

INVESTIGATION OF THE CATALYTIC ACTIVITY OF HYDRATED LIME Ca(OH)₂ IN THE PROCESS OF TRANSESTERIFICATION OF VEGETABLE OILS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:

Currently, humanity is facing two existential problems: the constant reduction of fossil fuel supplies, primarily crude oil, and global climate change, which is a direct consequence of the increasing use of fossil fuels both in industry and in the transport sector [1, 2]. One of the possible solutions for these problems are biofuels, fuels obtained from renewable raw materials, as it is biodiesel [2], which attracted attention due to characteristics such as high degradability, non-toxicity and low emission of carbon monoxide, particulate matter and unburned hydrocarbons, as well as the possibility of being used either in a mixture with fossil with diesel or independently as 100% biodiesel fuel [3, 4, 5, 6]. Heterogeneous catalysts in transesterification processes, i.e. biodiesel production, have been an area of significant and extensive research for many years. It is noticeable that there are significantly fewer works in which the application of Ca(OH)₂ was investigated, and the published works show conflicting results, both in terms of its catalytic activity and in terms of the achieved yield of fatty acid methyl esters (FAME). The main goal of this work was to analyze the physico-chemical, chemical, mineralogical, morphological and surface characteristics of hydrated lime produced by Stamal Ltd. Kreševo, with the aim of examining the possibility of its application as a catalyst in the process of transesterification of vegetable oils. The obtained results unequivocally show that by using this hydrated lime as a catalyst in the transesterification process of rapeseed oil, it is possible to achieve a yield of methyl esters that meets the minimum limit of 96.5% prescribed by the European standard for biodiesel, EN 14214.

KEYWORDS: biodiesel, heterogeneous catalysts, hydrated lime

INTRODUCTION

Biodiesel is a liquid biofuel that consists of monoalkyl esters of vegetable oils, animal fats, or other lipid raw materials such as used cooking oil. Due to its physicochemical properties similar to conventional diesel, biodiesel can be used in unmodified compression ignition engines, either in its pure form (designated as B100), or in blends with petroleum diesel [7, 8, 9] where it further improves lubricity and increases fuel cetane number. Among the existing methods of biodiesel production, the conventionally applied method is the transesterification of vegetable oils with alcohol, typically methanol (so-called methanolysis) in the presence of a catalyst, which converts oil triglycerides into alkyl esters, whereby biodiesel is produced as the main product and crude glycerol as a by-product [10, 11].

Although the transesterification reaction that produces biodiesel from triacylglycerol raw materials is balanced and the transformation basically occurs by mixing the reactants, the use of a catalyst increases the solubility of alcohol in oil and thereby accelerates the reaction [12], which enables the reaction to take place at low and moderate temperatures. The main process conditions whose optimization is of great importance for the efficient production of biodiesel include: molar ratio of alcohol to oil, type and amount of catalyst, temperature and reaction time [13, 14].

Homogeneously catalyzed transesterification reactions, which are dominant in industrial practice today, are typically fast and require a smaller amount of catalyst than heterogeneously catalyzed ones [15]. In general, it can be said, and this is confirmed by published research, that alkaline-catalyzed reactions take place much faster than acid-catalyzed ones. Kinetic coefficients for alkaline catalysts were two to

four orders of magnitude higher than those of acidic catalysts [16]. In addition, a very important feature of alkaline catalysts is that they are significantly less corrosive to industrial equipment than acidic ones, so it is not surprising that commercial biodiesel synthesis processes on an industrial scale are usually carried out with highly alkaline homogeneous catalysts, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaOCH_3) and potassium methoxide (KOCH_3) [17, 18, 19, 20, 21]. The

introduction of heterogeneous catalysts into the commercial process of biodiesel production could reduce its cost and make it competitive with fossil diesel, given the number of advantages these catalysts offer, including higher reaction rates, easy separation from products, and reusability [22]. Heterogeneous catalysts in transesterification processes, i.e. biodiesel production, have been an area of significant and extensive research for many years.

Table 1. Review of literature references in which $\text{Ca}(\text{OH})_2$ was used as a catalyst for transesterification of various vegetable oils

Catalyst type	Raw material (oil)	T (°C)	Methanol/oil ratio	Catalyst (wt.%)	Time (min)	Biodiesel yield (wt.%)	Reference
$\text{Ca}(\text{OH})_2$	Oilseed rape	65	0,225 mol/50 cm^3	0,0075 mol	150	/	[25]
$\text{Ca}(\text{OH})_2$	Soy	65	12:1 mol	14 mmol	60	12	[26]
$\text{Ca}(\text{OH})_2$	Sunflower	50	12:1 mol	Equivalent to 1% NaOH	1440	<70	[27]
$\text{Ca}(\text{OH})_2$	Soy	300	39,4:1 mol	0,68	10	98	[28]
$\text{Ca}(\text{OH})_2$	Soy	70	9:1 mol (ethanol)	13,8	600	<15	[29]
$\text{Ca}(\text{OH})_2$	Sunflower	60	6:1 mol	5	120	>90	[30]
$\text{Ca}(\text{OH})_2$	Barbados nut	65	20 wt% CH_3OH	1,5	60	76,75	[31]
$\text{Ca}(\text{OH})_2$	Peanuts (raw oil)	78	9:1 mol (ethanol)	1,0	180	8,08	[33]
$\text{Ca}(\text{OH})_2$	Peanuts (raw oil)	100	12:1 mol (ethanol)	2,0	120	<10	[32]
$\text{Ca}(\text{OH})_2$	Sunflower	60	6:1 mol	1,5	60	<20	[34]
$\text{Ca}(\text{OH})_2$	Soy	60	50 vol.% CH_3OH	3,8	120	100	[35]
$\text{Ca}(\text{OH})_2$	Castor oil	60	51 vol.% CH_3OH	1,6	120	93,5	[36]
$\text{Ca}(\text{OH})_2$	Oilseed rape	60	12:1 mol	5	180	>90	[37]
$\text{Ca}(\text{OH})_2$	Sunflower	60	25 vol.% CH_3OH	4	120	93,23	[24]
$\text{Ca}(\text{OH})_2/\text{KF}$	Palm oil	65	12:1 mol	5	1	97,6	[38]

There is a significant number of published results of the catalytic activity of different types of catalysts, where there are significant differences regarding the optimal process conditions, and in some cases also regarding the existence of the catalytic activity of certain compounds, which generally depends on their nature, size and specific surface area of the particles, and the applied reaction conditions [23, 24]. Given that Bosnia and Herzegovina has a significant number of limestone deposits of different composition and several production capacities of $\text{Ca}(\text{OH})_2$, the application of hydrated lime as a catalyst for obtaining biodiesel could economically significantly improve

both the industry itself related to the production of limestone-based products (by creating new market for products), as well as the industrial production of biodiesel (lower-price catalysts, less environmental burden), which would further result in market, environmental and numerous other advantages.

The largest number of studies on methanolysis with the use of calcium-based catalysts refers to the application of calcium oxide [24], due to its low cost, good catalytic properties and the possibility of recycling without a major reduction in catalytic activity [23]. On the other hand, there is a relatively small number of researches based on the application

of Ca(OH)₂ as a catalyst, for the reason that for a long time it was considered that it has no significant catalytic activity in the process of transesterification of vegetable oils.

A literature review of references in which the influence of Ca(OH)₂ as a catalyst in the process of transesterification of various vegetable oils was investigated is given in table 1.

MATERIAL AND METHODS

MATERIAL

The following materials were used in the experimental part of the research:

- commercial hydrated lime (Stamal Ltd. Kreševo),
- refined rapeseed oil (Bimal Ltd. Brčko),
- methanol p.a. (Fluka),
- other materials and chemicals needed to carry out the necessary analyses.

METHODS

Determination of structural properties of the catalyst was done using the X-ray diffraction (XRD) method. The diffractograms of the samples were recorded on an automatic X-ray powder diffractometer Philips PW1710, at an operating voltage of $U = 40\text{kV}$ and a current of $I = 30\text{mA}$. $\text{CuK}\alpha$ radiation with a wavelength of $\lambda = 1.54056 \text{ \AA}$ was used, monochromatized using a graphite monochromator. Before starting the recording of the samples, the accuracy of the diffractometer device was controlled using the basic program PW-1844. The step size was $0.02^\circ 2\theta$ with a time delay of 1 second at each step. The angular recording interval was $2-80^\circ 2\theta$. Diffraction data were collected at room temperature. Based on the obtained values of intensity I (imp) and interplanar distances d (Å), by comparison with literature data and ICDD standards, identification was made.

The determination of the chemical composition of the catalyst was carried out using the method of X-ray fluorescence analysis (XRF) on a Bruker S8 Tiger XRF spectrometer, at the operating voltage of the spectrometer X-ray tube 40 kV , the maximum current 10 mA and the maximum power of the X-ray tube 400 W .

The catalyst composition was determined by thermal analysis methods (TG/DTG), using a Q600 thermal analyzer (TA Instruments, New Castle, DE, USA). Analyzes were performed in a corundum cone, in a nitrogen atmosphere at a flow rate of $100 \text{ cm}^3/\text{min}$ and at a heating rate of $20^\circ\text{C}/\text{min}$. The mass of the sample by measurement was $2-3 \text{ mg}$. The reference sample was an empty cone. The temperature interval

of the analysis ranged from room temperature to 1000°C .

The determination of the morphological properties of the catalyst was performed using scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS) on a JEOL JSM 6420 LV device at an accelerating voltage of 20 kV . Catalyst samples were prepared for analysis by being coated with a 15 nm thick layer of gold with a density of 19.32 g/cm^3 . The element used for optimization is nickel.

The textural properties of the catalyst (specific surface area, mean pore diameter and total pore volume) were determined by the Brunauer–Emmett–Teller (BET) method. Sample preparation for analysis was done by activation at 400°C for 2 hours, followed by degassing in a nitrogen atmosphere at 400°C for 1 hour. The device on which the analysis was performed is Micromeritics - Gemini VII, Version 5.0, Model 2390, and the measurement was based on the static monomolecular adsorption of nitrogen N_2 at the temperature of its liquid aggregate state (-196°C) in the carrier gas stream.

A laser diffraction particle size analyzer, Malvern Mastersizer 2000, was used to determine the granulometric composition of the catalyst. The device works on the principle of diffraction of red and blue laser light on particles in dispersions. The system consists of a Mastersizer 2000 optical system and a Hydro 2000 dispersion unit for the characterization of dispersions in liquid dispersants and a computer with installed software.

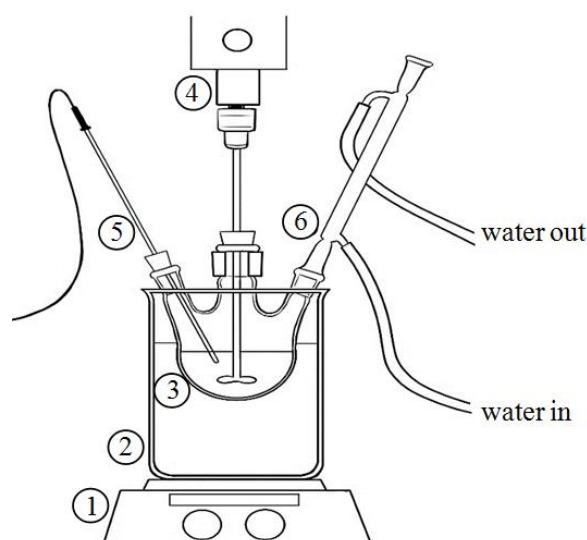


Figure 1. Laboratory apparatus for obtaining biodiesel

The apparatus that was used to carry out the heterogeneous-catalyzed methanolysis of rapeseed oil (Figure 1) consisted of the following components:

1. Electric heater with thermostat,
2. Glass cup,
3. Three-necked flask with a volume of 500 cm³ with a round bottom,
4. Mechanical mixer,
5. Temperature probe i
6. Water cooler

To test the influence of the amount of added catalyst on the transesterification of rapeseed oil, that is, on the yield of FAME and the basic characteristics of the obtained biodiesel sample, catalyst concentrations (wt.%) of 2, 3, 4 and 5 were used in relation to the mass of rapeseed oil. The reaction time was 120 min, and the temperature at which the reaction was carried out was 60°C. A methanol/oil volume ratio of 0.25 was used in all experiments. The mixing was more intense at the beginning of the experiments, considering the nature of the ingredients in the initial mixture, and after homogenization, the mixing was constant and amounted to 1000 rpm. After the expiry of the set methanolysis time, the liquid phase was separated from the catalyst by a vacuum pump and left for 24 h in a funnel to separate the fractions of biodiesel (methyl ester) and glycerol based on their different specific gravity. Then the

lower (glycerol) phase was discharged from the funnel, and the separation of fine catalyst particles and residual glycerol from the biodiesel fraction was performed by centrifugation at 3000 rpm (Eppendorf Centrifuge 5702) for 10 min at room temperature. The biodiesel thus obtained was further analyzed for fatty acid methyl esters (FAME) content.

Determination of FAME content was performed on a gas chromatograph 7890A with FID detector and automatic sampler 7683B, manufactured by Agilent Technologies, according to the standard SRPS EN 14103, April 2008, identical to EN 14103:2003. The aforementioned standard defines the determination of the ester content in fatty acid methyl esters intended for use as pure biofuel or as a component for mixing fuel oil and diesel fuel.

RESULTS

The morphology of the surface of the hydrated lime produced by Stamal, used as a catalyst, is presented in Figure 2. SEM photographs show an uneven morphology in the form of aggregates consisting of irregularly stacked Ca(OH)₂ crystals of different sizes and shapes, resulting in "open" structure of the material.

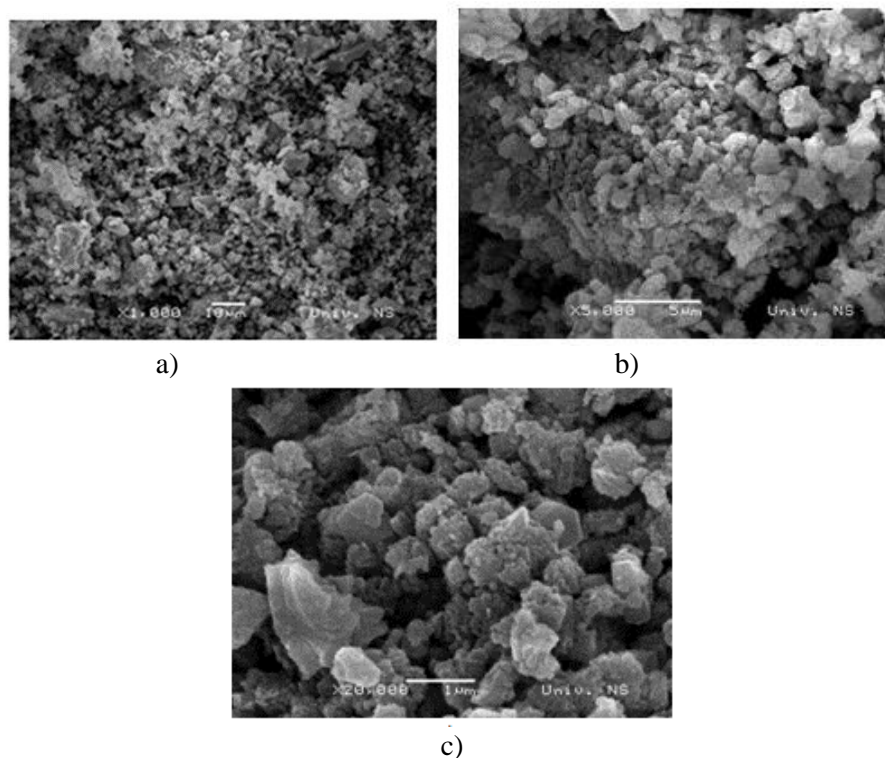


Figure 2. SEM photos of unused hydrated lime produced by Stamal, at magnifications of: a) 1000, b) 5000, c) 20000

The textural parameters of hydrated lime are as follows: the sample has an average pore diameter of

2.0 (nm) and pore volume (0.007 cm³/g), and therefore a relatively small specific surface (11.01 m²/g).

Energy dispersive X-ray spectroscopy (EDS), which was performed in combination with SEM, shows the elemental composition (wt.%) of the lime sample (Fig. 3): 39.07 Ca, 47.68 O, 11.56 C, 0.51 Mg,

0.39 Al, 0.56 Si and 0.24 Fe. Carbon, which is registered in the sample in a slightly larger amount, can also be an indication of the presence of a carbonate phase (CaCO₃).

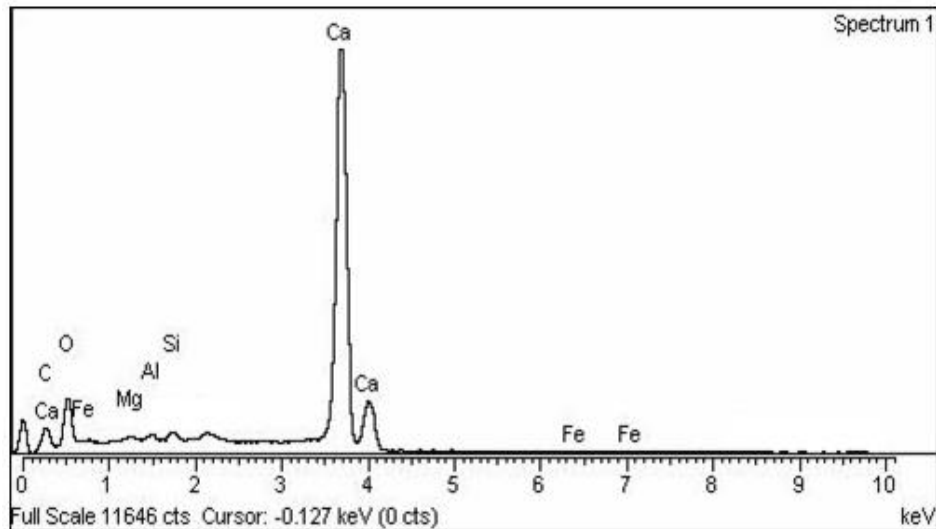


Figure 3. EDS spectrum of Stamal hydrated lime

Stamal hydrated lime particles have a narrow size range (1–80 μm) which is shown in Figure 4. In addition, they can be characterized by a bimodal distribution of particle sizes, where a slightly larger part of the particles is in the 11–70 μm range, and the rest in the 1–10 μm. About 10 vol.% of the particles

have a diameter smaller than 2.56 μm, about 50 vol.% of the particles are smaller than 9.926 μm, while 90 vol.% of them are characterized by a diameter below 34.6 μm. The average diameter of the particles is 14.73 μm.

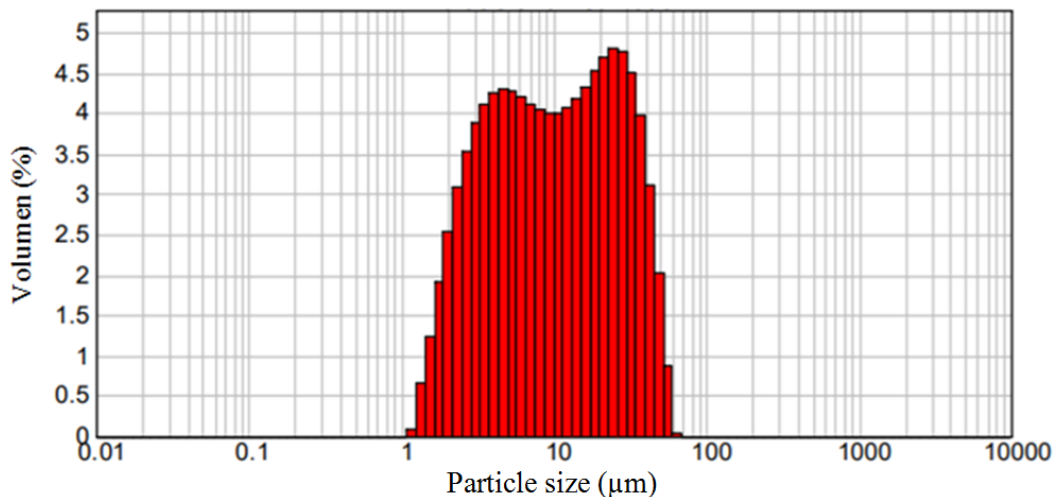


Figure 4. Particle size distribution of Stamal hydrated lime

The results of the XRF analysis of Stamal hydrated lime, which show its chemical composition in the form of oxides, are shown in Table 2. The largest part of the sample is CaO (63.63 wt.%), while SiO₂ was detected in a much lower concentration (1.58 wt.%), and other

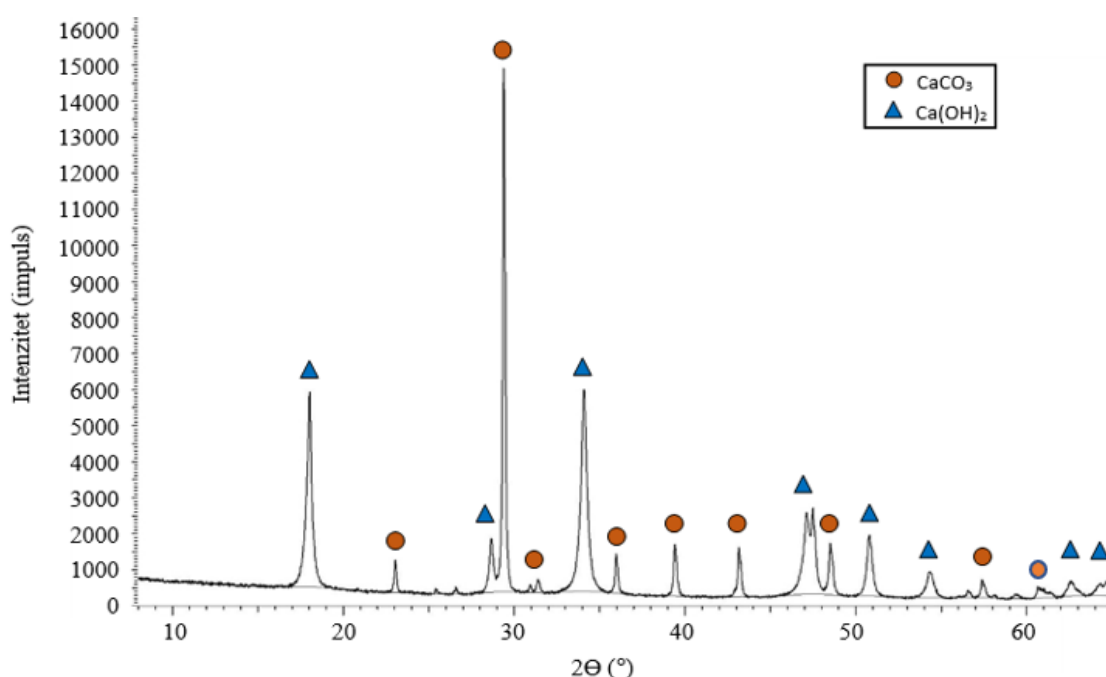
elements are present in very small amounts (<1.00 wt.%). The resulting loss on ignition (LOI) is related to the removed water and CO₂ from Ca(OH)₂ and CaCO₃ after exposing the sample to high temperature.

Table 2. Chemical composition of hydrated lime produced by Stamal Ltd. Kreševo

Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	LOI	Sum
wt.%	1.58	0.68	0.44	63.63	0.97	0.51	0.016	0.075	0.018	0.017	0.009	31.71	99.66

The XRD diagram of Stamal hydrated lime is given in Figure 5. The diffractogram shows two components of the catalyst: portlandite – Ca(OH)₂, with the two most intense peaks around 2 θ values of 18° and 34°, and calcite – CaCO₃, with the most intense peak at 2 θ values between 29° and 30°. Given

that calcite was identified by this method, the earlier assumption from EDS results about its presence can be confirmed. According to the XRD results of the quantitative analysis, the sample contains 89.63 wt.% portlandite, which corresponds to 67.83 wt.% CaO, and this is in good agreement with the XRF results.

**Figure 5.** XRD diagram of Stamal hydrated lime

Thermochemical changes of Stamal hydrated lime, which were examined by TG/DTG analysis, i.e. the weight loss profile when heated in a stream of nitrogen (N₂) is shown in Figure 6.

The weight loss of 0.7% in the temperature interval up to 300°C can be attributed to the loss of adsorbed water, which the Stamal sample contained in a relatively small amount.

Upon further heating to 500°C, the weight of the sample decreased by an additional 11.2%, which was caused by the dehydroxylation of Ca(OH)₂. In the temperature interval 500-770°C, the weight of the sample decreased by an additional 18.8%, as a result of the decomposition of the present CaCO₃ into CaO and CO₂, which is in accordance with other characterization results presented previously.

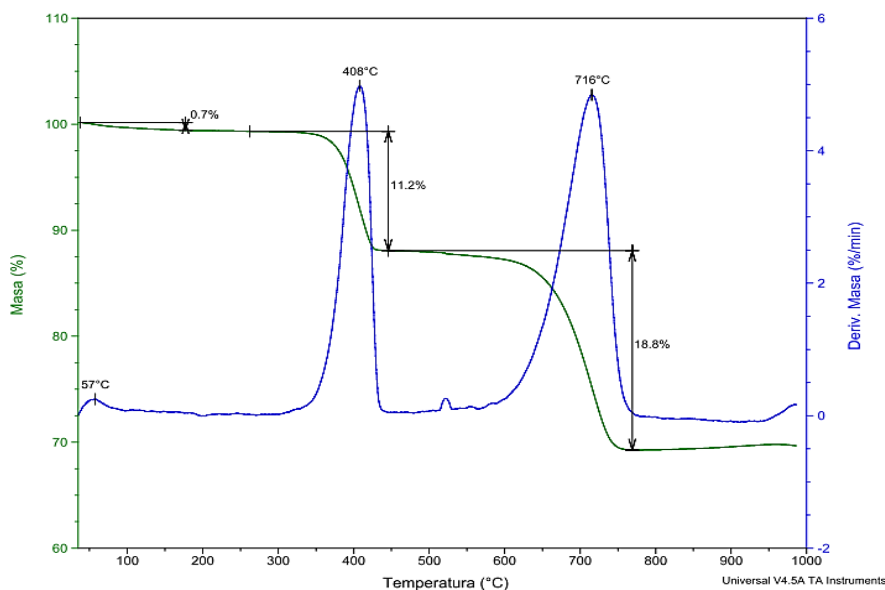


Figure 6. TG/DTG profile of Stamal hydrated lime

Figure 7 shows a diagram of the influence of the amount of catalyst (Stamal hydrated lime) on the yield

of methyl esters, by carrying out the transesterification of refined rapeseed oil.

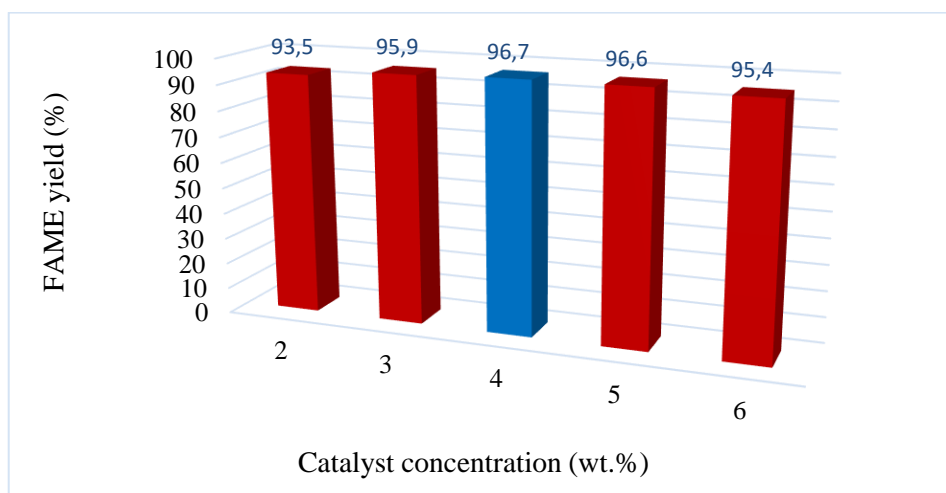


Figure 7. Influence of Stamal catalyst concentration on FAME yield

By using Stamal hydrated lime in a concentration of 2 wt.%, a yield of methyl esters of rapeseed oil of 93.5% was achieved. Although the FAME yield achieved is significant, the applied catalyst concentration did not yield a yield of rapeseed oil methyl esters that meets the minimum limit of the European standard EN 14214 of 96.5% [39]. This yield can be explained by the insufficient number of active sites for the reaction of reactants [40], i.e. relatively small specific surface area of the catalyst. Increasing the concentration of hydrated Stamal lime from 2 to 3 wt.% led to an increase in the yield of MEMK, which after a reaction time of 120 minutes

was 95.9%. This yield at a catalyst concentration of 3 wt.% is due to the relatively low content of Ca(OH)₂ determined by XRD analysis (Fig. 5) and TG/DTG analysis (Fig. 6), i.e. due to the highest content of calcium carbonate (CaCO₃) which were shown by TG/DTG analysis (Figure 6) and XRF analysis (Table 2). Calcium carbonate has been shown to have very little or no catalytic activity, i.e. much lower than calcium hydroxide [26]. By increasing the concentration of Stamal hydrated lime to 4 wt.%, the yield of rapeseed oil methyl esters increased slightly and reached its maximum (96.7%), and by further increasing the catalyst concentration to 5 and 6 wt.%,

the FAME yield gradually decreased to 96.6% and 95.4%.

CONCLUSION

Obtaining biodiesel by transesterification of rapeseed oil with the use of hydrated lime produced by Stamal Ltd. Kreševo, without prior activation of the catalyst, is possible to achieve a yield of methyl esters that meet the minimum limit of 96.5% prescribed by the European standard for biodiesel, EN 14214.

Under the conditions of a volume ratio of methanol to oil of 0.25, a temperature of 60°C, a duration of the transesterification reaction of 120 minutes, a catalyst concentration of 4 wt.% and a mixing speed of 1000 rpm, by a batch process of methanolysis with Stamal hydrated lime, as heterogeneous catalyst, the maximum yield of rapeseed oil methyl esters of 96.7% was achieved. The content of calcium hydroxide in hydrated lime is correlated with its catalytic ability in the transesterification reaction.

The content of $\text{Ca}(\text{OH})_2$ in the sample of hydrated lime produced by Stamal is average when it comes to products of this type and amounted to 89.63 wt.% for the tested sample, and the maximum yield of biodiesel obtained under the mentioned transesterification conditions was 96.7%. The presence of a crystalline phase of calcium carbonate in hydrated lime is associated with a lower catalytic activity of lime, which additionally depends on the content and location of CaCO_3 in the catalyst structure. Given that a significant content of calcium carbonate and an average content of $\text{Ca}(\text{OH})_2$ was found in the examined sample of hydrated lime, the catalytic activity of this lime is moderate.

The specific surface of Stamal hydrated lime of 11.4 (m^2/g) can also be considered as one of the reasons why this lime in the observed reaction conditions showed moderate catalytic activity, considering that to achieve a significant conversion of fatty acids into their methyl esters of 96.7%, it was necessary to use a catalyst in a concentration of 4 wt.%. From the obtained results it is evident that the concentration of hydrated lime as a catalyst can be taken as a very important factor on which the efficiency of the transesterification of vegetable oils with the aim of obtaining biodiesel depends. Lower concentrations will not ensure the smooth progress of the transesterification reaction, because not enough active sites will be provided. On the other hand, excessive catalyst concentrations can cause a decrease in the conversion of triacylglycerols into their methyl esters because they usually lead to an increase in the

viscosity of the reaction mixture, which leads to difficult mass transfer.

The lowest yield of methyl esters (93.5%) was achieved when the catalyst was used in a concentration of 2 wt.%. By increasing the concentration of the catalyst to 3 wt.%, an increase in the yield of methyl esters to 95.9% was recorded, so that the maximum value of the yield of FAME of 96.7%, which is in accordance with the minimum requirement of the European standard EN 14214 for biodiesel, was achieved when the catalyst was used in amount of 4 wt.%. A further increase in the catalyst concentration (5 wt.% and 6 wt.%), led to a partial decrease in the yield of methyl esters (96.6% and 95.4%) from the previously achieved maximum (96.7%).

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