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APPLICATION OF DOLOMITE AS A HETEROGENEOUS CATALYST OF BIODIESEL SYNTHESIS

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Abstract. Some of the more recent methods of obtaining biodiesel are based on heterogeneous catalysis, which has the advantage of multiple uses of a catalyst. Natural minerals, such as dolomite, opoca and serpentinites, could be promising for use in biodiesel synthesis. The purpose of this study was to optimise the reaction conditions for biodiesel synthesis from sunflower oil and methanol using dolomite as a catalyst. Optimum reaction conditions for the transesterification of sunflower oil with methanol, using dolomite calcined at the temperature of 850 °C, have been identified: the amount of the catalyst – 6%, the molar ratio of methanol to oil – 8:1, the reaction duration – 5 hours and the reaction temperature – 60 °C. The amount of Fatty Acid Methyl Esters (FAME) of the sunflower oil obtained – 97.6%. FAME is in conformity with the EN 14214:2003 standard, when 500 ppm of antioxidant Ionol and 500 ppm of depressant Infineum R-442 are added. The Cold Filter Plugging Point (CFPP) of FAME is reduced to7 °C by adding 500 ppm of Infineum R-442. This product can be used in summer in the countries that are placed in Class E, including Lithuania. It has been established that dolomite without regeneration can be used for the transesterification of sunflower oil 2 times.

Keywords: biodiesel, dolomite, heterogeneous catalysis, methanol, oil.

Introduction

As environmental pollution increases due to greenhouse gas emissions, EU legal and regulatory documents promote, as much as possible, the use of fuels obtained from renewable energy sources. The majority of studies globally are related to the improvement of conventional biofuel production technologies by applying the chemical process of transesterification of oil with methanol. Some of the more recent methods of obtaining biodiesel are based on heterogeneous catalysis (Endalew *et al.* 2011), which has the advantage of multiple uses of a catalyst. In biodiesel synthesis, biocatalysts can also be used more than once; however, they are very expensive and become inactive at a temperature of above 60 °C or in a case in which there is a larger amount of methanol (Shimada *et al.* 2002; Watanabe *et al.* 2007).

Scientists have examined many different heterogeneous catalysts that accelerate the process of the transesterification of vegetable oil (MacLeod *et al.* 2008; Arzamendi *et al.* 2007). For the purposes of studies of biodiesel synthesis, metal oxides, hydroxides, complex compounds (Faungnawakij *et al.* 2012), silicates (Long *et al.* 2014) and ion-exchange resins (Shibasaki-Kitakawa *et al.* 2007) have been used.

The catalysis efficiency of alkaline earth oxides can be ranked as follows: BaO > SrO > CaO > MgO. In biodiesel production, metal oxide compounds are also used as catalysts. The comparison of the efficiency of pure CaO and CaO–MgO has made it possible to establish the following under the same transesterification conditions: Ca/Mg = 1:3, catalyst dosage 1.0 wt%, methanol: soybean oil molar ratio of 12:1, 70 °C, 2 hours, and the respective amounts of the esters obtained are equal to 92.8 and 98.4% (Fan *et al.* 2016). Studies of the use of an alkali-doped metal oxide ($LiNO_3$/CaO, $NaNO_3$/CaO, KNO_3/CaO and $LiNO_3$/MgO) for biodiesel production have made it possible to establish that under the same conditions of synthesis (60 °C, 3 hours, 6:1 molar ratio of methanol to oil, 5% of the catalyst), the degree of transesterification received is equal to 85…100%. The best efficiency was demonstrated by $NaNO_3$/CaO (calcined) and KNO_3/CaO (calcined). It is noteworthy that the calcination of a catalyst produces a positive effect (MacLeod *et al.* 2008).

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For biodiesel synthesis, Gui *et al.* (2016) used cottonseed oil, methanol and sodium silicate calcined at 400 °C, with 2 hours as a catalyst. The maximum output of biodiesel, 98.9 %, was obtained when the molar ratio of methanol to oil was 12:1, the reaction temperature was equal to 65 °C, the duration was 3 hours, and the catalyst was 2 w% of the amount of oil.

Having conducted thorough studies of the use of ion-exchange resins (cation-exchange resins and anion-exchange resins) for biodiesel synthesis using ethanol, researchers determined that anion-exchange resins are significantly more efficient than cation-exchange resins (Shibasaki-Kitakawa *et al.* 2007). The scientists continued their research using ion-exchange resins as catalysts and established that they were suitable not only as catalysts but also as sorbents of by-products (glycerol and water) and that the biodiesel obtained was in conformity with the requirements of the standard without downstream purification (Shibasaki-Kitakawa *et al.* 2007).

Natural minerals, such as dolomite, opoca and serpentinites, could be promising while using them in biodiesel synthesis. It is known that metal oxides are used in heterogeneous catalysis (Faungnawakij *et al.* 2012), while dolomite and opoca include, in their composition, calcium and magnesium carbonates, which can be thermally broken down to oxides. Since dolomite is a very common mineral in nature, it is not very expensive as a catalyst. Researchers (MacLeod *et al.* 2008; Gui *et al.* 2016; Niu *et al.* 2014; Shajaratun Nur *et al.* 2014) who examined biodiesel synthesis by applying the heterogeneous catalysis method and used methanol as a transesterification agent have identified various transesterification conditions. Canola oil transesterification with methanol under heterogeneous catalysis using calcined at 850 °C dolomite is reported by Ilgen (2011). The highest biodiesel yield of 91.78%, was obtained when the molar ratio of methanol to oil was 6:1, the reaction temperature – 67.5 °C, duration – 3 hours, and the catalyst content – 3 w% of the amount of oil. Ngamcharussrivichai *et al.* (2010) determined, that calcined at 800 °C dolomite was active, giving the palm kernel oil methyl esters content of 98.0%, at the methanol/oil molar ratio – 30:1, temperature – 60 °C, reaction time – 3 hours, catalyst – 6 w% (form the weight of oil). However, the results have not been found using sunflower oil and methanol, with dolomite as a catalyst.

The purpose of this study was to optimise the reaction conditions for biodiesel synthesis from sunflower oil and methanol using dolomite as a catalyst, to obtain biodiesel quality that meets the requirements of EN 14214:2003 standard.

1. Materials and methods

Sunflower oil was obtained from a local market.

The fatty acid composition of oil was analysed by the Clarus 500 gas chromatograph equipped with Flame Ionization Detector (FID) according to the requirements of the standard EN ISO 5508:1990. The fatty acid composition of oil used for experiments was the following: myristic acid (C14:0) – 0.01%, palmitic acid (C16:0) – 3.2%, palmitoleic acid (C16:1) – 0.13%, heptadecanoicacid (C17:0) – 0.07%, stearic acid (C18:0) – 3.20%), oleic acid (C18:1) – 27.70%, linoleic acid (C18:2) – 63.62%, linolenic acid (C18:3) – 0.16%, arachidic acid (C20:0) – 0.24%, eicosenoic acid (C20:1) – 0.15%, behenic acid (C22:0) – 0.50%, erucic acid (C22:1) – 0.1% and lignocericacid (C24:0) – 0.15%. The density of oil was – 0.915 g/cm^3 (at 15 °C), acid value – 0.11 mg KOH/g, iodine value – 119 g/100g.

Methanol (99.5%) was obtained from Sigma-Aldrich (UK), while dolomite was obtained from JSC Agromax (Lithuania), and its chemical composition (expressed in oxides) is as follows: CaO – 29.5%, MgO – 19.4%, SiO_2 – 3.1% and Fe_2O_3 – 0.3%. Before it was used for synthesis, dolomite was calcined under the temperature of 850 °C for 4 hours, which caused the calcium and magnesium carbonates to be fully broken down to oxides (Sendžikienė *et al.* 2012). Other analytical grade reagents were obtained from Fluka (UK).

Transesterification tests were conducted in a conical flask, which was connected to a condenser, a thermometer with a temperature controller and a mixer (at a constant mixing speed of 200 min^{-1}). The necessary amount of sunflower oil was poured into the flask and heated until the necessary temperature by constantly stirring it. Once the temperature of the oil reached the set value, the methanol was poured, and the necessary amount of the catalyst – dolomite – was added. Following a lapse of the intended time period, the catalyst was filtered. The remaining mixture was washed with water 2 times, and surplus alcohol and water were removed with the help of a vacuum rotary evaporator. Transesterification tests were performed under the following conditions: the molar ratio of methanol to oil – 3:12, the amount of dolomite – 4…8% of the amount of oil (mass), the temperature – 40…65 °C and the reaction duration – 2…9 hours.

The amount of the Fatty Acid Methyl Esters (FAME) of sunflower oil was determined by applying gas chromatography methods with a Clarus 500 chromatograph (Perkin Elmer). The chromatoghaph was equipped with a capillary column (14 m – 0.53 mm –16 μm) and a FID under temperature programming conditions. Hydrogen was used as the carrier gas.

In the case of the transesterification degree being higher than 80%, the amount of methyl esters was established by applying the method indicated in the EN 14203:2004 standard. When the transesterification degree did not exceed 80%, it was established in accordance with the methodology provided in the EN 14105:2011 standard by identifying the amounts of partial glycerides (monoglycerides, diglycerides, triglycerides) and calculating the degree of transesterification (Sendžikienė *et al.* 2016).

Physical and chemical properties of biodiesel were determined on the basis of the requirements of the EN 14214:2003 standard. Density and viscosity were

measured with the viscometer Stabinger SVM 3000. Density was measured according to the requirements of the EN ISO 12185:1996 standard. Viscosity was measured according to the requirements of the EN ISO 3104:1996 standard. Water content was measured according to the EN ISO 12937:2000 standard requirements, acid value – by using analyser Titrino plus according to the requirements of the EN 14104:2003 standard, copper strip corrosion was evaluated according to the requirements of EN ISO 2160:1998 standard, oxidation stability – by applying the Rancimat method (EN 14112:2016). The oxidation stability of FAME produced was increased by applying an antioxidant Ionol (JSC Pemco Chemicals, Norway). Cold Filter Plugging Point (CFPP) tests were performed according to the requirements of the DIN EN 116:2018-04 standard. For the performance of CFPP tests, the thermostatic bath Proline RP-84 (Lauda, Germany) was used. The volume of the samples was 45 ml. Temperature was decreased in steps by 1 degree each time until the liquid was not able to run through the filter any more. The depressants Wintron XC-30 (Biofuel Systems Group Limited, UK) and Infineum R-442 (Infineum GmbH, UK) were used for reducing the CFPP of FAME. All experiments were performed in triplicate. Mean values as well as uncertainty limits are presented as results.

The filtered catalyst (dolomite) was regenerated with hexane by adding 20 times more of it than the catalyst; the mixture was stirred for 30 minutes; dolomite was separated by filtering and dried under the temperature of 110 °C.

2. Results and discussion

Figures 1…3 demonstrate the dependence of the degree of transesterification on the reaction parameters (i.e., the duration, temperature, amount of the catalyst-dolomite, molar ratio of methanol to oil).

Figure 1 shows the dependence of the degree of transesterification on the amount of methanol and the reaction temperature, when the reaction duration is 6 hours and the amount of the catalyst is equal to 6% of the amount of oil.

The results of the tests demonstrated that under a temperature of 40 °C, the degree of transesterification reaches only 23%, when the molar ratio of methanol to oil is equal to 10:1 or higher. As the reaction temperature increases, the degree of transesterification also increases. The highest degree of transesterification is obtained when the process temperature is equal to 55 °C and the molar ratio of methanol to oil is 9:1 and higher. The amount of esters in compliance with the requirements of the standard (higher than 96.6%) is obtained when the molar ratio of methanol to oil is 8:1 and the reaction temperature is 60 °C or when the molar ratio is equal to 9:1 and the temperature is 65 °C. Nearly the similar results of transesterification of canola oil with application of dolomite as catalyst were obtained by Ilgen (2011). The process of transesterification with methanol was examined at room temperature and at

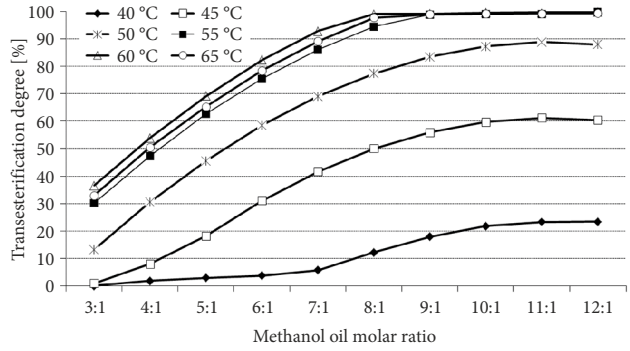

Figure 1. Dependence of the degree of transesterification on the molar ratio of methanol to oil and the reaction temperature, when the process lasts 6 hours and the amount of the catalyst is equal to 6%

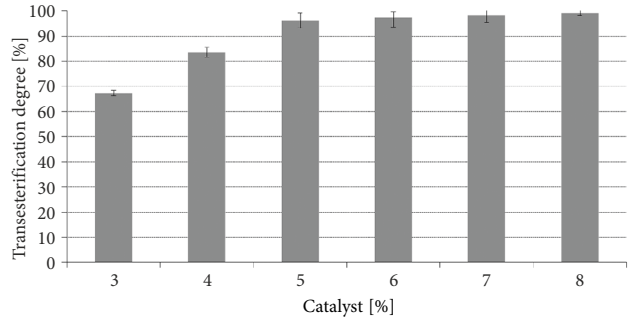

Figure 2. Dependence of the degree of transesterification on the amount of the catalyst, when the process lasts 6 hours, the molar ratio of methanol to oil is equal to 8:1 and the reaction temperature is 60 °C

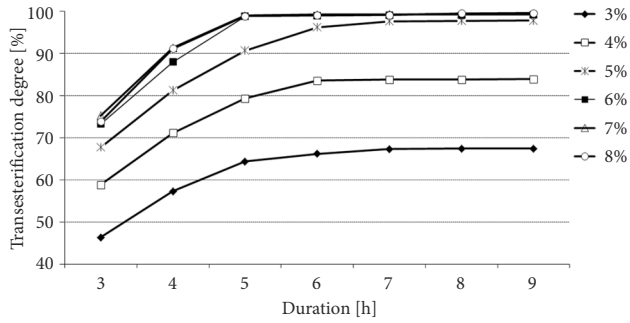

Figure 3. Dependence of the degree of transesterification on the catalyst amount and the reaction duration, when the process temperature is equal to 60 °C and the molar ratio of methanol to oil is 8:1

temperatures of 60 and 67.5 °C, when the other reaction parameters were constant. It was found that the degree of transesterification was equal to 30.82, 86.1 and 91.78%, respectively.

The our obtained results presented in the Figure 1 shows that the degree of transesterification consistently increases as the molar ratio of alcohol increases, at lower reaction temperatures (40, 45, 50 °C), while at a temperature of 55 °C or higher, the degree of transesterification remains almost the same when the molar ratio of alcohol to oil is equal to 10:1 or higher. The results obtained differ

from the test results published by other researchers: Ilgen (2011) established that the degree of transesterification increased from 67.98 to 91.78% as the molar ratio was increased from 3:1 to 6:1, while the increase to 9:1 and 12:1 resulted in a lower degree of transesterification.

Other researchers established a considerably higher optimum molar ratio of methanol to oil. Buasri *et al.* (2015) examined the transesterification of jatropha oil with methanol using microwaves and identified that approximately 95% of methyl esters were obtained in 4 minutes, under a molar ratio of methanol to oil of 18:1 and using a small amount (4%) of a heterogeneous catalyst – dolomite. Heterogeneous catalysis tests conducted by Niu *et al.* (2014) using palm kernel oil demonstrate that if dolomite calcined at 750 °C is used as a catalyst, the output of methyl esters obtained reaches 96%, when 4% of the catalyst is used and the molar ratio of methanol to oil is equal to 12:1. Ngamcharussrivichai *et al.* (2007) suggests using an even higher molar ratio for the transesterification of palm kernel oil with methanol. He indicates that under the temperature of 59.9 °C and using 6% of calcined dolomite, it is possible to obtain the output of 98% of palm kernel oil methyl esters in 3 hours, when the molar ratio of methanol to oil is equal to 50:1. In another study, Jaiyen *et al.* (2015) used 10% of calcined dolomite and obtained an output of 98.6% of palm kernel oil methyl esters using the molar ratio of methanol to oil of 30:1 under the temperature of 60 °C and with the reaction duration of 3 hours.

Figure 2 demonstrates the dependence of the degree of transesterification on the amount of the catalyst and the process temperature, when the process lasts for 6 hours and the molar ratio of methanol to oil is equal to 8:1.

The provided results make it obvious that when the catalyst amount is increased to 6%, the amount of esters obtained increases consistently. If the catalyst amount is increased even more, the increase in the amount of esters obtained is insignificant under the same process temperature and duration and with the same molar ratio of methanol to oil. Therefore, the catalyst amount of 6% was chosen as the optimum amount. These results almost correlate with the published results of heterogeneous catalysis using dolomite for the transesterification of various types of oil with methanol: many authors state that the optimum catalyst amount is 4…10% of the amount of oil (Buasri *et al.* 2015; Ngamcharussrivichai *et al.* 2007; Niu *et al.* 2014).

A much smaller optimum amount of the catalyst, while using canola oil and dolomite as a catalyst, is specified by Ilgen (2011). He established that the optimum amount of dolomite is much smaller and is equal to 1.5%, and when he increased the catalyst amount even further, the amount of ester obtained – according to his report – did not change and reached 91.78%.

The duration has considerable impact on the efficiency of the transesterification process. Figure 3 shows the dependence of the degree of transesterification on the catalyst amount and the reaction duration, when the process temperature is equal to 60 °C and the molar ratio of methanol to oil is 8:1.

The provided data makes it possible to conclude that at the temperature of 60 °C and with the molar ratio of methanol to oil set at 8:1, the process duration has a major impact on the output of the esters. If the process lasts less than 5 hours, then the degree of transesterification does not reach 96.5% as required by the standard. The degree of transesterification of 98.78% is obtained when the process lasts for 5 hours and the catalyst amount is equal to 6%. The degree of transesterification of 97.64%, which is in compliance with the standard, is also obtained when the reaction lasts for 7 hours and the catalyst amount is 5%.

To summarise the results of the tests, it is possible to maintain that the optimum conditions of the transesterification process of sunflower oil with methanol using calcined (850 °C) dolomite are the following: the catalyst amount of 6%, the molar ratio of methanol to oil of 8:1, the process temperature of 60 °C and the duration of 5 hours. The degree of transesterification of the biodiesel obtained is equal to 98.78±0.15%, and the ester content is 97.6±0.09%. Our results are nearly in compliance with the results of other authors: Ilgen (2011) examined the transesterification of canola oil with methanol using calcined (850 °C) dolomite and established the following optimum conditions: the temperature of 60 °C, also; the molar ratio of methanol to oil of 6:1; the duration of 3 hours only; and the catalyst amount of 3%. However, the degree of transesterification reached 91.78% and was not in compliance with the requirements of the standard.

The physical and chemical properties of Methyl Esters of Sunflower oil (SME) were examined and compared with the requirements of the EN 14214:2003 standard (Table).

The data presented in the Table show that the quality of SME is in compliance with all of the requirements of the standard, except for the oxidation stability, which reaches only 4.3 hours, and the CFPP, which is too high to use SME as fuel in any period of year. Similar results were also obtained by other researchers who examined the properties of FAME (Santos *et al.* 2013; Dunn *et al.* 2015).

Aiming to increase the stability for oxidation and improve the low temperature properties of SME, possibilities to use additives were examined. In our previous studies we established that antioxidant Ionol is effective for increase of oxidation stability of FAME produced from camelina sativa oil as well as depressants Wintron XC-30 or Infineum R-442 are effective for the improvement of the cold flow properties of FAME (Zaleckas *et al.* 2012). Therefore, to improve the oxidation stability of SME, 500 ppm of the antioxidant Ionol was added. The increase of oxidation stability 4.3…9.1 hours was observed. The requirements for the CFPP of fuel depend on the climatic conditions of the country where it is used. During summer, the CFPP of fuel should be a minimum of –5 °C in the climatic zone (Class E), to which Lithuania belongs. Evaluation of the effectiveness of depressants on the CFPP of our produced SME demonstrated that when 1500 ppm of Wintron

Table. The physical and chemical properties of methyl esters of SME

Parameter	EN 14214:2003 requirements		SME
	min	max	
Ester content [%]	96.5	–	97.6±0.15
Density at 15 °C [kg/m^3]	860	900	877±0.31
Viscosity at 40 °C [mm^2/s]	3.50	5.00	4.8±0.02
Sulfur content [mg/kg]	–	10	6±0.005
Monoglyceride content [%]	–	0.70	0.50±0.15
Diglyceride content [%]	–	0.20	0.17±0
Triglyceride content [%]	–	0.20	0.04±0
Free glycerol content [%]	–	0.02	0.01±0
Total glycerol content [%]	–	0.25	0.21±0.15
Cetane number	51.0	–	54.1±0.15
Acid value [mg KOH/g]	–	0.5	0.3±0.002
Iodine value [g J2/100 g]	–	120	119±0.15
Moisture content [mg/kg]	–	500	150±0.15
Phosphorus content [ppm]		10	8±0.05
Copper strip corrosion (3 hour at 50 °C)	1 class		1±0.003
Oxidation stability 110 °C [hours]	8		4.3±0.01
CFPP [°C]	–5 °C (in summer) –26 °C, –32 °C (in winter)		–3±0.002

XC-30 is added, the CFPP of SME is equal to minus 12 °C, while the 1200 ppm dosage of Infineum R-442 reduces the CFPP of SME to the minus 13 °C. Further research showed that the optimum amount of Infineum R-442, which reduces the temperature of SME to minus 7 °C, is equal to 500 ppm.

To reduce costs of biodiesel production, it is important to examine whether a catalyst can be used more than once. To conduct further tests, dolomite that was filtered after synthesis was used (Figure 4). The synthesis was performed for 5 hours under the temperature of 60 °C, with the catalyst amount of 6% and the molar ratio of methanol to oil of 8:1. Biodiesel in conformity with the requirements of the standard is obtained when using dolomite 2 times: when calcinated dolomite as catalyst was used for transesterification of the first portion of oil the degree transesterification of 98.78±0.15% was observed, after repeated usage of dolomite for the transesterification of the second portion of oil, the 98.16±0.13% degree of transesterification was achieved. In the case of dolomite usage for the third time, comparatively high degree of transesterification was achieved, namely, 95.72±0.17%; however, such a degree is no longer in compliance with the requirements of the standard.

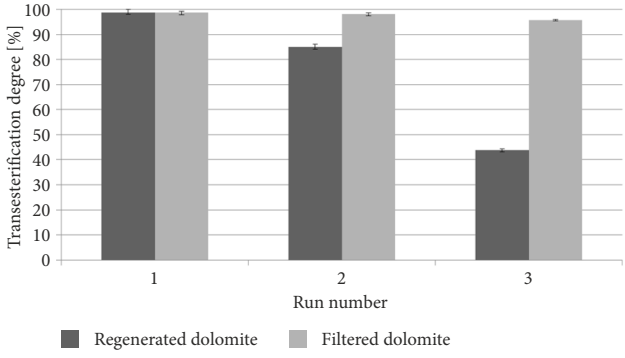

Figure 4. Dependence of the degree of transesterification on multiple usage of dolomite

Ilgen (2011) also examined possibilities for using dolomite as a catalyst multiple times. He established that dolomite could be used as a catalyst for 3 cycles, and when the process lasted 3 hours, the amount of dolomite was 4.5%, the temperature was 67.5 °C and the molar ratio of methanol to canola oil was 6:1. Because the degree of transesterification decreased only by 1.5% each time, however, the maximum transesterification degree of the biodiesel obtained reached 91.78%.

Tests were also conducted following regeneration, i.e., the filtering, washing and drying, of the dolomite (Figure 4). When dolomite was used for the second time, the transesterification degree obtained was 85.05±0.12%, while if it was used for the third time, it was only 43.8±0.04%. Such a reduction in the catalyst efficiency could be explained by the fact that in the presence of water in the solution, calcium and magnesium oxides turn into hydroxides, which do not act as catalysts in the process of transesterification of oil. In this case, the dolomite should be additionally calcinated at high temperatures before the usage as catalyst for transesterification. This is economical unprofitable, therefore it could be stated that dolomite has a limited reusability in biodiesel production reaction.

Conclusions

The process of biodiesel fuel synthesis with application of heterogeneous catalysis for sunflower oil transesterification using dolomite as catalyst was studied. The optimal reaction conditions of the transesterification of sunflower oil with methanol were established: the catalyst amount – 6%, the molar ratio of methanol to oil – 8:1, the reaction duration – 5 hours and the reaction temperature – 60 °C. The amount of FAME of sunflower oil obtained was 97.6%.

Under above mentioned optimal conditions produced SME met the standard requirements set for biodiesel fuel with respect to almost all properties except for oxidation stability and CFPP. It was found that SME are in conformity with the EN 14214:2003 standard, when 500 ppm of antioxidant Ionol and 500 ppm of depressant Infineum R-442 are added. The CFPP of FAME is reduced to –7 °C if 500 ppm of Infineum R-442 is added. This product can be used in summer in the countries that are placed in Class E, including Lithuania. It has been established that dolomite as catalyst without regeneration can be used for the transesterification of sunflower oil 2 times.

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