INTERESTERIFICATION OF RAPESEED OIL WITH METHYL FORMATE FOR PRODUCTION OF INNOVATIVE BIODIESEL FUEL

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Abstract

During the production of biodiesel, a by-product - the glycerol phase is formed (about 10% of the obtained biodiesel). The interesterification of vegetable oil using carboxylate esters of low molecular weight does not produce glycerol, instead its compounds (mono-, di- and triformyl glycerides) are obtained in a mixture with fatty acid alkyl esters (conventional biodiesel). Such a product can be used as fuel for diesel engines. The aim of the work was to investigate the possibilities of application of methyl formate in the biotechnological production of biodiesel. The industrial enzyme preparation Lipozyme TL IM was used as a catalyst for interesterification. The influence of the amount of catalyst, the molar ratio of methyl formate to oil and the duration of the process on the yield of biodiesel was evaluated. The highest yield of rapeseed oil methyl esters was obtained under the following conditions: 14-15% of the enzyme preparation Lipozyme TL IM (based on the weight of the oil), molar ratio of methyl formate to oil - 40:1, duration - 60 h. Under these conditions, an 81.6% yield of rapeseed oil methyl esters was obtained.

Keywords: *biodiesel, methyl formate, interesterification, lipase*

1. INTRODUCTION

Most often, biodiesel is produced by applying the chemical process of transesterification of oil with methanol [1]. In addition to biodiesel, a by-product is formed - the glycerol phase (about 10% of the obtained product), the composition of which varies depending on the applied biodiesel production technology. The glycerol phase consists of 80-90% glycerol. In addition, the glycerol phase contains such impurities as fatty acid methyl esters (FAME), soaps, alcohol and water [2]. Pure glycerol is used in the paper, ester, tobacco, cellulose, food and pharmaceutical industries [3,4]. It can also be used in the production of feeding stuffs or wood briquettes [5]. Only in some industries, e.g., energy production, the glycerol phase can be used directly without purification. Before use in the food, cosmetic, pharmaceutical industry, impurities from glycerol phase must be removed. Generally, glycerol phase is refined to produce the pure glycerol, which can be used in the industries mentioned above. For glycerol refining technology to be profitable, large quantities of the glycerol phase are required, which are not produced in smaller scale biodiesel plants. In addition, the refining process requires high energy and material costs [6,7]. Another problem faced by biodiesel producers is the surplus of glycerol on the market, which has resulted from the intensive development of biodiesel production in the EU and other countries. Conventional industries are no longer able to use the glycerol produced during the production of biodiesel and it is necessary to look for a new way of using glycerol. The market price of glycerol is falling, and at the same time, the profitability of biodiesel producers.

The biodiesel production process would become more economically efficient if by-products were not formed. One such possibility is to replace the methanol used in the oil transesterification process with carboxylate esters of low molecular mass. During such a process, glycerol, a byproduct of conventional biodiesel production, is not formed [8,9], and its derivatives (esters of glycerol and carboxylic acids of low molecular weight) are formed which are soluble in biodiesel. They increase the yield of biodiesel. The smallest carbon chain carboxylate ester is methyl ester of formic acid - methyl formate. The interesterification of triglycerides with methyl formate take place in 3 stages: in the first stage, triglyceride (TG) reacts with methyl formate (MF), forming fatty acid methyl ester (FAME – conventional biodiesel) and monoformyl diglyceride (MFDG), which in the second stage react with next molecule of methyl formate, forming FAME and diformyl monoglyceride (DFMG), which in the

third stage reacts with MF, and the final products are formed – FAME and triformylglyceride (TFG) (Fig. 1).

Triglyceride + Methyl formate ↔ Fatty acid methyl ester + Monoformyldiglyceride

Monoformyldiglyceride + Methyl formate ↔ Fatty acid methyl ester + Diformylmonoglyceride

Diformylmonoglyceride + Methyl formate ↔ Fatty acid methyl ester + Triformylgliceride

Fig. 1. Principal scheme of triglyceride interesterification with methyl formate

The mixture obtained during the interesterification process has better low-temperature properties than pure fatty acid alkyl esters (conventional biodiesel). In colder climate zones, the use of biodiesel is also slowed down by the fact that diesel used in the winter season must meet the requirements of the second arctic class, i.e. cold filter plugging point (CFPP) must be below -32 °C. This reason forces to look for ways to reduce the CFPP of biodiesel. Industrial depressants, which need to be added in large quantities to fatty acid methyl esters, greatly increase the cost of the product. One of the possible ways to lower CFPP is the addition to biofuel the esters of glycerol and carboxylic acids of low molecular wight [10]. A method of converting crude glycerol (obtained during transesterification) into glycerol triacetate was studied. The mixture of glycerol triacetate with methyl or ethyl esters of fatty acids makes it possible to obtain biodiesel with improved properties, especially at low temperatures [11] (EP 1985684B1 2009), and avoid the expensive glycerol purification procedure [7].

The use of various alkyl acetates for interesterification of rapeseed oil using sodium methoxide catalysts was investigated by Z. Sustere et al. (2016). The optimal molar ratio of alkyl acetates to oil was 36:1 when process temperature was near the boiling point of alkyl acetates. The obtained yield of fatty acid alkyl esters was 93%, 89%, 87% and 88% accordingly when methyl, ethyl, propyl and isopropyl acetates were used for interesterification [12]. Researchers from some countries have analyzed the application of methyl and ethyl acetates in biodiesel production by using enzymatic catalysts and different types of oil [13,14]. It was established that during such a process not only no by-products are formed, but also enzymes are not inactivated as happens when using methanol for oil transesterification [15]. Methyl formate, which is obtained from methanol, could be also used for the transesterification of vegetable oil. Methyl formate can be produced in various ways: partial oxidation of methanol on active platinoid heterogeneous catalysts with oxygen deficiency; applying the carbonization of methanol to methyl formate with sodium methylate; carbonization of methanol with carbon monoxide using copper, platinum and anionic groups and other similar heterogeneous catalysts; dehydrogenation of methanol with copper and other heterogeneous catalysts [16]. Research on the use of methyl formate in the synthesis of biofuel from rapeseed oil using chemical catalyst (28.6% sodium methoxide solution in methanol) has been started. It was established that at a temperature of 27 °C, with a molar ratio of catalyst to oil of 0.16:1, a molar ratio of methyl formate to oil of 18:1, and a reaction time of 60 min., a biodiesel yield of 88.3% is obtained [17]. However, there is little data on the use of methyl formate in the biotechnological synthesis of biodiesel, such research has only just begun. The aim of our work is to investigate the possibilities of using methyl formate in the production of biodiesel using industrial enzymatic preparation Lipozyme TL IM as catalysts.

2. MATERIALS AND METHODS

2.1. Materials

Materials used for research:

- refined rapeseed oil that meets the quality requirements of edible oil;
- methyl formate, analytical grade, JSC Labochema (Lithuania);

• enzyme preparation Lipozyme TL IM (lipase from *Thermomyces lanuginosus*, immobilized on silica gel, activity ≥3,000 U/g, Novozymes, Denmark).

2.2. Methods

The studies on interesterification of rapeseed oil with methyl formate using biocatalysts were carried out in a thermostatically controlled laboratory reactor equipped with a condenser, a thermometer with a temperature controller and a mixer (stirred at a constant rotation frequency of 250 min^{-1}). The required amount of rapeseed oil was poured into the reactor, the catalyst was added and the required amount of methyl formate was added. The reaction was carried out for the specified time with constant stirring. After the specified time, the mixture was filtered for removal of biocatalyst. Excess methyl formate was evaporated from the remaining mixture. The resulting product (a mixture of biodiesel (rapeseed oil fatty acid methyl esters) and formylglycerol) was analyzed by gas chromatography using a Perkin Elmer Clarus 500 chromatograph (detector - FID, column - Restek MXT-Biodiesel TG (0.15 m – 0.32 mm – 0.10 µm) according to the EN 14105 standard. The ester content was evaluated according to the content of formylglycerides in the sample. The yield (%) of rapeseed oil methyl esters (RME) was calculated based on the experimental content of RME in the reaction product, obtained by gas chromatography, and the theoretical amount of RME that can be obtained after the reaction of all triglyceride molecules. The theoretical RME amount is 84% [17].

3. RESULTS AND DISCUSSIONS

The efficiency of the interesterification process and the yield of biodiesel are determined by three main factors: the amount of methyl formate (expressed as molar ratio of methyl formate to oil), the amount of catalyst in the reaction medium (calculated on the basis of oil) and the duration of the process. The process of interesterification takes place in three stages (Fig. 1). Three molecules of methyl formate are required to react with one triglyceride molecule. The interesterification process is reversible, therefore, in order to obtain a higher product yield, it is appropriate to increase the amount of reactants or to remove the formed products from the reaction medium. The process is catalytic, so the yield of reaction products also depends on the amount of catalyst. As with other enzymatic processes, the yield of products from the interesterification process also depends on the duration. In the first stage of the research, the influence of the amount of enzyme on the yield of rapeseed oil methyl esters (RME) was evaluated. The process was carried out at 15:1 to 40:1 molar ratio of methyl formate to oil, with a process time of 20 h and a temperature of 20 ºC. The content of the enzyme preparation Lipozyme TL IM varied from 9 to 17 wt% of the oil content. The temperature of the process was chosen close to the boiling point of methyl formate, based on the findings of other scientists that it is inappropriate to carry out biodiesel synthesis processes at a temperature not higher than the evaporation temperature of the acyl receptor. The obtained research results are presented in Fig. 2.

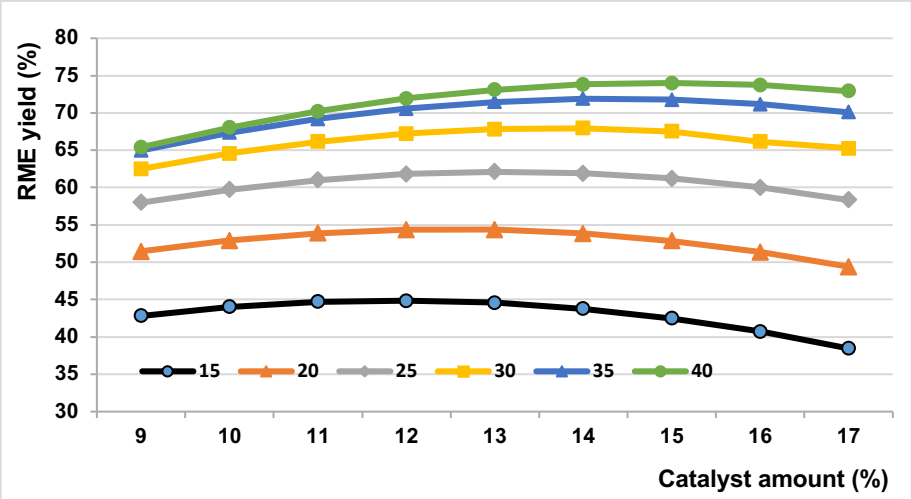

Fig. 2. Influence of Lipozyme TL IM amount on RME yield

As can be seen from the presented data, increasing the amount of catalyst increases the yield of RME. But up to a certain value. Higher RME yield depending on the molar ratio of methyl formate to oil were obtained at 13 to 15 wt% of catalyst (from oil content). Our previous studies also showed that using another enzymatic preparation, Lipozyme RM IM, the interesterification of rapeseed oil with methyl formate requires a large amount of enzymatic preparation, which reached 13%. The fact that heterogeneous enzyme catalysts have a lower catalytic activity than chemical catalysts in interesterification reactions and therefore require a larger amount of them in order to obtain a high product yield is also noted by other researchers. When studying interesterification with ethyl acetate, they used the enzyme Novozyme 435 and it was found that its optimal amount is 10 % [18]. Du et al. (2004) used methyl acetate and Novozyme 435 as a catalyst for the interesterification of vegetable oil, and the optimal determined amount was 30 % [19]. Other authors, using methyl or ethyl acetates for interesterification process, obtained higher than 90 % yield of esters than using from 10 to 20% of this enzyme preparation [15,20].

Taking into account the fact that the molar ratio of methyl formate to oil also affects the yield of the product, research was conducted analyzing the influence of amount of methyl formate on the yield of RME. The amount of catalyst was chosen as the one that gave a higher yield of RME in previous studies, it was between 13 and 15 %. The obtained research results are presented in Fig. 3.

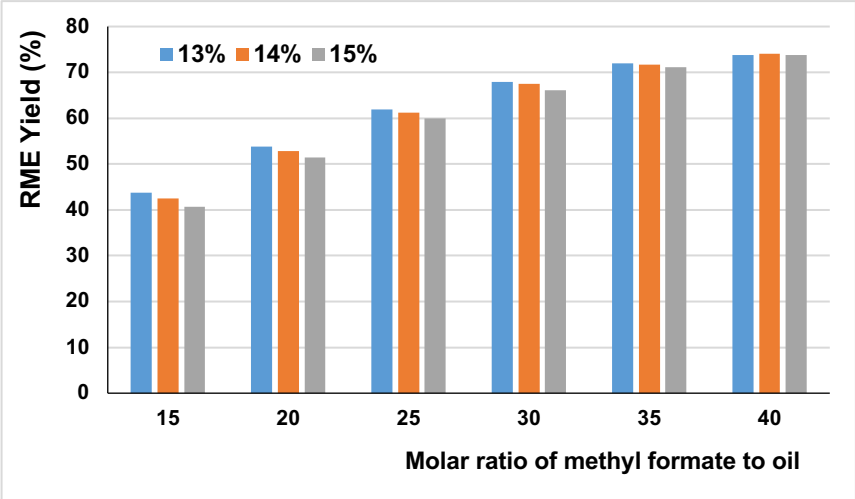

Fig. 3. Dependence of RME yield on molar ratio of methyl formate to oil when catalyst amount was 13%, 14% and 15%

From the data presented, it can be seen that by increasing the molar ratio of methyl formate to oil, a higher yield of esters is obtained, which reaches 74% at a molar ratio of 40:1. It can also be seen from the obtained data that the amount of enzyme has a significant influence on the yield of RME at a lower molar ratio, while at a higher molar ratio, the influence of different amounts of enzyme on the yield of RME is smaller. However, for maximum yield and at a 40:1 molar ratio of methyl formate to oil, the optimal amount of Lipozyme TL IM is 14%, as the RME yield is slightly higher at this amount than with 13 or 15% ferment preparation. The importance of the molar ratio in the yield of interesterification products is discussed by other scientists who used various acyl receptors for interesterification of triglycerides. They state that high yield of methyl esters is obtained only at high molar ratios of methyl formate to oil. Applying the chemical process of interesterification, 88.3% yield of RME was obtained at a molar ratio of 18:1 [17]. Casas et al. (2013, 2011) used 50:1 and 48:1 molar ratio for oil interesterification with methyl acetate and obtained 94.8% and 95.1% of esters even using different chemical catalysts [21,22]. Using methyl formate by the method of enzymatic catalysis, 67.9% yield of RME was obtained only at a molar ratio of 32:1 [23].

The duration of the reaction is one of the more important factors influencing the output of biotechnological processes. In order to evaluate the influence of the process duration on the process of interesterification of rapeseed oil with methyl formate, the tests were carried out by changing the process duration from 6 to 48 hours, with a molar ratio of methyl formate to oil of 40:1, the amount of enzyme – 14% and 15%, and the temperature - 20 °C. The obtained results are presented in Fig. 4.

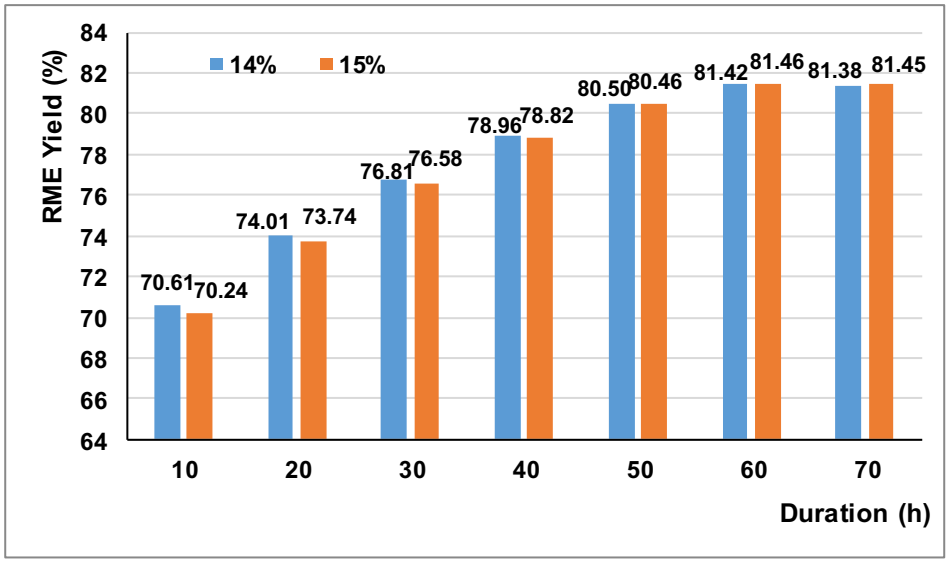

Fig. 4. Dependence of RME yield on process duration when catalyst amount is 14% and 15% and molar ratio of methyl formate to oil is 40:1

The presented data show that the yield of methyl esters increases as the process duration increases. During 10 h of interesterification, the yields of esters reach 70.6 and 70.2% using 14 and 15% of the enzyme preparation, respectively. After increasing the duration to 50 h, the yield of RME increased more significantly and reached 80.5 and 80.49%, respectively. Further increasing the process time, the increase in RME yield was not so significant and at 60 h of interesterification, the RME yield reached 81.42 and 81.55%, respectively. Increasing the duration from 60 h to 70 h did not increase the yield of esters, so it can be stated that the optimal duration of this process using Lipozyme TL IM as a catalyst is 60 h. The same trend is confirmed by the results of research on the amount of formyl glycerides in the reaction product (Fig. 5). As the yield of RME increased, the concentration of formyl glycerides in the reaction product gradually increased.

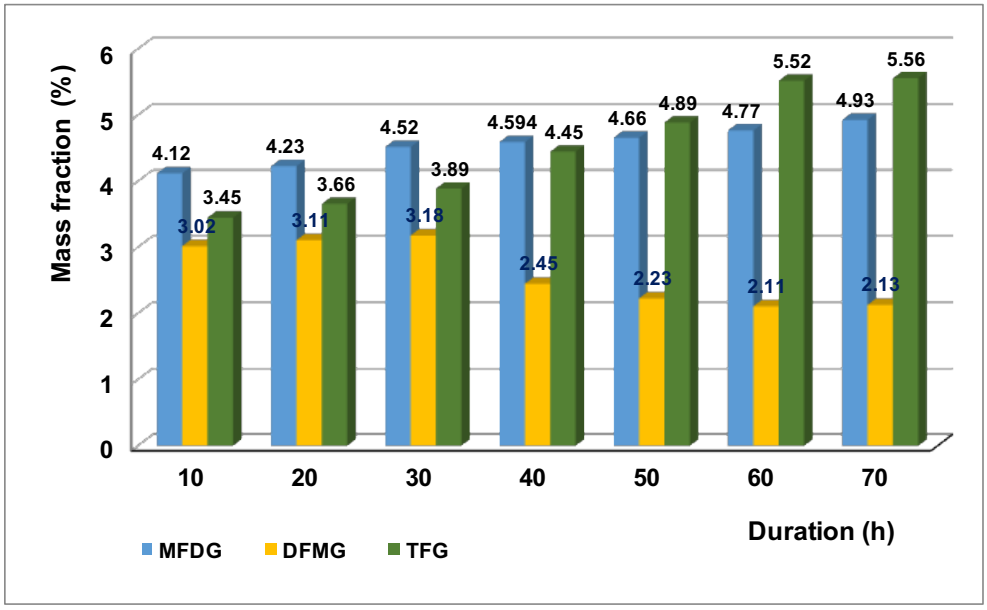

Fig. 5. Dependence of composition of formylglycerides in reaction product on the process duration when catalyst amount is 14% and molar ratio of methyl formate to oil is 40:1

The obtained data show that as the process duration increases, the amount of trifomilglycerol also increases, which reaches 5.52% at a process duration of 60 h. As time increases, the amount of monoformyldiglycerides and triformylglycerides in the reaction product increases, while the amount of diformylmonoglycerides decreases. This shows that the amount of glycerol compounds formed in the second and third stages increases, while the amount of compounds formed in the first stage decreases, i.e. the shift of the reaction towards the formed products. The amount of MFDG is higher than that of DFMG, indicating that the first step of interesterification determines the joint rate of the interesterification process, and the final step retains incompletely reacted glycerol intermediates in the product. After 60 h, the amount of triformylglycerol in the product reaches 5.52%, product also contains 2.11% diformylmonoglicerides and 4.77% monoformyldiglycerides. Amount of triformylglycerol after 60 h does not differ much when the process duration is extended to 70 h.

Many scientists who studied the interesterification process emphasize the importance of the process duration for the yield of the obtained products. The optimal process duration of 40 h was determined by enzymatic interesterification of rapeseed oil with methyl formate [23] using enzymatic catalyst Lipozyme RM IM. The results of interesterification studies with methyl acetate also confirmed that longer durations are required for enzymatic catalysis. Only less than 50% yield of esters was obtained in 48 h using waste canola oil. Usai et al. (2010) obtained only 82% yield of olive oil methyl esters in 96 h [24], while Surendhiran et al. 2014 indicates a yield of 85.3% seaweed oil methyl esters obtained in 60 h [25]. Meanwhile, interesterification processes using chemical homogeneous catalysts are faster. Using alkaline catalysts for oil interesterification with ethyl acetate within 20 min. 77% yield of esters was obtained [26]. Using alkaline homogeneous catalysts, a 90% yield of ethyl esters was obtained within 20 h [27]. A longer optimum process time was found using acid catalysts. Using p-toluenesulphonic acid for interesterification with ethyl acetate, only 73.5% esters yield was obtained in 40 h. A shorter process duration of 10.8 h was observed for interesterification using a magnetic solid acid catalyst [28]. An even shorter process duration is indicated by Ribeiro et al. (2017; 2018), who conducted studies of the effectiveness of niobium phosphate and ɣ-Aluminum (γAl_2O_3) catalysts in the interesterification of oils with methyl acetate [29,30]. Our data show that enzymatic interesterification with methyl formate occurs more slowly compared to chemical catalysis, the process must be carried out for a longer time.

Summarizing the results of the research, it can be stated that in order to obtain a high product yield in the interesterification process of rapeseed oil using Lipozyme TL IM as a catalyst, it is appropriate to use 14 to 15% of the catalyst Lipozyme TL IM, a higher product yield is obtained in 60 h at the molar ratio of methyl formate to oil 40:1.

4. CONCLUSIONS

The biotechnological method of interesterification of oil with methyl formate can be applied in the production of biodiesel. The industrial enzyme preparation Lipozyme TL IM is an effective catalyst in biodiesel synthesis. Its optimal amount is from 14 to 15 w% (from oil mass). The yield of biodiesel during the interesterification process depends on the amount of catalyst, the amount of methyl formate and the duration of the process. By increasing these parameters, the yield of biodiesel increases. The enzymatic process is more complicated than the interesterification using chemical catalysts: even in order to obtain a higher product yield, the enzymatic catalysis requires a larger catalyst and acyl receptor amoiunt, and a longer process duration. The highest yield of rapeseed oil methyl esters was obtained during the transesterification process at 20 °C with a molar ratio of methyl formate to oil of 40:1, with a process duration of 60 hours. Under these conditions, the yield of rapeseed oil methyl esters reached over 81%. The reaction product contained 5.52% of triformylglycerol, 2.11% diformylmonoglycerides and 4.77% monoformyldiglycerides.

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REFERENCES

1. Basha, SA, Gompa, KR&Jebaraj, S 2009, ‘A review on biodiesel production, emissions and performance’, Renewable and Sustainable Energy Reviews, vol, 13, no. 6-7, pp. 1628–1634.
2. Ayoub, M & Ahmad, ZA 2012, ‘Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry’, *Renewable and Sustainable Energy Reviews*, vol. 16, no. 5, pp. 2671–2686.
3. Behr, A & Oberdorf, L 2001, ‘Verfahrensentwicklung der säurekatalysierten Veretherung von Glycerin mit Isobuten zu Glycerintertiärbutylethern’, *Chemie-Ingenieur-Technik*, vol. 73, no. 11, pp. 1463–1467.
4. Karinen, RS & Krause, AOI 2006, ‘New biocomponents from glycerol’, *Applied Catalysis A: General*, vol. 306, pp. 128–133.
5. Saoharit, N & Khanal, SK 2011, ‘Biodiesel-derived crude glucerol bioconversion to animal feed. A sustainable option for a biodiesel refinery’, *Bioresource Technology*, vol. 102, no, 10, pp. 5808–5814.
6. Azita, J, Hasheminejad, M, Tahvildari, K & Tabatabaei M 2012, ‘High quality potassium phosphate production through step-by-step glycerol purification: A strategy to economize biodiesel production’, *Bioresource Technology*, vol. 104, pp. 788–790.
7. Quispe, CAG, Coronado, CJR & Carvalho, JrJA 2013, ‘Glycerol: production, consumption, prices and new trends in combustion’, *Renewable and Sustainable Energy Reviews*, vol. 27, pp. 475–493.
8. Huang, X, Bi, J, Wang, J, Ouyang, J, Xiao, Y, Hao, H, Wang, Y & Yin, Q 2015, ‘Liquid–liquid equilibrium of binary and ternary systems composed by palm oil or palm oil fractions with methanol/ethanol and water’, *Fluid Phase Equilibria*, vol. 404, pp.17-25.

9. Alavianmehr, MM, El-Shaikh, M, Akbari, F & Behjatmanesh-ardakani, R 2017, 'A new equation of state for modeling thermodynamic properties of some fatty acids alkyl esters, methyl ester-based biodiesels and their blends', *Fluid Phase Equilibria*, vol. 442, pp. 53–61.
10. Wessendorf, R 1995, 'Glycerinderivate als Kraftstoffkomponenten', *Erdöl und Kohle, Erdgas, Petrochemie vereinigt mit Brennstoff-Chemie*, vol. 48, no. 3, pp. 138–142.
11. *EP 1985684B1,* Process to obtain biodiesel fuel with improved properties at low temperature and comprising glycerine acetates, August 2009.
12. Sustere, Z, Murnieks, R & Kampars V 2016, 'Chemical interesterification of rapeseed oil with methyl, ethyl, propyl and isopropyl acetates and fuel properties of obtained mixtures', *Fuel Processing Technology*, vol. 149, pp. 320–325.
13. Kumar, MM, Reddy, JRC, Rao, BVSK & Prasa, RBN 2007, 'Lipase-mediated conversion of vegetable oils into biodiesel using ethyl acetate as acyl acceptor', *Bioresource Technology*, vol. 98, no. 6, pp. 1260–1264.
14. Chinh, NH, Liang, SH, Chenc, SH, Suc, CH, Linc, JH & Chien-Chung Chienc, CC 2018, 'Enzymatic production of biodiesel from insect fat using methyl acetate as an acyl acceptor: Optimization by using response surface methodology', *Energy Conversion and Management*, vol. 158, pp. 168–175.
15. Nguyen, HC, Liang, SH, Doan, TT, Su, CH & Yang, PC 2017, 'Lipase-catalyzed synthesis of biodiesel from black soldier fly (*Hermetica illucens*): optimization by using response surface methodology', *Energy Conversion and Management*, vol. 14, pp. 335–342.
16. Kaiser, D, Beckmann, L, Walter, J & Bertau, M 2021, 'Conversion of Green Methanol to Methyl Formate', *Catalysts*, 11, 869, < https:// doi.org/10.3390/catal11070869>.
17. Sustere, Z & Kampars V 2017, 'The influence of acyl and alcohol moieties of carboxylate esters on rapeseed oil chemical interesterification', *Materials, Methods & Technologies*, vol. 11, pp. 1–7.
18. Modi, MK, Reddy, JRC, Rao, B & Prasa RBN 2007, 'Lipase-mediated conversion of vegetable oils into biodiesel using ethyl acetate as acyl acceptor', *Bioresource Technology*, vol. 98, pp. 1260–1264.
19. Du, W, Xu, Y, Liu, D & Zeng, J 2004, 'Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors', *Journal of Molecular Catalysis B: Enzymatic*, vol. 30, pp. 125–129.
20. Tavares, GR, Goncalves, JE, Santos,WD & Silva C 2017, 'Enzymatic interesterification of crambe oil assisted by ultrasound', *Industrial Crops and Products*, vol. 97, pp. 218–223.
21. Casas, A, Ramos, MJ & Perez A 2011, 'New trends in biodiesel production: chemical interesterification of sunflower oil with methyl acetate', *Biomass and Bioenergy*, vol. 35, pp. 1702–1709.
22. Casas, A, Ramos, MJ & Perez A 2013, 'Methanol-enhanced chemical interesterification of sunflower oil with methyl acetate', *Fuel*, vol. 106, pp. 869–872.
23. Makareviciene, V, Sendzikiene, E, Gaide, I & Kazancev, K 2022, 'Application of methyl formate in the process of biotechnological interesterification of triglycerides for the production of biodiesel', *Biomass Conversion and Biorefinery*, < https://doi.org/10.1007/s13399-022-03390-4>.
24. Usai, EM, Gualdi, E, Solinas, V & Battistel E 2010, 'Simultaneous enzymatic synthesis of FAME and triacetyl glycerol from triglycerides and methyl acetate', *Bioresource Technology*, vol. 101, pp. 7707–7712.
25. Surendhiran, D, Vijay, M & Sirajunnisa AR 2014, 'Biodiesel production from marine microagla *Chlorella salina* using whole cell yeast immobilized on sugarcane bagasse', *Journal of Environmental Chemical Engineering*, vol. 2, pp. 294–1300.

26. Miesiac, I, Rogalinski, A & Jozwiak P 2013, 'Transesterification of triglycerides with ethyl acetate', *Fuel*, vol. 105, pp. 169–175.
27. Galia, A, Centineo, A, Saracco, G, Schiavo, B & Scialdone O 2014, 'Interesterification of rapeseed oil catalyzed by tin octanoate', *Biomass and Bioenergy*, vol. 67, pp. 193–200.
28. Wu, H, Liu, Y, Zhang, J & Li G 2014, '*In situ* reactive extraction of cottonseeds with methyl acetate for biodiesel production using magnetic solid acid catalysts', Bioresource Technology, vol. 174, pp. 182–189.
29. Ribeiro, JS, Celante, D, Brondani, LN, Trojahn, DO, Silva, C & Castilhos, F 2018, 'Synthesis of methyl esters and triacetin from macaw oil (*Acrocomia aculeata*) and methyl acetate over γ-alumina', *Industrial Crops and Products*, vol. 124, pp. 84–90.
30. Ribeiro, JS, Celante, D, Simões, SS, Bassaco, MM, Silva, C & Castilhos F 2017, 'Efficiency of heterogeneous catalysts in interesterification reaction from macaw oil (*Acrocomia aculeata*) and methyl acetate', *Fuel,* vol. 200, pp. 499–505.