15th Scientific/Research Symposium with International Participation
„METALLIC AND NONMETALLIC MATERIALS“, B&H, 24th-25th April 2025

THE INFLUENCE OF TEMPERATURE AND REACTION TIME ON THE YIELD OF FATTY ACID METHYL ESTERS IN THE TRANSESTERIFICATION OF RAPESEED OIL

Azra Halilović, Amna Karić
University of Zenica, Faculty of Engineering and Natural Sciences, Zenica
Bosnia and Herzegovina

Sabina Begić, Zoran Iličković
University of Tuzla, Faculty of Technology, Tuzla, Bosnia and Herzegovina

Keywords: methanolysis, FAME (Fatty Acid Methyl Esters), temperature, time, comercial hydrated lime

ABSTRACT

The depletion of fossil fuel reserves and the increasing environmental concerns regarding their production and combustion have led to an exponential rise in interest in biofuels [1], among which biodiesel has attracted attention due to its characteristics such as high biodegradability, non-toxicity, and low emissions of carbon monoxide, particulate matter, and unburned hydrocarbons [2,3]. Biodiesel produced from edible oils is currently more expensive than conventional petroleum fuels [4]. In light of this, significant attention has been devoted to research on its production, with the aim of making it more sustainable and cost-effective [5]. Various parameters governing the kinetics of transesterification can contribute to the commercial performance of the overall process [6]. Key reaction conditions that must always be optimized for efficient biodiesel production include the molar ratio of alcohol to oil, the type and amount of catalyst, as well as the reaction temperature and time [7,8].

The aim of this study was to carry out the transesterification reaction of rapeseed oil with methanol (methanolysis) using commercial hydrated lime $Ca(OH)_2$ as a heterogeneous catalyst. The reaction conditions that were varied included reaction temperature (25, 45, and 60 °C) and reaction time (60, 120, and 180 minutes). The obtained results showed that the optimal temperature for the methanolysis process is 60 °C, with an optimal reaction time of 120 minutes.

1. INTRODUCTION

Biodiesel is a mixture of monoalkyl esters of long-chain fatty acids, derived from various raw materials such as vegetable oils, animal fats, or other lipids, also known as triacylglycerols (TAG), or more simply, triglycerides [9]. Since methanol is the most commonly used alcohol in biodiesel production, another name for biodiesel is fatty acid methyl esters.

Compared to conventional diesel, the combustion of biodiesel generally produces lower hydrocarbon emissions [10,11]. This is due to the higher oxygen content in biodiesel, which leads to an increase in gas temperature and a reduction in the possible incomplete combustion. For a similar reason, the use of biodiesel as a fuel can reduce CO emissions from internal combustion engines [12].

Industrial biodiesel production plants must deliver a product of the required quality at the lowest possible cost, which significantly limits the number of available production technologies. Consequently, most plants produce biodiesel from edible vegetable oil through an alcoholysis process (typically methanolysis) using homogeneous alkaline catalysts such as sodium and potassium hydroxides and alkoxides [13,14,15]. The investigated types of heterogeneous alkaline catalysts include oxides of alkali and transition metals, as well as their combinations, metals and metal oxides on supports, zeolites, hydrotalcites, and biomass-based catalysts [5].

Published studies on the influence of key transesterification reaction conditions on biodiesel yield and properties include investigations of the molar ratio of alcohol to oil, catalyst amount, reaction temperature, and reaction time [16]. The factor that is usually the easiest to control is the reaction temperature at which the transesterification process occurs. Reaction temperature is one of the most important parameters affecting biodiesel production yield. A higher temperature enables more active particle movement and increased collisions between particles, resulting in a higher reaction rate. On the other hand, maintaining a high temperature requires high-temperature conditions and leads to high operational costs [14]. Reaction time is an important parameter that allows reactants to undergo the reaction and convert into the desired product. It is particularly significant in biodiesel production using heterogeneous catalysis, as achieving the same yields as homogeneous catalysis sometimes requires up to five times longer reaction time [17]. However, exceeding the optimal reaction time may lead to a reverse reaction within the reaction medium, ultimately reducing the overall biodiesel yield [14].

2. EXPERIMENTAL PART

The subject of this research is the methanolysis process of rapeseed oil using commercial hydrated lime. Within this scope, the efficiency of the process was examined depending on the reaction temperature and time.

2.1. Material and methods

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.,
- other materials and chemicals needed to carry out the necessary analyses.

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 $U = 40kV$ and a current of $I = 30mA$. CuKα radiation with a wavelength of $\lambda = 1.54056$ Å 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 0.02º 2θ with a time delay of 1 second at each step. The angular recording interval was 2-80º 2θ. 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 methanolysis process was carried out under defined process conditions. Accordingly, the catalyst concentration (wt.%) relative to the mass of the rapeseed oil used was 4 wt.%. The volumetric methanol-to-oil ratio was 0.25. The stirring speed during the reaction was kept constant at 1000 rpm. The process parameters varied during the methanolysis of rapeseed oil using hydrated lime as a catalyst were reaction temperature and reaction time.

To examine the influence of reaction temperature and time on the yield of fatty acid methyl esters (FAME), the catalyst amount relative to the mass of rapeseed oil (wt.%) was used as determined in a previously conducted and published study on the investigation of the catalytic activity of hydrated lime $Ca(OH)_2$ in the process of transesterification of vegetable oils. The optimal concentration, which resulted in the highest FAME yield, was found to be 4 wt.% [18]. The reaction times were 60 minutes, 120 minutes, and 180 minutes, with the reactions conducted at a temperature of 60°C. The reaction temperatures were 25°C, 45°C, and 60°C, with the reactions carried out for a duration of 120 minutes.

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 cm^3 with a round bottom,
4. Mechanical mixer,
5. Temperature probe i
6. Water cooler

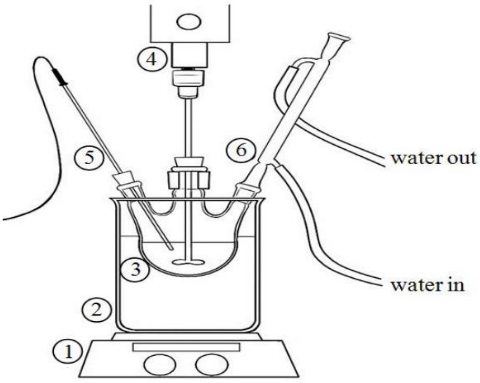

Figure 1. Laboratory apparatus for obtaining biodiesel

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 minutes 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.

3. RESULTS AND DISCUSION

3.1. Characterisation of the catalyst

The XRD diagram of Stamal hydrated lime is given in Figure 2. The diffractogram shows two components of the catalyst: portlandite – $Ca(OH)_2$, with the two most intense peaks around 2Θ values of 18° and 34°, and calcite – $CaCO_3$, with the most intense peak at 2Θ values between 29° and 30°. According to the XRD results of the quantitative analysis, the sample contains 89.63 wt.% portlandite,

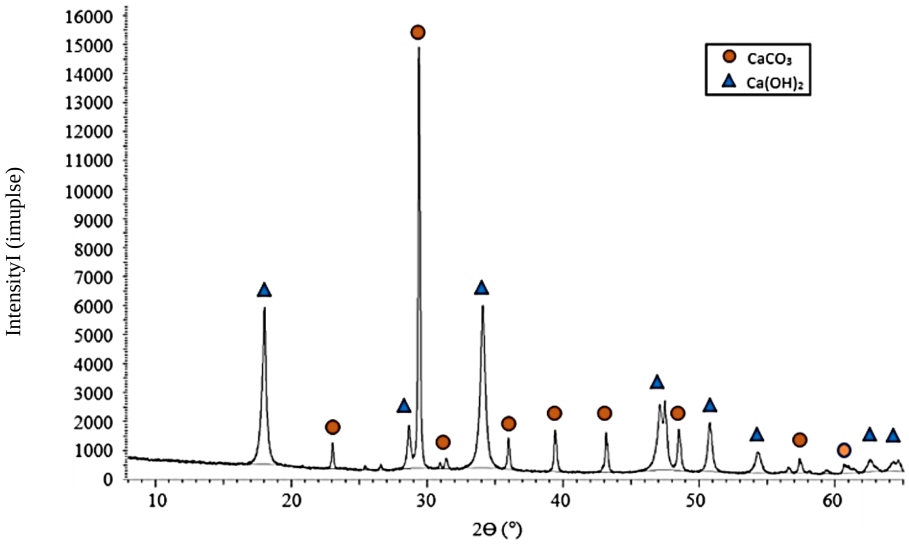

Figure 2. XRD pattern of Stamal hydrated lyme

3.2. Influence of Methanolysis Parameters on FAME Yield

The effect of transesterification reaction temperature on FAME yield is shown in Figure 3. Conducted methanolysis experiments at temperatures of 25, 45 and 60°C, in reaction time of 120 minutes resulted in the exponential growth of FAME yield, that is, an almost negligible yield (6.57%) was achieved at the lowest temperature, and increasment thetemperature to 45°C and 60°C, gave higher yields (22.67 and 96.7 %). The yield of FAME achieved at 60°C meets the yield requirement of the European standard for biodiesel [19].

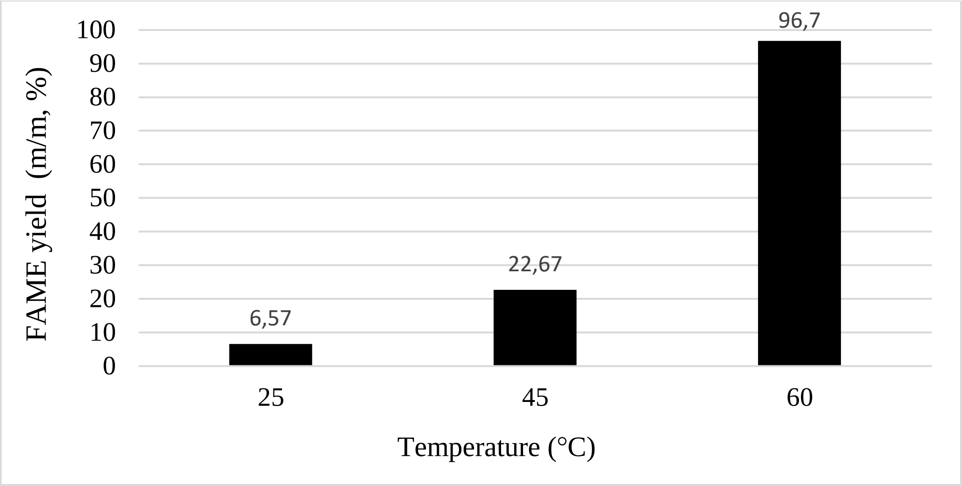

Figure 3. Effect of temperature on FAME yield
Process conditions: methanol:oil volume ratio 0.25, catalyst loading 4 wt%,reaction time 120 minutes

The effect of temperature on reaction rate plays a crucial role, as rate constants depend on temperature [17]. Temperature can influence transport phenomena in heterogeneous catalysis. A temperature higher than the boiling point of alcohol is undesirable due to evaporation [20], which is why the transesterification reaction temperature should be lower than the boiling point of the alcohol. The effect of temperature on yield is also related to the solubility of the catalyst in the reaction medium [21]. The observed yield trend is similar to that of the methanolysis of soybean oil using hydrated lime [22], where the authors reported that no conversion was achieved at a transesterification temperature of 25°C, while at higher reaction temperatures (35, 45, 55, and 60°C), FAME yields increased (2, 19, 57, and 100%). The increase in yield with reaction temperature results from a higher reaction rate and improved contact between reactants due to the reduction in oil viscosity [23].

The effect of transesterification reaction time on FAME yield is shown in Figure 4. During the first 60 minutes of methanolysis, a methyl ester yield of 87.81% was obtained, which increased to 96.7% during the additional 60 minutes,indicating the importance of ensuring sufficient time for the conversion of reactants into a product. The yield of FAME achieved after 120 minutes meets the yield requirement of the European standard for biodiesel [18]. The yield obtained after 180 minutes was 97.81 and meets the yield requirement of the European standard for biodiesel [19].

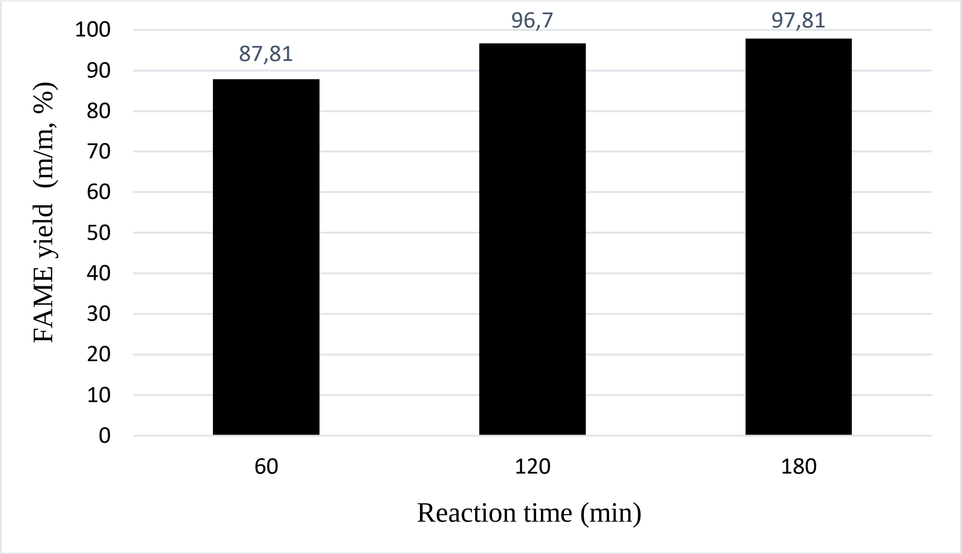

Figure 4. Effect of reaction time on FAME yield
Process conditions: methanol:oil volume ratio 0.25, catalyst loading 4 wt%, temperature 60 °C

In the case of using the Stamal catalyst, further extending the reaction time to 180 minutes resulted in an additional increase in FAME yield to 97.81%. In the transesterification of sunflower oil using hydrated lime, an increase in methyl ester yield was also observed after a reaction time of 180 minutes [24]. However, increasing the reaction time to 180 minutes led to a decrease in yield to 96.40% when using commercial hydrated lime Ingram Ltd. as a heterogeneous catalyst in a previously conducted study [25]. This trend—where yield increases over time up to a certain point before subsequently decreasing—was also observed in the methanolysis of sunflower oil [26] using hydrated lime. The reduction in yield observed with excessive reaction time is associated with the reversibility of the transesterification reaction [27,28,29].

4. CONCLUSION

The minimum temperature for conducting methanolysis using hydrated lime should be close to the boiling point of methanol to achieve a high biodiesel yield. Under the highest tested methanolysis temperature of 60°C, the use of Stamal hydrated lime resulted in the highest methyl ester yield of 96.7%, whereas a significantly lower yield of 22.67% was obtained at 45°C, and a very low yield of 6.57% at 25°C.

The transesterification reaction catalyzed by hydrated lime requires a certain amount of time to achieve an adequate conversion of reactants. The determined minimum methanolysis duration required to obtain a methyl ester content that meets the European biodiesel standard EN 14214 is 120 minutes. Extending the reaction time further leads to higher energy costs with only a slight additional increase in biodiesel yield, which, in the case of Stamal hydrated lime, increased by 1.11% after 180 minutes. Additionally, excessive reaction time may result in a reverse reaction, consequently leading to lower yields.

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