/desorption method by using a Micromeritics ASAP 2010 with helium as carrier gas. Structural analysis in order to reveal crystal structure of catalysts, X-ray diffraction analysis, was performed on a XRD Philips APD-1700 diffractometer with anticathode and mono-chromator at 55 mA and 40 kV. Crystallite size was calculated by applying the Scherer equation.

Morphological properties of the bulk catalysts were determined by a scanning electron microscopy, SEM JOEL JSM-6460L, at accelerating voltage of 25 kV and magnification up to 100.000 ×. Thermal features of the solid catalysts were examined using thermogravimetric (TG) and differential thermal analyses (DTA) on a Baehr

STA 503 in an inert atmosphere. These measurements were done in the temperature range 25–1000°C using a heating rate of 10°C/min. Surface basic properties of the calcium oxide samples were considered by FTIR spectroscopy on a Win Bomem 1000 instrument in the region 4000–400 $cm^{-1}$. Catalysts surfaces were exposed to phenol (ex. weak acidic properties) vapours to study the basic nature of catalysts active sites, and afterwards exposed to vacuum in order to remove any physically adsorbed vapours.

*Reaction procedures*. Methanolysis of sunflower oil was conducted in a stirred, high pressure, commercial reactor Parr 4520 over the prepared and activated CaO catalysts. The catalyst dosage was 1 wt. % relative to the total reactants weight, the molar ratio (methanol to oil) 6:1 (wt.:wt.), different selected reaction temperatures (60, 80, 100 and 120°C), and pressures (5, 10, 15 and 20 bar), and constant stirring rate of 250 rpm. The constant selected reaction temperature was maintained during 5.5 h, and reaction products were taken after each 1 h of a single reaction run. The zero point of the reaction run was the moment when the chosen temperature was reached in the batch reactor.

Reaction products and fatty acid profile of the sunflower oil were characterised by gas chromatography, GC HP 5890 Series II with a FID detector, according to standardised procedure given by SRPS EN 14103. The working conditions of GC analysis were: 30 m long capillary column (0.3 μm layer of polyethylene glycol), flow of helium of 2 $cm^3$/min, the analyte at 210°C during 10 min. Methyl heptadecanoate (99%, Fluka Co.) was used as the internal standard for the quantitative analysis and a standard mixture of methyl esters in qualitative analysis.

The particular catalysts efficiency was judged based on the FAME yield as in our previous paper[5].

*Mathematical (model) approach in process parameters optimisation. Nonlinear regression model*. In a number of experiments/reaction runs it can be seen the connection between two or more variables (in our case – process parameters). The correlation/ratio of two or more variables is analysed by correlation and regression model(s).

The correlation analysis involves the strength and direction of the relationship. Numerically, it is shown over the correlation coefficient ($r$). The values of the linear correlation coefficients range from –1 to +1. The strength of the association/relationship (the interpretation is the same for negative values of the correlation coefficient) is interpreted as follows: $r \approx 0.00$ means that there is no relationship between variables, while for $r \geq 0.70$ there is a strong correlation between the variables.

The coefficient of determination $r^2$ is the proportion of common variance of two variables. Regression analysis involves the shape and direction of correlation and analysis in terms of independent/dependent (predictor/outcome) variables with the aim of predicting. In the regression model, the knowledge of the values of the independent variables makes possible a prediction of the values of dependent variables. Generally speaking, whenever there is a significant correlation between the two variables the value of one variable can be used to predict the value of other variables.

The simplest regression analysis is a single regression, when considering two variables $y$ and $x$. It is searched a function φ such that $y \approx \varphi(x)$. The function φ is called the regression of $y$ on $x_1, x_2, ..., x_p$, and is chosen so that the mean square deviation that is referred as:

$$E(y - \varphi(x_1, x_2, \ldots, x_p))^2 \tag{1}$$

has to be the smallest one.

If φ dependence between variables $y$ and $x$ is linear, i.e. in relation

$$y = a_0 + a_1x + a_2x^2 + \ldots + a_nx^n \tag{2}$$

then it is said that φ is polynomial nonlinear regression. The unknown parameters $a_0, a_1, a_2, ..., a_n$ are determined by the method of the smallest squares based on the condition that the mean square deviation:

$$E(y - (a_0 + a_1x + a_2x^2 + \ldots + a_nx^n))^2 \tag{3}$$

has to be the smallest one.

If the degree of the polynom $n = 1$ it is a simple linear regression, if $n = 2$ it is a quadratic regression function, if $n = 3$ it is a cubic regression function.

## RESULTS AND DISCUSSION

### ESSENTIAL CaO-CATALYST STRUCTURAL PROPERTIES

Based on the TG results of calcium oxide based catalysts (Table 1), there are three weight losses: the first corresponding to the removal of physisorbed and/or rarely chemisorbed water (up to 120°C in DTA curve), the second occurring as the result of $Ca(OH)_2$ dehydration (up to 450°C in DTA curve), and the third one attributed to $CaCO_3$ decomposition (at 540–640°C in DTA curve) (DTA curves not shown)[6]. The estimated content of calcium hydroxide in the non-calcined CaO catalyst (precursor) was relatively high around 65%, and of calcium carbonate less than 10% (Table 1). When high(er) calcination temperatures are applied over CaO-based precursor materials smaller weight percentages of calcium hydroxide and carbonate are detected in the CaO-750 and CaO-900 catalysts (Table 1). This is crucial fact bearing in mind that the authors predict that chemical composition and purity of the CaO catalyst are key factors regarding catalytic efficiency in sunflower oil methanolysis. In addition, the authors claim that small ingredients of calcium hydroxide and carbonate (lower than 3–5%) (Table 1) would not have extremely negative impact on the FAME yield and process parameters.

**Table 1**. Crystal phases and relevant weight percentages in CaO-based catalysts

| Catalyst | Crystal phases in TG/DTA curves and weight losses (%) | | |
|---|---|---|---|
| | water up to 120°C | calcium hydroxide up to 450°C | calcium carbonate at 540–640°C |
| Non-calcined CaO | 12.0 | 65.0 | 8.0 |
| CaO-750 | 6.5 | 9.5 | 2.5 |
| CaO-900 | 5.0 | 3.5 | 1.0 |

On the other side, some authors have given much severe opinion claiming that even small content of calcium carbonate would deactivate CaO catalysts in transesterification of plant oil(s)[22,23]. Besides, these authors have published minor catalytic efficiency over CaO catalyst in the presence of calcium hydroxide. Similarly, Kouzu et al.[24] have registered a fast deactivation of CaO catalysts exposed to air during preparation procedure under atmospheric conditions.

In our case, calcium hydroxide and carbonate can be generated in the CaO-precursor material during the CaO catalyst preparation and application in the biodiesel synthesis in ambient conditions. DTA curves indicate that decomposition temperatures of calcium hydroxide and carbonate are shifted to higher temperatures when higher calcination temperatures are used in the catalyst preparation and activation procedures. These transition and/or decomposition temperatures are comparable or slightly lower than in literature[25,26].

The XRD results are in line with thermal properties of the CaO-based catalysts. In non-calcined CaO-precursor three different crystal phases were registered in the XRD pattern: CaO, $Ca(OH)_2$ and $CaCO_3$ (Fig. 1). The volume fractions of the relevant XRD peaks for CaO and calcium hydroxide are completely comparable while the fraction of calcium carbonate is considerably lower. The authors think that all these crystal phases may be present in the CaO catalyst due to possible existence of starting impurities in the precursor material and also interaction with moisture and $CO_2$ in the ambient circumstances during activation and testing of the catalyst.

Thermal activation procedures over CaO precursors have resulted in catalysts with much lower fractions of calcium hydroxide and carbonate when compared with CaO crystal phase existence. This especially stands for the CaO-900 catalyst calcined at higher temperature. In both catalysts, CaO-750 and CaO-900, the principal phase is CaO crystal phase followed with only negligible intensity of detected calcium carbonate and hydroxide phases. The intensity of the pure CaO crystal phase is higher in parallel with higher calcination temperature applied (Fig. 1). It is believed that the CaO phase may be essential one for the catalytic efficiency in the transesterification of plant oil[5]. Thus, we can expect equally favourable catalytic activity in the sunflower oil methanolysis over CaO-900 catalyst.

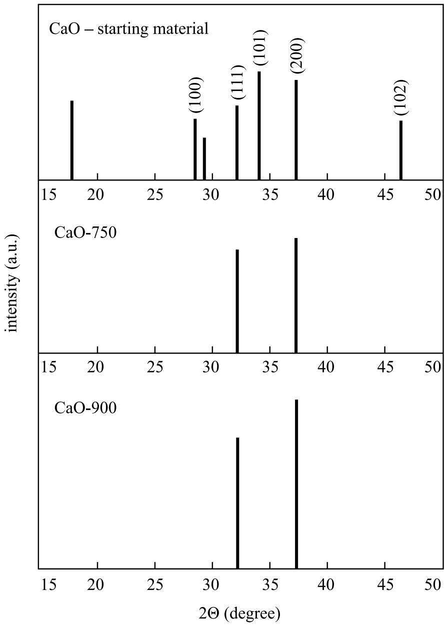

**Fig. 1**. XR diffractograms of the CaO-starting material and catalysts

In parallel with the calcination temperature increase the CaO peak width broadening resulted in larger CaO crystallites generated at higher temperatures. Taking in mind that we have registered almost pure CaO crystal phase after catalyst activation at 750°C, we can predict that thermal activation procedure at optimum temperature is crucial before catalyst use in the test reaction. Based on the TG/DTA and XRD results we have assumed that catalytic efficiency in the sunflower oil methanolysis in biodiesel synthesis would be expressed in order: CaO > $Ca(OH)_2$ > $CaCO_3$. The carbonates are known to exhibit no activity[23] in the transesterification of different plant oils while calcium hydroxide is reported to show a slight reactivity[22]. We think that thermal procedures at temperatures over 750°C would lead to bare CaO catalyst, which would be active and selective in the plant oils transesterification reactions.

The morphological properties – surface of the non-calcined CaO-starting material was characterised with the existence of relatively great particles aggregates-like (Fig. 2). After the calcination of the CaO-precursors at 750 and/or 900°C, nano-size crystallites were observed surrounded with larger pores (Fig. 2). These pore systems may enable the triglycerides transfer to and contact with catalytically active sites inside the catalyst pores during the transesterification reaction[6]. These data are in line with the XRD results on the essential crystal phase and crystallite size (Table 1, Fig. 1). After the reaction, the bulk catalyst underwent to a deactivation while a coalescence of the catalytic material occurred. The deactivation phenomenon resulted in the blockage of the reactant molecules interaction with the catalytic active sites inside the catalyst bulk.

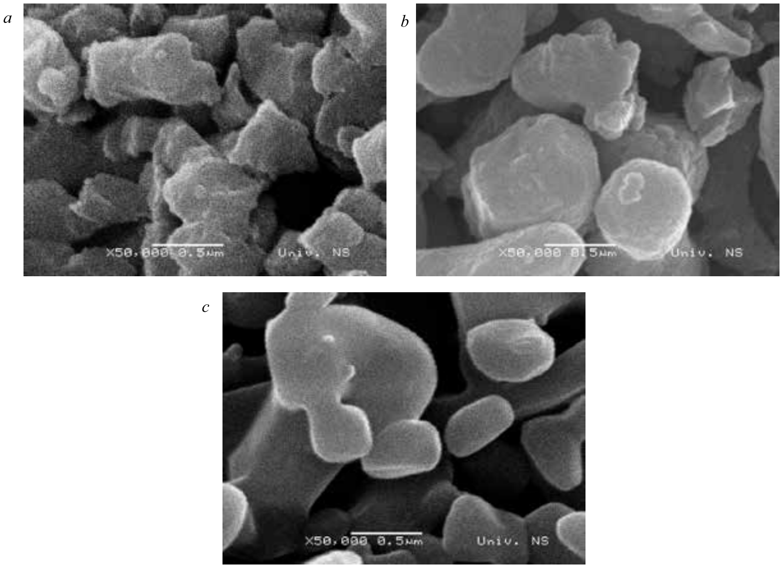

**Fig. 2**. SEM images of the CaO-starting material and catalysts: *a* – CaO-precursor; *b* – CaO-750; *c* – CaO-900

The textural features of the CaO catalysts are summarised in Table 2. The increase of the calcination temperature from 750 to 900°C has caused a slight decrease of the BET surface area (from 4.9 to 4.4 $m^2/g$) and the broadening of the average pore diameters (from 12.5 to 13.1 nm). The mean pore diameter has become greater starting from the non-calcined CaO to catalyst CaO-900 calcined at the highest temperature. The sintering process has begun after thermal treatment of calcination and resulted in a consolidation of the CaO-based catalytic material[6,27]. The relevant textural properties of both catalysts, CaO-750 and CaO-900, such as BET surface area, mean pore diameter and pore volume, are comparable and presented changes only in a small extent (Table 2).

**Table 2**. BET surface area, mean pore diameter and pore volume for the CaO-catalysts

| Catalyst | BET surface area ($m^2/g$) | Mean pore diameter (nm) | Pore volume ($cm^3/g$) |
|---|---|---|---|
| CaO-750 | 4.9 | 12.5 | 0.019 |
| CaO-900 | 4.4 | 13.1 | 0.023 |

The authors think that textural properties of the catalytic materials are in dependence on the precursor type and the thermal history and/or activation realised. These properties may significantly influence the catalytic efficiency of the CaO-based solid catalyst in the transesterification of the plant oils. The mean pore diameter and pore volume are favourable for liquid-solid phase interaction in contact reactant – catalyst and may provide the adequate surface area for the conversion of large triglycerides molecules.

Based on the FTIR spectra (not shown) of the catalytic samples before and after the adsorption of phenol as test molecule for the basic catalytic sites, it may be said that the vibrations of molecular phenol adsorbed were completely absent in the CaO-900 catalyst calcined at the highest temperature. This means that probably dissociative adsorption of phenol occurred onto the strongest basic catalytic active sites present in/at the CaO-900 catalyst bulk/surface. The corresponding deprotonating of phenol over/on strong basic sites resulted in a generation of phenolate anions that may be linked to metal (oxide) cations, in our experiment $Ca^{2+}$ ions. The presence of vibrations that indicates the potential physisorption of molecular phenol in the CaO-750 catalyst may be related to the existence of the catalytic active basic sites of lower strength or active sites of other type. We presume that the existence of the catalytic active basic sites of the strongest strengths ($Ca^{2+}$ ions) is essential for the catalytic efficiency in the methanolysis of the sunflower oil.

## CaO-CATALYST EFFICIENCY IN THE METHANOLYSIS OF SUNFLOWER OIL UNDER DIFFERENT PROCESS PARAMETERS

*Effect of reaction temperature on the FAME yield*. The reaction temperature was varied in the range of 60–120°C. The FAME yield increased with the increasing the reaction temperature up to 100°C, and then decreased at 120°C (Fig. 3). The reaction rate was relatively slow at lower reaction temperatures, and especially slow at the lowest process temperature of 60°C below the methanol boiling point. The optimum reaction/process temperature was 100°C when during the reaction run the FAME yield increased and only slightly decreased after 5.5 h. In the biodiesel synthesis over the heterogeneous catalyst (CaO), the reaction takes place in the multi-phase system, liquid-liquid-solid phase (ex. oil-methanol-catalyst), where the reaction may be slowed down due to possible diffusion restrictions on the interface (contacts) between different phases, and limited mass-transfer process[28]. In general, at higher reaction temperatures methanol vapourised and formed bubbles which can affect the reaction rate on the three-phase interface like in our case at 120°C. In addition, the reaction temperature may influence the density of the plant oil and the obtained biodiesel fuel. Therefore, it may indirectly affect the multi-phase system of the reaction mixture, and consequently the reaction rate. Similarly to Patil et al.[29], we have found that the reaction temperature of 100°C is the optimum one in the transesterification of the plant oil.

We have selected the CaO-900 catalyst to be applied in the transesterification of the sunflower oil due to established relation of the positive CaO structural properties and catalytic efficiency in the test reaction. Namely, we propose that there is a direct link between favourable textural properties (type of the pore system and specific surface area), the essential CaO crystal phase and crystallites up to 25 nm in size, the type and strength of the basicity of the catalytically active base sites[2,6].

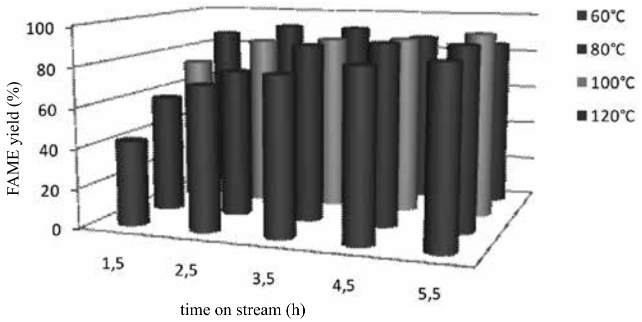

**Fig. 3**. FAME yield as a function of the reaction temperature and time

*Effect of reaction pressure on the FAME yield*. The reaction pressure was changed in the range of 5–20 bars at reaction temperature of 80°C. After the first 4 h of the reaction run, the FAME yield increased with the increasing the reaction pressure up to 15 bars, and it was higher when the process was carried out under the pressure of 10 bars (Fig. 4). The FAME yield was greater when higher process pressure of 15 bars was applied at the last 2 h of the reaction run. The reaction rate and biodiesel yield was very slow at the highest reaction pressure during the whole reaction run.

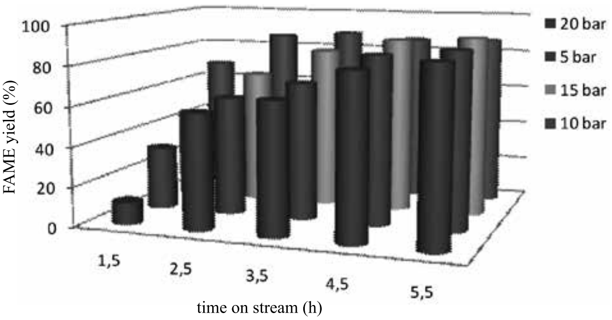

**Fig. 4**. FAME yield as a function of reaction pressure and time

It seems that the reaction pressure influence on the FAME yield is not simple but multi-sided one. Namely, after 4 h of the reaction time-on-stream, the FAME yield was not influenced only by the reaction pressure[5]. The conversion of reactants in the biodiesel synthesis reached maximum at 10 bars while further increase of the process pressure resulted with completely negative impact.

## REGRESSION MODEL DEVELOPMENT

*Mathematical optimisation of process temperature*. The experimental design over process parameters: temperature ($T$), pressure ($P$) and time of the reaction run ($t$) that may affect the FAME yield was developed. For the purpose of interrogation of interaction factors, experiments were performed with a variety of different physical parameters.

Based on the regression analysis of the experimental results dealing with the FAME yield (%) as a function of reaction temperature and time-on-stream (h), polynomial equations of third order were determined in which the dependent variable was FAME yield and the independent variable was time of the reaction run. The obtained resulting models (Table 3, Fig. 5) of depending of FAME yield in the product of time of the reaction run for different reaction temperatures are shown:

- temperature 60°C

$$\text{FAME yield (\%)} = -1.92541 + 3.60625t - 1.33036t^2 + 0.215t^3;$$

- temperature 80°C

$$\text{FAME yield (\%)} = -24.6402 + 44.5942t - 4.84714t^2 + 0.103333t^3;$$

- temperature 100°C

$$\text{FAME yield (\%)} = -1.56681 + 70.7281t - 17.4887\mathrm{t}^2 + 1.3675t^3;$$

- temperature 120°C

$$\text{FAME yield (\%)} = 85.4902 - 0.873542t + 0.23125t^2 - 0.0258333t^3. \qquad (4)$$

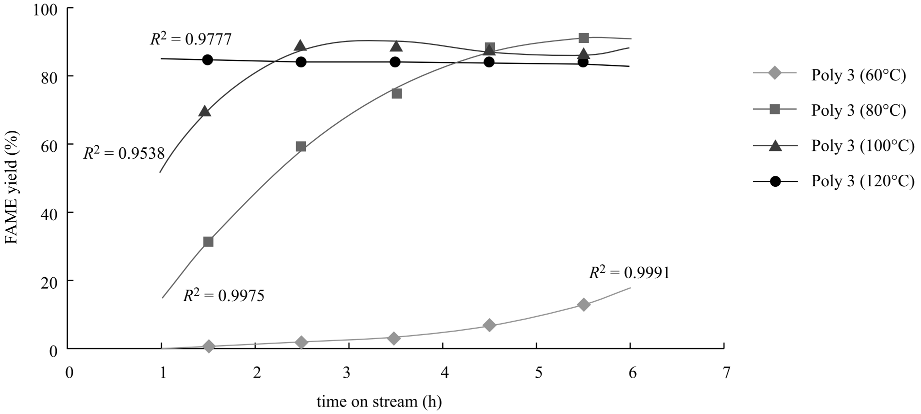

**Fig. 5**. Obtained results and polynomial model of third order in dependence of FAME yield in product of time-on-stream for different process temperatures

**Table 3**. Parameters of the polynomial model of third order

| Temperature (°C) | Parameter | Estimate | Standard error | *T*-statistic | *P*-value |
|---|---|---|---|---|---|
| 60 | constant | –1.92541 | 2.63891 | –0.729623 | 0.5987 |
| | $t$ | 3.60625 | 2.72955 | 1.32119 | 0.4125 |
| | $t^2$ | –1.33036 | 0.843935 | –1.57637 | 0.3599 |
| | $t^3$ | 0.215 | 0.0800025 | 2.68742 | 0.2268 |
| 80 | constant | –24.6402 | 21.3606 | –1.15353 | 0.4547 |
| | $t$ | 44.5942 | 22.0943 | 2.01835 | 0.2928 |
| | $t^2$ | –4.84714 | 6.83123 | –0.709557 | 0.6071 |
| | $t^3$ | 0.103333 | 0.647579 | 0.159569 | 0.8993 |
| 100 | constant | –1.56681 | 31.3449 | –0.0499863 | 0.9682 |
| | $t$ | 70.7281 | 32.4215 | 2.18152 | 0.2736 |
| | $t^2$ | –17.4887 | 10.0242 | –1.74465 | 0.3313 |
| | $t^3$ | 1.3675 | 0.950266 | 1.43907 | 0.3866 |
| 120 | constant | 85.4902 | 1.23634 | 69.1478 | 0.0092 |
| | $t$ | –0.873542 | 1.27881 | –0.683091 | 0.6185 |
| | $t^2$ | 0.23125 | 0.395387 | 0.58487 | 0.6631 |
| | $t^3$ | –0.0258333 | 0.0374815 | –0.689229 | 0.6158 |

**Table 4**. Regression analysis (ANOVA)

| Temperature (°C) | Source | Sum of squares | Df | Mean square | *F-r*atio | *P*-value |
|---|---|---|---|---|---|---|
| 60 | model | 98.3147 | 3 | 32.7716 | 355.57 | 0.0384 |
| | residual | 0.0921657 | 1 | 0.0921657 | | |
| | total (corr.) | 98.4069 | 4 | | | |
| 80 | model | 2392.56 | 3 | 797.519 | 132.07 | 0.0630 |
| | residual | 6.03877 | 1 | 6.03877 | | |
| | total (corr.) | 2398.59 | 4 | | | |
| 100 | model | 267.255 | 3 | 89.0849 | 6.85 | 0.2684 |
| | residual | 13.0033 | 1 | 13.0033 | | |
| | total (corr.) | 280.258 | 4 | | | |
| 120 | model | 0.88465 | 3 | 0.294883 | 14.58 | 0.1871 |
| | residual | 0.02023 | 1 | 0.02023 | | |
| | total (corr.) | 0.90488 | 4 | | | |

Df – degree of freedom.

**Table 5**. Estimation of the polynomial models of third order

| Temperature (°C) | *R*-squared (%) | *R*-squared (adjusted for Df) (%) | Standard error of estimation | Mean absolute error |
|---|---|---|---|---|
| 60 | 99.9063 | 99.6254 | 0.303588 | 0.116114 |
| 80 | 99.7482 | 98.9929 | 2.457390 | 0.939886 |
| 100 | 95.3603 | 81.4410 | 3.606000 | 1.379200 |
| 120 | 97.7643 | 91.0574 | 0.142232 | 0.054400 |

In general, for the determination of the polynomial model it should be checked *P*-value with the highest degree of the polynomial, which ranges from 0.226783 to 0.899265. Since the *P*-value is higher than 0.05 for all reaction temperatures, this value is not statistically significant at a confidence level of 95% or higher one, and therefore, it should be considered a reduction of the degree of polynomial models for one.

For the applied reaction temperatures of 60°C, the *P*-value is smaller than 0.05 (Table 4), which indicates that there is a statistically significant correlation between the FAME yield in the product and the time of the reaction run at confidence level of 95%. On the contrary, for the applied reaction temperatures of 80, 100 and 120°C, the *P*-value is higher than 0.05.

The quality of the mathematical model is defined by a parameter $R^2$ that indicates that the fitted model accounts a variability of the FAME yield (%) for different temperatures from 95.3603% (at 100°C) to 99.9063% (at 60°C) (Table 5). Adjusted *R*-square statistics, which is more suitable for comparing models with different numbers of independent variables, amounts from 81.441% (at 100°C) to 99.6254% (60°C). The standard estimation error, which shows the standard deviation of the residuals ranges from 0.142232 to 3.606, mean absolute error, which shows the average value of the residuals ranges from 0.0544 to 1.3792 (Table 5).

*Mathematical optimisation of process pressure*. Based on the regression analysis of the experimental results dealing with the FAME yield as a function of reaction pressure and time-on-stream at 80°C, polynomial equations of third order were determined in which the dependent variable was FAME yield (%) and the independent variable was time of the reaction run (h). The obtained resulting models (Table 6, Fig. 6) of depending of FAME yield in the product of time of the reaction run for different reaction pressures are shown:

- pressure 5 bars

$$\text{FAME yield (\%)} = -32.0346 + 55.75t - 9.42143t^2 + 0.6t^3;$$

- pressure 10 bars

$$\text{FAME yield (\%)} = -3.19107 + 72.425t - 18.4357t^2 + 1.5t^3;$$

- pressure 15 bars

$$\text{FAME yield (\%)} = -10.0288 + 46.8146t - 7.04464t^2 + 0.341667t^3;$$

- pressure 20 bars

$$\text{FAME yield (\%)} = -129.234 + 134.21t - 30.1839t^2 + 2.35833t^3. \qquad (5)$$

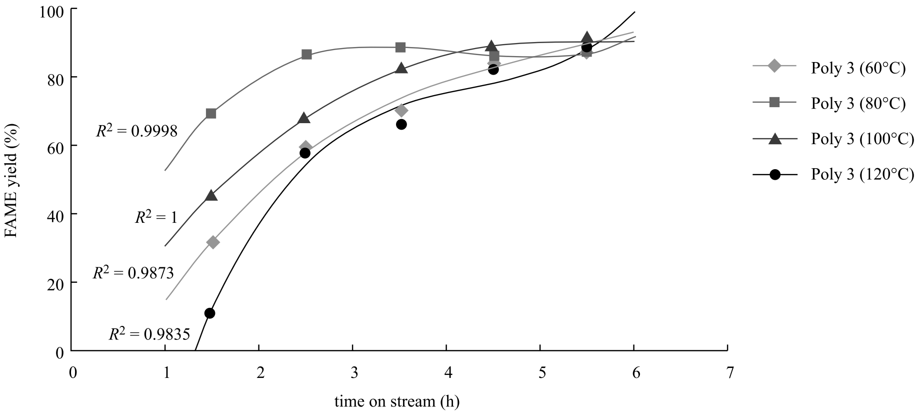

**Fig. 6**. Obtained results and polynomial model of third order in dependence of FAME yield in product of time-on-stream for different process pressures

**Table 6**. Parameters of the polynomial model of third order

| Pressure (bar) | Parameter | Estimate | Standard error | *T*-statistic | *P*-value |
|---|---|---|---|---|---|
| 5 | constant | –32.0346 | 44.8823 | –0.713748 | 0.6054 |
| | $t$ | 55.75 | 46.4239 | 1.20089 | 0.4421 |
| | $t^2$ | –9.42143 | 14.3535 | –0.656383 | 0.6302 |
| | $t^3$ | 0.6 | 1.36067 | 0.440959 | 0.7356 |
| 10 | constant | –3.19107 | 2.07788 | –1.53573 | 0.3674 |
| | $t$ | 72.425 | 2.14925 | 33.6977 | 0.0189 |
| | $t^2$ | –18.4357 | 0.664516 | –27.7431 | 0.0229 |
| | $t^3$ | 1.5 | 0.0629941 | 23.8118 | 0.0267 |
| 15 | constant | –10.0288 | 0.311682 | –32.1765 | 0.0198 |
| | $t$ | 46.8146 | 0.322388 | 145.212 | 0.0044 |
| | $t^2$ | –7.04464 | 0.0996774 | –70.6744 | 0.0090 |
| | $t^3$ | 0.341667 | 0.00944911 | 36.1586 | 0.0176 |
| 20 | constant | –129.234 | 67.4273 | –1.91664 | 0.3061 |
| | $t$ | 134.21 | 69.7433 | 1.92435 | 0.3051 |
| | $t^2$ | –30.1839 | 21.5635 | –1.39977 | 0.3949 |
| | $t^3$ | 2.35833 | 2.04416 | 1.15369 | 0.4546 |

**Table 7**. Regression analysis (ANOVA)

| Pressure (bar) | Source | Sum of squares | Df | Mean square | *F*-ratio | *P*-value |
|---|---|---|---|---|---|---|
| 5 | model | 2070.91 | 3 | 690.304 | 25.89 | 0.1413 |
| | residual | 26.6606 | 1 | 26.6606 | | |
| | total (corr.) | 2097.57 | 4 | | | |
| 10 | model | 262.983 | 3 | 87.661 | 1534.07 | 0.0185 |
| | residual | 0.0571429 | 1 | 0.0571429 | | |
| | total (corr.) | 263.04 | 4 | | | |
| 15 | model | 1427.89 | 3 | 475.964 | 370193.89 | 0.0012 |
| | residual | 0.00128571 | 1 | 0.00128571 | | |
| | total (corr.) | 1427.89 | 4 | | | |
| 20 | model | 3592.7 | 3 | 1197.57 | 19.90 | 0.1608 |
| | residual | 60.1716 | 1 | 60.1716 | | |
| | total (corr.) | 3652.87 | 4 | | | |

**Table 8**. Estimation of the polynomial models of third order

| Pressure (bar) | *R*-squared (%) | *R*-squared (adjusted for Df) (%) | Standard error of estimation | Mean absolute error |
|---|---|---|---|---|
| 5 | 98.729 | 94.916 | 5.16339 | 1.97486 |
| 10 | 99.978 | 99.913 | 0.23905 | 0.09143 |
| 15 | 99.999 | 99.999 | 0.03586 | 0.01371 |
| 20 | 98.353 | 93.411 | 7.75703 | 2.96686 |

In general, for the determination of the polynomial model it should be checked *P*-value with the highest degree of the polynomial, which ranges from 0.0176 to 0.7356 (Table 6). Since the *P*-value is higher than 0.05 for reaction pressures of 5 and 20 bars, this value is not statistically significant at a confidence level of 95% or higher one, and therefore, it should be considered a reduction of the degree of polynomial models for one.

For the applied reaction pressures of 10 and 15 bars, the *P*-value is smaller than 0.05 (Table 7), which indicates that there is a statistically significant correlation between the FAME yield in the product and the time of the reaction run at confidence level of 95%. On the contrary, for the applied reaction pressures of 5 and 20 bars, the *P*-value is higher than 0.05.

The quality of the mathematical model is defined by a parameter $R^2$ that indicates that the fitted model accounts a variability of the FAME yield (%) for different pressures from 98.353% (under 20 bars) to 99.999% (under 15 bars) (Table 8). Adjusted *R*-square statistics, which is more suitable for comparing models with different numbers of independent variables, amounts from 93.411% (under 20 bars) to 99.999% (under 15 bars). The standard estimation error, which shows the standard deviation of the residuals ranges from 0.03586 to 7.75703, mean absolute error, which shows the average value of the residuals ranges from 0.01371 to 2.96686 (Table 8).

The developed mathematical regression model for optimisation of process parameters showed that the optimum reaction temperature would be 60°C and the optimum reaction pressure 15 bars. On the other side, the experimental results presented that the optimum reaction temperature is 100°C and reaction pressure of 10 bars. Liu et al.[28] and Zhao et al.[3] have reported that the optimum temperature in transesterification of the selected plant oils (soybean and canola oils) catalysed by CaO to obtain biodiesel was 65°C.

In our case, the discrepancy between the obtained experimental data and mathematically optimised parameters may be due to insufficient number of individual measurements for development of the mathematical model(s) or it may be caused by laboratory errors occurred during the performance of some experiments.

## CONCLUSIONS

Calcium oxide as a solid base after activation at higher optimised temperature may be used as very active and selective catalyst in transesterification of refined sunflower oil with methanol in order to produce biofuel. A number of essential structural features of the CaO catalyst like acceptably large specific surface area and especially pore diameters on meso/macro dimensions, the essential crystal phase of bare CaO with crystallites up to limited dimensions, and the total amount and strength of the basic catalytically active sites on the $Ca^{2+}$ cations are all together responsible for its favourable catalytic efficiency.

It is possible to evaluate and optimise simultaneously a number of process parameters that could influence the biodiesel yield by using the mathematical model – regression analysis. In addition, this mathematical model would be very useful in maximising the biofuel yield while reducing production costs in case when an adequate number of measurements are provided.

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