Membrane Filtration as an Environmentally Friendly Method for Crude Biodiesel Purification

M. Ostojčić,[a] *S. Brkić,*[a] *M. Tišma,*[a] *B. Zelić,*[b] and *S. Budžaki*[a*]

[a] Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek,
Franje Kuhača 20, HR-31 000 Osijek, Croatia

[b] University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19,
HR-10 000 Zagreb, Croatia

Abstract

Biodiesel is the first alternative fuel the physicochemical properties of which are regulated by appropriate standards: American ASTM D 6751 and European standard EN 14214. The process of biodiesel production consists of three main phases: 1) preparation of feedstock, 2) transesterification, and 3) processing of the reaction product – purification of crude biodiesel to meet the specification provided by the previously mentioned standards. The purification process of crude biodiesel is usually carried out by two notable techniques: wet and dry washing. The most commonly used process is wet washing. A major drawback in the use of water in purification process is the generation of a large amount of wastewater that greatly increases biodiesel production costs, followed by drying of the product, which requires an additional amount of energy and is time consuming. The greatest disadvantage of dry washing using different ion-exchange resins is the inability to remove glycerol and methanol from crude biodiesel to those limits prescribed by EN 14214, followed by the disposal problem of spent ion-exchange resins. Because of the aforementioned, the use of membrane technology in the process of biodiesel purification has appeared as an alternative for the existing purification techniques. The membrane filtration is environmentally friendly and requires less energy. By membrane filtration, the glycerol, methanol, and water contents in biodiesel can be decreased to the amounts prescribed by the standards. In the frame of this review article, the short overview of the possibility of using ultra- and/or micro-filtration in the purification process of biodiesel is presented.

Keywords

Biodiesel, purification, membrane filtration, glycerol, methanol

1 Introduction

Internal combustion engines are appropriated to drive on fossil fuel. In particular, diesel engines run on mineral diesel. These engines can, without major modifications, run on biodiesel due to similar properties of diesel and biodiesel. Prior to its use, biodiesel needs to satisfy the prescribed quality standards EN 14214.[1]

Biodiesel is defined as a mixture of fatty acid methyl esters (FAME) of vegetable and/or animal oils and fats. Minimum percentage of FAME in biodiesel needs to be 96.5 % according to EN 14214:2014 standard.[1] The composition and quality of biodiesel depend on several factors, most of all on the quality of feedstock from which it is produced, and the applied technology. The most commonly used technology is based on transesterification reactions[2–4] with different catalysts, chemical (acid or base) and/or biocatalyst (enzymes lipase and other esterases). For biodiesel production, feedstock such as edible vegetable oils,[5] animal fats,[6] non-edible/waste oils and fats[4,5] or microalgae oils[3] can be used. The selection of catalysts depends on the feedstock used. The crude biodiesel needs to be purified after its production in order to conform quality standards. The most used methods for biodiesel purification are wet and dry washing. Due to their great shortcomings in terms

of industrial ecology and environmental protection, membrane purification technology has emerged as an alternative method.

The aim of this work was to conduct a literature survey related to the purification of crude biodiesel with an emphasis on membrane filtration. Presented is a short overview of the possibility of using ultra- and/or micro-filtration in the purification process of biodiesel.

2 Biodiesel production

Nowadays, transesterification reaction of triacylglycerols from oils and fats in presence of methanol to produce fatty acid methyl esters (FAME) and glycerol as a by-product is the most commonly used method for biodiesel production. Stoichiometrically, in transesterification three moles of methanol and one mole of triacylglycerols yield three moles of FAME and one mole of glycerol. This reaction consists of three successive reversible reactions with formation of di- and mono-glycerides as intermediate products.

Considering the catalyst, as already mentioned, biodiesel production can be chemically or enzymatically catalysed. On the industrial level, potassium hydroxide is the most often used catalyst, and although it gives high biodiesel yields in a short reaction time, there are also shortcomings such as high energy demand, and formation of soaps as by-prod-

* Corresponding author: Assoc. Prof. Sandra Budžaki
e-mail: sandra.budzaki@ptfos.hr

ucts along with glycerol.[7] It is known that cca 0.2 tons of wastewater are generated *per* 1 ton of biodiesel produced. When using lipases as biocatalysts in biodiesel production, those problems can be minimized or even eliminated.[8] Lipase can be used as immobilized[9,10] or free[11,12] originating from different organisms such as filamentous fungi,[13] bacteria and yeasts,[14] marine organisms,[15] plants and animals.[16] It should be noted here that, during the biocatalytic production of biodiesel, there are no other by-products except glycerol, and thus the purification of such biodiesel is easier to perform compared to the biodiesel produced by chemically catalysed transesterification.

3 Biodiesel purification

Biodiesel purification is one of the steps in downstream processing of biodiesel along with 1) Biodiesel-glycerol separation (decantation); 2) Glycerol purification; 3) Biodiesel wash water treatment; 4) Alcohol recovery; and 5) Biodiesel additives.[17] Initially, after transesterification reaction, products are allowed to settle to give the phase separation: crude biodiesel as upper layer and crude glycerol as lower layer. After that, each phase separately passes purification processes.

Crude biodiesel contains impurities like methanol, free glycerol, soap, FFA, water, residual catalyst, and glycerides.[18] The type and amount of impurities depend largely on used feedstock, catalyst, and process conditions. However, all mentioned impurities could greatly reduce the thermal and oxidative stability of biodiesel, as well as adversely affect the engines and their shelf life. According to the standards mentioned previously, the limit values for some of the impurities are listed in Table 1.

Table 1 – Maximal values for impurities in biodiesel according to EN 14214 standard

Tablica 1 – Maksimalne vrijednosti onečišćenja u biodizelu sukladno normi EN 14214

Impurities	EN 14214
Water, max [mg/kg]	500
Methanol, max [% wt]	0.20
Total glycerol, max [% wt]	0.25
Free glycerol, max [% wt]	0.02
Monoglycerides, max [% wt]	0.70
Diglycerides, max [% wt]	0.20
Triglycerides, max [% wt]	0.20

To meet the limits (Table 1), the purification of crude biodiesel is necessary regardless which feedstock, catalysts, and process conditions were applied for production. It is preferred for the alcohol to be removed before crude biodiesel purification, like wet washing, to minimize methanol content in wastewater. When recovered, methanol can be reused if the water content is less than 0.1 %.[19]

4 Conventional purification technologies

4.1 Wet washing

Conventional methods for crude biodiesel purification are wet and dry washing. Because methanol and glycerol are highly soluble in water, wet washing is very effective in removing these impurities and is the most frequently used. Generally, for the removal of water-soluble impurities in biodiesel, like soaps, catalyst, glycerol, and alcohol,[18] water is the mostly used washing agent.[20] Usually, this method includes two steps, washing with acidified and pure water. For soap removal, it is recommended to apply neutral water in the first washing step to avoid the soap hydrolysis and acidification of the product. Mechanical mixer, mist washing or bubble washing can be used in the process of wet washing.[21] Mixing is a very simple method, but due to high intensity and emulsion formation, it is not recommended.[22] In mist washing, the nozzles make and spray a fine, gentle mist,[21] which floats over the surface of biodiesel[23] and reduces separation time of biodiesel from water[22] that is used for purification. Because of the significant amounts of water required, this method is not cost-effective nor environmentally friendly. On the other hand, bubble-washing is highly recommended and can be easily implemented to the existing technology by aeration from the bottom of washing vessel.[22]

Abbaszadeh et al.[21] investigated the influence of water type (tapped, distilled, and water with 3 % phosphoric acid), water to biodiesel ratio (0.5, 1, 1.5 *v/v*), and temperatures (30, 45, and 60 °C) on biodiesel purification. They applied bubble-washing technique. The results showed that, for catalyst and soap removal, the best process conditions were as follows: acidified wash water, $T = 60\,°C$, and water to biodiesel ratio = 1.5 *v/v*. For the water residue removal, the best process conditions were application of tap wash water at 60 °C and water to biodiesel ratio 0.5 *v/v*. On the other hand, *Predojević*[24] reported that there was no significant change in biodiesel properties between the types of water, distilled or acidified, applied in the washing process. Regardless of the good purification results achieved by this method, it has great drawbacks. The method is timely and energy intensive, and generates large amounts of wastewater. Purification of 1 l of biodiesel yields 10 l of wastewater[18] as highly organic effluent mostly consisting of the impurities withdrawn from crude biodiesel, including water, residual biodiesel, residual catalyst, methanol, glycerol, soaps, and unreacted oil. According to *Bashir et al.*[25] less contaminated wastewater can be produced when 5 % water pre-wash of crude biodiesel is implemented before the usual wet washing. This way, the amount of fresh water used for purification was reduced by 60 %. In addition, drying of the product after purification required additional amounts of energy and time.

4.2 Dry washing

To overcome the drawbacks of wet washing, the dry washing method is usually used. The main reason why the dry washing method is used is to replace the water washing purification process with an environmentally-friendly water-free method. In dry washing, for the removal of im-
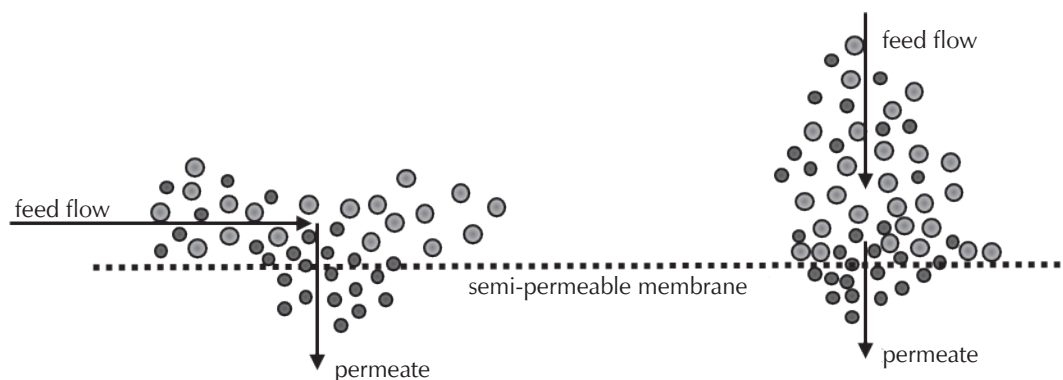
Fig. 1 – Configuration of membrane flow filtration: a) cross flow, and b) dead-end flow filtration
Slika 1 – Konfiguracija protoka membranske filtracije: a) poprečni protok i b) filtracija u mrtvom prolazu

purities from biodiesel, waterless washing agents, such as adsorbents and acid resins, are used. These agents can be used either as a fixed layer in a column or as suspended in biodiesel. After purification, they are removed by filtration. The filtration, adsorption, ion exchange, and glycerol/soap interaction, are the main mechanisms for crude biodiesel purification process by dry washing.[20] Methanol and glycerol cannot be completely removed by waterless washing agents. Therefore, it is necessary to remove them during the previous separation and evaporation stages as much as possible. *Faccini et al.*[26] compared dry washing method using commercial adsorbents, such as Magnesol, silica, Amberlite and Purolite, with wet washing using acidified water. Their results showed that most of the impurities were effectively removed by dry washing, and the inorganic matrices, Magnesol and silica, were successfully applied as adsorbents for removal of both inorganic and organic components. In addition, inorganic matrices gave better results in comparison with organic resins. In order to reduce the costs, as well as to be more environmentally friendly, natural adsorbents, like agro-industrial waste and/or waste/by-products from food industry, can be used.[27–31]

Despite all the good results, the main disadvantages of dry washing processes for crude biodiesel purification are related to the commercial adsorbents price and their reuse and disposal.[29] On the other hand, the great advantage is the use of natural adsorbents (waste/by-products from food industry and/or agro-industrial waste), while good results have already been achieved as reported previously.

5 Membrane technology for biodiesel purification

Nowadays, researchers are more and more focused on membrane purification processes in order to overcome all the deficiencies of the aforementioned conventional purification methods. Along with extraction by ionic liquids or deep eutectic solvents, membrane separation technology (MST)[32] is one of the novel biodiesel purification methods. Membrane technology is based on the application of semi-permeable membranes, certain phys-

ical and chemical structures for the selective transport of matter through the membrane by the action of a driving force (usually pressure). Depending on the pore size of the membrane, membrane processes can be divided as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) whereby the membrane pore size ranges from 0.1–10 μm, 0.01–0.1 μm, 0.001 – 0.01 μm, and 0.0001–0.001 μm, respectively. There are two different flow filtration configurations: cross flow and dead-end filtrations (Fig. 1). Each has its advantages and disadvantages. Dead-end filtration configuration (Fig. 1a) is easy to set up and is most commonly used on a laboratory scale. Longitudinal flow (Fig. 1b) of the feed flow flushes (cleanses) the membrane surface, thus reducing polarization of concentration and preventing particle deposition on the membrane as opposed to dead-end flow filtration configuration. The membrane technology in cross-flow is more costly and labour intensive than dead-end membrane technology.

It can be applied to economize biodiesel production and purification. Biodiesel can be produced in a membrane reactor[33] where FAME, glycerol, and methanol can be selectively permeated during transesterification reaction or where the unreacted oil can be separated from FAME.[34] With this type of reactor, in biodiesel production, the number of purification steps as well as energy and time can be reduced. When biodiesel is produced by conventional methods, purification can be carried out by membrane separation technology. Membrane properties are a) selectivity – function of material properties from which the membrane is made; b) bandwidth – the amount of permeate at working pressure, and c) productivity – function of material properties and the thickness of the film ("cake") on the membrane. Membranes are selective either by their pore size or because of their chemical affinity for permeating components. Membrane separation is a promising technology because of its stable effluent quality, zero chemical needs,[35] low energy consumption, greater separation efficiency, reduced number of processing steps, ecological acceptability, and the high quality of the final product[36]. Micro- (0.2 μm) and ultrafiltration (0.05 μm) processes are the most often used for biodiesel refining. The pore size of the membrane plays the most significant role. It is im-

Table 2 – Selected studies for glycerol removal by membrane separation technology
Tablica 2 – Odabrane studije uklanjanja glicerola membranskom tehnologijom

Type of membrane (*i.d.* = inner diameter, [mm]; *o.d.* = outer diameter, [mm]; *l* = length, [mm])	Filtration area/m²	Pore size	*T*/°C	*p*/bar	Flux	Glycerol content after purification/wt.% (optimal conditions)	Refs
Ceramic (*o.d.* = 26 mm, *l* = 250 mm)	0.04500	0.1 μm 0.2 μm 0.6 μm	60	1.5	300 l m⁻² h⁻¹	0.0108 (0.1 μm; 300 l m⁻² h⁻¹)	*Wang et al.*, 2009[39]
α-Al₂O₃/TiO₂ (*i.d.* = 7 mm, *l* = 250 mm)	0.00500	0.2 μm 0.4 μm 0.8 μm	60	1–3	12.2–83.6 kg m⁻² h⁻¹	0.0400 (2 bar)	*Gomes et al.*, 2010[40]
Polyacrylonitrile	0.02760	100 kDa	25	5.52	10 l m⁻² h⁻¹	0.0130	*Saleh et al.*, 2010a[41]
Ceramic (*i.d.* = 5 mm, *l* = 590 mm)	0.00927	0.2 μm 0.05 μm	0 5 25	5.52 2.07	–	0.0180 (0.05 μm; 25 °C; 3 h)	*Saleh et al.*, 2011[48]
α-Al₂O₃/TiO₂ (*i.d.* = 7 mm, *l* = 250 mm)	0.00500	0.2 μm 0.1 μm 0.05 μm 20 kDa	50	1–3	–	0.0200 (0.05 μm and 20 kDa; 1 bar, 60 kg m⁻² h⁻¹; addition of 10 % acidified water)	*Gomes et al.*, 2013[50]

portant to estimate the size of the molecule and droplets of impurities in crude biodiesel in order to choose appropriate membrane.[37] For biodiesel purification, ceramic or polymeric membranes can be used with different configurations, such as hollow fibre, spiral or tubular. According to *Atadashi et al.*,[18] membrane processes have shown potential for the removal of unreacted triacylglycerols, catalyst, glycerol, soap, and methanol. Ceramic membranes are more suitable for purification due to their well-defined pores that do not tend to change shape and size. On the other hand, polysulfonic membranes will change the shape and size of their pores during continuous use, which will affect their lifetime. One of the major drawbacks of ceramic membranes is their relatively high price.

In membrane separation technology, the separation unit usually consists of feed and permeate reservoirs, heating equipment, pump, and valves for monitoring pressure along with an adequate membrane. An example of an experimental set up is given by *Atadashi et al.*[38] Process parameters that can be regulated are temperature, transmembrane pressure, and flow rate. The temperature can vary in the range from 30 to 70 °C,[38–40] pressure from 1 to 5.52 bar, and flow rate from 60 to 150 l min⁻¹.[38] Selected studies for glycerol removal by membrane separation technology are given in Table 2. Presented is a review on optimal temperature, pressure, and flow rate for biodiesel purification, depending on the type of membrane used and the size of the pores. For glycerol removal, *Saleh et al.*[41] proposed the use of polymeric membranes. They published that the concentrations of water, methanol, and soap in the crude biodiesel are crucial for the efficiency of glycerol removal. Unlike conventional separation processes, small amounts of water are needed (2.0 g of water *per* 1 l of treated biodiesel *vs.* the current 10 l of water in conventional processes).[42] The presence of methanol, unlike the addition of water,[42,43] reduces the efficiency of glycerol

separation by the membrane. The best results for glycerol retention and stabilized permeate flux were achieved with the addition of 10 % acidified water,[40] where water also reduced membrane fouling. There are many papers dealing with the application of ceramic membranes in their studies of biodiesel purification.[18–20,38,40,43–45,46,47] *Saleh et al.*[48] pointed out the advantages of ceramic membranes, such as improved mechanical strength and rigidity, resistance to corrosion, bacterial attack and temperature differences, stability of operating characteristics, and the possibility of multiple regenerations. The aforementioned advantages are the reason why ceramic membranes can be used over a wide pH range and at high temperatures and pressures. In a few experiments of the same authors,[48] with ceramic membranes, using ultrafiltration and microfiltration at different temperatures, the values of glycerol content compliant to international standards for glycerol content in biodiesel were reached after 3 h using ultrafiltration membranes at 25 °C. *Gomes et al.*,[40] in their research, reached 99.6 % retention of glycerol using tubular Al₂O₃/TiO₂ ceramic membranes with pore size of 0.2 μm at 2.0 bar. They emphasised that, when applying pressures higher than 2 bar, reduced retention of glycerol occurred. The same observation was given by *Alves et al.*[47] They compared application of ceramic membrane and wet washing for glycerol removal.

Better results regarding glycerol removal were gained with wet washing in comparison with the application of ceramic membrane of 30 kDa at higher pressures (3–4 bar). The transmembrane pressure is the most significant factor for membrane separation technology where the optimal purification can be achieved by applying moderate pressures (2.0 bar). *Atadashi et al.*[46] used ceramic multi-channel tubular ultrafiltration membrane and recorded retention coefficients of 97.5 % for free glycerol and 96.6 % for soaps. *Torres et al.*[49] tested poly(vinylidene fluoride) and poly(sul-

fone) membranes. Under the same operating conditions (30 °C and 5 bar), with the addition of 0.5 wt% water, the poly(vinylidene fluoride) membrane showed a higher separation performance, with glycerol rejection higher by 19 % in comparison with poly(sulfone) membrane. Moreover, poly(vinylidene fluoride) membranes also showed better stability and resistance to solvents, alkalines, and temperature.

Generally, both types of membranes, polymer and ceramic, can be successfully used for the removal of soaps to reach the levels regulated by biodiesel standard specification. In reference to glycerol, only ultrafiltration membranes of 10 kDa are appropriate for the removal of glycerol so that the final concentration in the product is less than 0.02 wt%.[43]

After each purification process, it is necessary to clean the membrane to remove residual components in order to extend the self-life, efficiency, and repeatability of the membrane. The cleaning process is usually conducted in three steps. Firstly, the membrane is washed with water and detergent, then with 1 % NaOH circulating for cca 45 min, and finally with hot distilled water.[38,40]

Like any other method, MST also has some drawbacks. One of the major drawbacks for biodiesel purification at industrial level is undeveloped scale-up strategy, aside from the problems with maintenance due clogging and fouling, and resistance of membrane materials to the chemicals. The mentioned drawbacks are involve a temperature limitation, whereby the membranes made of polymers do not maintain their physical integrity at temperatures above 100 °C. However, despite all said, overall evaluation showed that membrane technology has the potential to replace both processes, wet and dry washing.[51]

6 Conclusion

Regardless of the disadvantages of membrane separation technology (temperature limitation, difficult scale-up, membrane fouling, clogging tendency, *etc.*), the purification process by MST is simpler and, most importantly, environmentally friendly in comparison with the conventional purification methods, wet and dry washing. The process still needs to be optimized to ensure that the final product meets biodiesel standard specifications, whereby membrane fouling and clogging tendency can be minimized by the proper selection of membrane materials. The good results obtained up to date in biodiesel purification process by applying MST in laboratory, continue to inspire many researchers to further improve this technology and develop an efficient strategy of scale-up technology. Biodiesel purified by membrane filtration technology is a high quality product that is produced in an energy efficient process, in which negligibly small quantities of wastewater are generated. Therefore, membrane separation technology can be labelled as eco-friendly technology representing a novel process window for both the academic and the industrial community.

References
Literatura

1. CEN, European Committee for Standardization: Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods. EN 14214:2008.

2. *D. Y. C. Leung, X. Wu, M. K. H. Leung*, A review on biodiesel production using catalyzed transesterification, Appl. Energy **87** (2010) 1083–1095, doi: https://doi.org/10.1016/j.apenergy.2009.10.006.

3. *M. D. Macías-Sánchez, A. Robles-Medina, E. Hita-Peña, M. J. Jiménez-Callejón, L. Estéban-Cerdán, P. A. González-Moreno, E. Molina-Grima*, Biodiesel production from wet microalgal biomass by direct transesterification, Fuel **150** (2015) 14–20, doi: https://doi.org/10.1016/j.fuel.2015.01.106.

4. *T. Maneerung, S. Kawi, Y. Dai, C. H. Wang*, Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure, Energy Convers. Manage **123** (2016) 487–497, doi: https://doi.org/10.1016/j.enconman.2016.06.071.

5. *S. Budžaki, A. Šalić, B. Zelić, M. Tišma*, Enzyme-catalysed biodiesel production from edible and waste cooking oils, Chem. Biochem. Eng. Q. **29** (3) (2015) 329–333, doi: https://doi.org/10.15255/CABEQ.2015.2177.

6. *I. B. Banković-Ilić, I. J. Stojković, O. S. Stamenković, V. B. Veljković, Y. T. Hung*, Waste animal fats as feedstock for biodiesel production, Renew. Sust. Energ. Rev. **32** (2014) 238–254, doi: https://doi.org/10.1016/j.rser.2014.01.038.

7. *H. H. Mardhiah, H. C. Ong, H. H Masjuki, S. Lim, H. V. Lee*, A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils, Renew. Sust. Energ. Rev. **67** (2017) 1225–1236, doi: https://doi.org/10.1016/j.rser.2016.09.036.

8. *M. Babaki, M. Yousefi, Z. Habibi, M. Mohammadi, P. Yousefi, J. Mohammadi, J. Brask*, Enzymatic production of biodiesel using lipases immobilized on silica nanoparticles as highly reusable biocatalysts: effect of water, t-butanol and blue silica gel contents, Renewable Energy **91** (2016) 196–206, doi: https://doi.org/10.1016/j.renene.2016.01.053.

9. *X. Zhao, F. Qi, C. Yuan, W. Du, D. Liu*, Lipase-catalyzed process for biodiesel production: Enzyme immobilization, process stimulation and optimization. Renew. Sust. Energ. Rev. **44** (2015) 182–197, doi: https://doi.org/10.1016/j.rser.2014.12.021.

10. *X. Wang, X. Qin, D. Li, B. Yang, Y. Wang*, One-step synthesis of high-yield biodiesel from waste cooking oils by a novel and highly methanol-tolerant immobilized lipase, Bioresour. Technol. **235** (2017) 18–24, doi: https://doi.org/10.1016/j.biortech.2017.03.086.

11. *Y. Li, W. Du, D. Liu*, Exploration on the effect of phospholipids on free lipase-mediated biodiesel production, J. Mol. Catal. B-Enzym **102** (2014a) 88–93, doi: https://doi.org/10.1016/j.molcatb.2014.01.018.

12. *Y. Li, W. Du, D. Liu*, Free lipase-catalyzed biodiesel production from phospholipids containing oils, Biomass Bioenergy **71** (2014b) 162–169, doi: https://doi.org/10.1016/j.molcatb.2014.01.018.

13. *E. C. G Aguieiras, E. D. Cavalcanti-Oliveira, D. M. G. Freire*, Current status and new developments of biodiesel production using fungal lipases, Fuel **159** (2015) 52–67, doi: https://doi.org/10.1016/ j.fuel.2015.06.064.

14. *M. Aarthy, P. Saravanan, M. K Gowthaman, C. Rose, N. R. Kamini*, Enzymatic transesterification for production of biodiesel using yeast lipases: An overview, Chem. Eng. Res. Des. **92** (2014) 1591–1601, doi: https://doi.org/10.1016/j.cherd.2014.04.008.

15. *A. Navvabi, M. Razzaghi, P. Fernandes, L. Karami, A. Homaei*, Novel lipases discovery specifically from marine organisms for industrial production and practical applications, Process Biochem. **70** (2018) 61–70, doi: https://doi.org/10.1016/j.procbio.2018.04.018.

16. *J. Sebastian, C. Muraleedharan, A. Santhiagu*, Enzymatic catalyzed biodiesel production from rubber seed oil containing high free fatty acid, Int. J. Green Energy **14** (2017) 687–693, doi: https://doi.org/10.1080/15435075.2017.1318754.

17. *M. Tabatabaei, K. Karimi, I. S. Horváth, R. Kumar*, Recent trends in biodiesel production, Biofuel Res. J. **7** (2015) 258–267, doi: https://doi.org/10.18331/BRJ2015.2.3.4.

18. *I. M. Atadashi, M. K. Aroua, A. R. A. Aziz, M. N. M. Sulaiman*, Refining technologies for the purification of crude biodiesel, Appl. Energy **88** (2011a) 4239–4251, doi: https://doi.org/10.1016/j.apenergy.2011.05.029.

19. *I. J Stojković, O. S. Stamenković, D. S. Povrenović, V. B. Veljković*, Purification technologies for crude biodiesel obtained by alkali-catalyzed transesterification. Renew. Sust. Energ. Rev. **32** (2014) 1–15, doi: https://doi.org/10.1016/j.rser.2014.01.005.

20. *V. B. Veljković, I. B. Banković-Ilić, O. S. Stamenković*, Purification of crude biodiesel obtained by heterogeneously-catalyzed transesterification, Renew. Sust. Energ. Rev. **49** (2015) 500–516, doi: https://doi.org/10.1016/j.rser.2015.04.097.

21. *A. Abbaszadeh, B. Ghobadian, G. Najafi, T. Yusaf*, An experimental investigation of the effective parameters on wet washing of biodiesel purification, Int. J. Automot. Mech. Eng. **9** (2014) 1525–1537, doi: https://doi.org/10.15282/ijame.9.2013.4.0126.

22. *M. Feizollahnejad, B. Ghobadian, A. Zenouzi, A. Motevali*, Comparison of mist circulation biodiesel water washing with traditional methods, Int. J. Renew. Energy Technol. Res. **2** (2013) 249–257.

23. *X. Fan, X. Wang, F. Chen*, Biodiesel production from crude cottonseed oil: An optimization process using response surface methodology, Open Fuels Energy Sci. **4** (2011) 1–8, doi: https://doi.org/10.2174/1876973X01104010001.

24. *Z. J. Predojević*, The production of biodiesel from waste frying oils: A comparison of different purification steps, Fuel **87** (2008) 3522–3528, doi: https://doi.org/10.1016/j.fuel.2008.07.003.

25. *M. A. Bashir, M. Thiri, X. Yang, Y. Yang, A. M. Safdar*, Purification of biodiesel via pre-washing of transesterified waste oil to produce less contaminated wastewater, J. Cleaner Prod. **180** (2018) 466–471, doi: https://doi.org/10.1016/j.jclepro.2018.01.126.

26. *C. S. Faccini, M. E. da Cunha, M. S. A. Moraes, L. C. Krause, M. C. Manique, M. R. A. Rodrigues, E. V. Benvenutti, E. B. Caramão*, Dry washing in Biodiesel Purification: a Comparative Study of Adsorbents, J. Braz. Chem. Soc. **22** (2011) 558–563, doi: https://doi.org/10.1590/S0103-50532011000300021.

27. *M. C. Manique, C. S. Faccini, B. Onorevoli, E. V. Benvenutti, E. B. Caramao*, Rice husk ash as an adsorbent for purifying biodiesel from waste frying oil, Fuel **92** (2012) 56–61, doi: https://doi.org/10.1016/j.fuel.2011.07.024.

28. *M. G. Gomes, D. Q. Santos, L. C. de Morais, D. Pasquini*, Purification of biodiesel by dry washing employing starch and cellulose as natural adsorbents, Fuel **155** (2015a) 1–6, doi: https://doi.org/10.1016/j.fuel.2015.04.012.

29. *M. J. Alves, Í. V. Cavalcanti, M. M. de Resende, V. L. Cardoso, M. H. Reis*, Biodiesel dry purification with sugarcane bagasse, Ind. Crops Prod. **89** (2016) 119–127, doi: https://doi.org/10.1016/ j.indcrop.2016.05.005.

30. *M. A. A. Farid, M. A. Hassan, Y. H. Taufiq-Yap, Y. Shirai, M. Y. Hasan, M. R. Zakaria*, Waterless purification using oil palm biomass-derived bioadsorbent improved the of biodiesel from waste cooking oil, J. Cleaner Prod. **165** (2017) 262–272, doi: https://doi.org/10.1016/j.jclepro.2017.07.136.

31. *L. S. Ott, M. M. Riddell, E. L. O'Neill, G. S. Carini*, From orchids to biodiesel: Coco coir as an effective drywash material for biodiesel fuel, Fuel Process. Technol. **176** (2018) 1–6, doi: https://doi.org/10.1016/j.fuproc.2018.02.023.

32. *M. Hasheminejad, M. Tabatabaei, Y. Mansourpanah, M Khatami Far, A. Javani*, Upstream and downstream strategies to economize biodiesel production, Bioresour. Technol. **102** (2011) 461–468, doi: https://doi.org/10.1016/j.biortech.2010.09.094.

33. *M. A. Dubé, A. Y. Tremblay, J. Liu*, Biodiesel production using a membrane reactor, Bioresour. Technol. **93** (2007) 639–647, doi: https://doi.org/10.1016/j.biortech.2006.02.019.

34. *P. Cao, A. Y. Tremblay, M. A. Dubé, K. Morse*, Effect of membrane pore size on the performance of a membrane reactor for biodiesel production, Ind. Eng. Chem. Res. **46** (2007) 52–58, doi: https://doi.org/10.1021/ie060555o.

35. *I. M. Atadashi, M. K. Aroua, A. R. A. Aziz, M. N. M. Sulaiman*, Membrane biodiesel production and refining technology: A critical review, Renew. Sust. Energ. Rev. **15** (2011b) 5051–5062, doi: https://doi.org/10.1016/j.rser.2011.07.051.

36. *C. de Morais Coutinho, M. C. Chiu, R. C. Basso, A. P. B. Ribeiro, L. A. G. Gonçalves, L. A. Viotto*, State of art of the application of membrane technology to vegetable oils: a review, Food Res. Int. **42** (2009) 536–550, doi: https://doi.org/10.1016/j.foodres.2009.02.010.

37. *M. L. Savaliya, B. D. Dhorajiya, B. Z. Dholakiya*, Current trends in separation and purification of fatty acid methyl ester, Sep. Purif. Rev. **44** (2015) 28–40, doi: https://doi.org/10.1080/15422119.2013.872126.

38. *I. M. Atadashi, M. K. Aroua, A. R. A. Aziz, M. N. M. Sulaiman*, High quality biodiesel obtained through membrane technology, J. Membr. Sci. **421-422** (2012) 154–164, doi: https://doi.org/10.1016/j.memsci.2012.07.006.

39. *Y. Wang, X. Wang, Y. Liu, S. Ou, Y. Tan, S. Tang*, Refining of biodiesel by ceramic membrane separation, Fuel Process. Technol. **90** (2009) 422–427, doi: https://doi.org/10.1016/j.fuproc.2008.11.004

40. *M. C. S. Gomes, N. C. Pereira, S. T. D. de Barros*, Separation of biodiesel and glycerol using ceramic membranes, J. Membr. Sci. **352** (2010) 271–276, doi: https://doi.org/10.1016/j.memsci.2010.02.030.

41. *J. Saleh, A. Y. Tremblay, M. A. Dubé*, Glycerol removal from biodiesel using membrane separation technology, Fuel, **89** (2010a) 2260–2266, doi: https://doi.org/10.1016/j.fuel.2010.04.025.

42. *J. Saleh, M. A. Dubé, A. Y. Tremblay*, Effect of soap, methanol, and water on glycerol particle size in biodiesel purification, Energy Fuels **24** (2010b) 6179–6186, doi: https://doi.org/10.1021/ef1011353.

43. *M. J. Alves, S. M. Nascimento, I. G. Pereira, M. I. Martins, V. L. Cardoso, M. Reis*, Biodiesel purification using micro and ultrafiltration membranes, Renewable Energy **58** (2013)

15–20, doi: https://doi.org/10.1016/j.renene.2013.02.035.

44. *M. Berrios, M. A. Martín, A. F. Chica, A. Martín*, Purification of biodiesel from used cooking oils, Appl. Energy **88** (2011) 3625–3631, doi: https://doi.org/10.1016/j.apenergy.2011.04.060.

45. *M. C. S. Gomes, P. A. Arroyo, N. C. Pereira*, Influence of oil quality on biodiesel purification by ultrafiltration, J. Membr. Sci. **496** (2015b) 242–249, doi: https://doi.org/10.1016/j.memsci.2015.09.004.

46. *I. M. Atadashi*, Purification of crude biodiesel using dry washing and membrane technologies, Alexandria Eng. J. **54** (2015) 1265–1272, doi: https://doi.org/10.1016/j.aej.2015.08.005.

47. *M. J. Alves, I. G. Pereira, V. L. Cardoso, M. H. M. Reis*, Biodiesel purification using ultrafiltration ceramic membranes, Procedia Eng. **44** (2012) 2045–2047, doi: https://doi.org/10.1016/j.proeng.2012.09.039.

48. *J. Saleh, M. A. Dubé, A. Y. Tremblay*, Separation of glycerol from FAME using ceramic membranes, Fuel Process. Technol. **92** (2011) 1305–1310, doi: https://doi.org/10.1016/j.fuproc.2011.02.005.

49. *J. J. Torres, N. E. Rodriguez, J. T. Arana, N. A. Ochoa, J. Marchese, C. Pagliero*, Ultrafiltration polymeric membranes for the purification of biodiesel from ethanol. J. Cleaner Prod. **141** (2017) 641–647, doi: https://doi.org/10.1016/j.jclepro.2016.09.130.

50. *M. C. S Gomes, P. A. Arroyo, N. C. Pereira*, Influence of acidified water addition on the biodiesel and glycerol separation through membrane technology, J. Membr. Sci. **431** (2013) 28–36, doi: https://doi.org/10.1016/j.memsci.2012.12.036.

51. *I. M. Atadashi, M. K Aroua, A. R. A. Aziz, N. M. N Sulaiman*, Crude biodiesel refining using membrane ultra-filtration process: An environmentally benign process, Egypt. J. Petrol. **24** (2015) 383–369, doi: https://doi.org/10.1016/j.ejpe.2015.10.001.

SAŽETAK

Membranska filtracija kao ekološki prihvatljiva metoda pročišćavanja sirovog biodizela

Marta Ostojčić,[a] *Sanja Brkić,*[a] *Marina Tišma,*[a] *Bruno Zelić*[b] *i Sandra Budžaki*[a*]

Biodizel je prvo alternativno gorivo čija su fizikalno-kemijska svojstva regulirana odgovarajućim standardima: američkim ASTM D 6751 i europskim standardom EN 14214. Proces proizvodnje biodizela sastoji se od tri glavne faze: 1) pripreme sirovine, 2) transesterifikacije i 3) obrade produkta reakcije – pročišćavanje sirovog biodizela kako bi se zadovoljile specifikacije koje su navedene u prethodno spomenutim standardima. Proces pročišćavanja sirovog biodizela obično se provodi dvjema tehnikama: vlažnim i suhim pranjem. Najčešće primjenjivani postupak je mokro pranje. Glavni nedostatak u upotrebi vode u procesu pročišćavanja je stvaranje velike količine otpadne vode koja uvelike povećava troškove proizvodnje biodizela nakon čega slijedi sušenje proizvoda, što zahtijeva dodatni utrošak energije i vremena. Najveći nedostatak suhog pranja s različitim ionsko-izmjenjivačkim smolama je nemogućnost uklanjanja glicerola i metanola iz sirovog biodizela do onih granica koje su propisane EN 14214 te problem odlaganja iskorištenih ionsko-izmjenjivačkih smola. Zbog toga se kao alternativa postojećim tehnikama pročišćavanja pojavila primjena membranske tehnologije u procesu pročišćavanja biodizela. Membranska filtracija je ekološki prihvatljiva i zahtijeva manje energije. Membranskom filtracijom može se smanjiti udio glicerola, metanola i vode u biodizelu do količina propisanih standardima. U okviru ovog rada prikazan je kratki pregled mogućnosti primjene ultra i/ili mikrofiltracije u procesu pročišćavanja biodizela.

Ključne riječi
Biodizel, pročišćavanje, membranska filtracija, glicerol, metanol

[a] *Sveučilište Josipa Juraja Strossmayera u Osijeku, Prehrambeno-tehnološki fakultet, Franje Kuhača 20, 31 000 Osijek*

[b] *Sveučilište u Zagrebu, Fakultet kemijskog inženjerstva i tehnologije, Marulićev trg 19, 10 000 Zagreb*