Ultrafiltration for Sustainable Biodiesel Purification. Part 1 – Overview of Production Methods, Principles, and Operating Modes

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Review
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Abstract

The increasing depletion of fossil fuel reserves, rising energy costs, and growing environmental concerns have intensified interest in sustainable biofuels, with biodiesel emerging as one of the most important alternatives to petroleum diesel. However, crude biodiesel produced by transesterification contains residual glycerol, methanol, soaps, catalysts, water, and glycerides that must be removed to meet international fuel standards such as EN 14214 and ASTM D6751. Conventional purification methods, including wet washing, dry washing, distillation, and liquid-liquid extraction, are often associated with high water and energy consumption, wastewater generation, and operational complexity. The aim of this work was to provide an integrated overview of biodiesel purification technologies, with particular emphasis on ultrafiltration (UF) as a sustainable membrane-based alternative for downstream biodiesel processing. The manuscript discusses UF principles, membrane materials, membrane configurations, filtration modes, operating parameters, and challenges related to membrane fouling, and process limitations relevant to industrial implementation. Analysis of the available literature indicates that UF offers significant environmental advantages over conventional purification methods, primarily through reduced water consumption, elimination of wastewater generation, and compatibility with continuous processing. Membrane material is crucial for successful UF in biodiesel processing. Ceramic membranes generally exhibit superior thermal and chemical stability, while polymeric membranes are more economical but more susceptible to swelling and fouling. Based on these considerations, UF is regarded as one of the most promising environmentally friendly technologies for sustainable biodiesel purification. However, further development of membrane materials and process optimisation are required for broader industrial application.

Keywords

Biodiesel purification, ultrafiltration membranes, transesterification, glycerol removal, renewable fuels

1 Introduction

In 2024, 86 % of the world's energy was derived from fossil fuels (oil, coal, and gas) (Fig. 1). However, the depletion of fossil fuel reserves, rising prices, and growing environmental concerns have increased demand for alternative energy sources, with biofuels emerging as a leading candidate.[1] Biofuels (biogas, biodiesel, bioethanol, and biohydrogen) are renewable solid, liquid or gaseous fuels derived from biological feedstock.[3,4] Among these, biodiesel is notable because it can be used in existing diesel engines and its physicochemical properties closely match those of petroleum diesel, enabling seamless transport, storage, and blending. These compatibility advantages reduce infrastructure and transition costs and can result in strong economic performance.[5] Reflecting these strengths, global biodiesel capacity has expanded rapidly in regions such as the United States, Brazil, and Europe, and it is widely used in blends like B5 (5 % biodiesel / 95 % diesel) and B20 (20 % biodiesel / 80 % diesel).[1] In addition, over the past decade, reported production growth of 4–14 % has been observed.[6] Despite the increasing number of reports on biodiesel production and purification[7–11], most published studies focus either on general purification technologies or on membrane applications without systematically integrating UF operating principles, membrane material selection, module configurations, and process limitations relevant to sustainable biodiesel purification. In addition, a previously published study[12] by our research group primarily addressed experimental investigations of membrane-assisted biodiesel purification and membrane selection.

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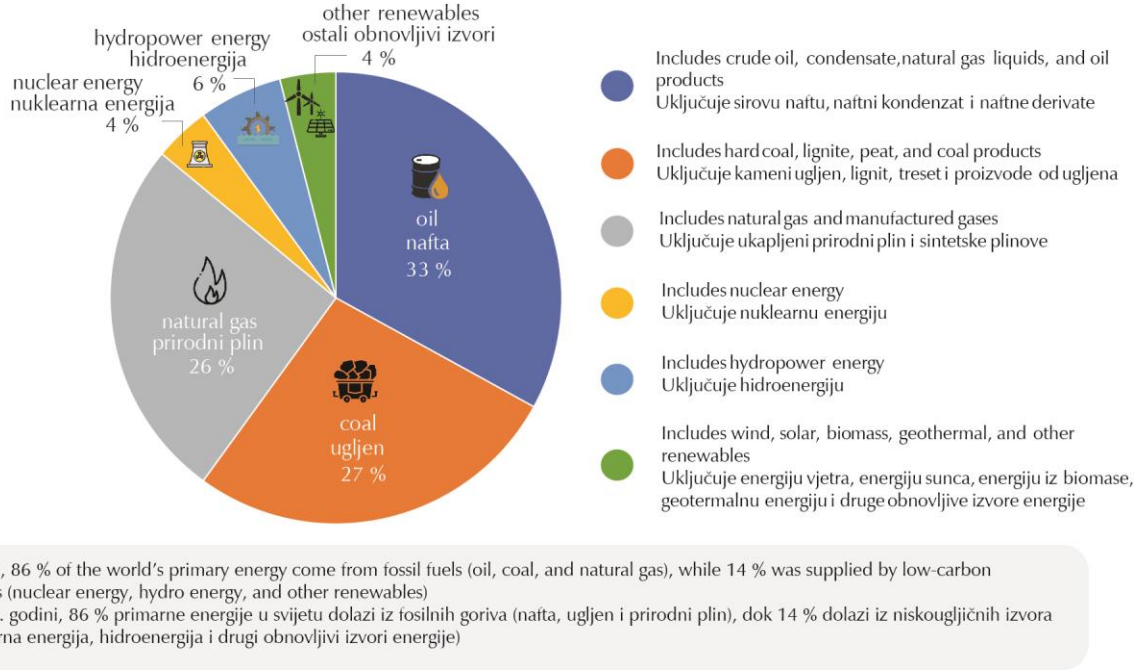


Fig. 1 – Global primary energy consumption by source[2]

Slika 1 – Globalna potrošnja primarnih izvora energije[2]

Therefore, the objective of this manuscript was not to provide a comprehensive review of all published studies, but rather to present an integrated overview of biodiesel purification technologies with particular emphasis on UF as a sustainable downstream processing approach. The manuscript summarises current knowledge regarding purification principles, membrane materials, filtration configurations, operational parameters, and process limitations relevant to future industrial implementation. Particular attention is given to the comparative analysis of UF and conventional purification technologies regarding sustainability, operational complexity, water consumption, and industrial applicability. The manuscript also highlights the major technical challenges associated with membrane fouling, process stability, and membrane durability, as well as the key research gaps limiting broader industrial application.

This paper is the first of two thematically connected segments related to UF as a sustainable biodiesel purification process. While Part 2 focuses on the experimental and mechanistic aspects of UF performance and membrane fouling behaviour, Part 1 provides an independent state-of-the-art overview of biodiesel purification technologies and the applicability of UF from technological and sustainability perspectives.

2 Biodiesel production and purification

2.1 Methods of biodiesel production

Various methods have been developed to address the challenges of biodiesel production, including direct blending, microemulsification, pyrolysis, and transesterification.[1] In direct blending, two viscous liquids, typically a renewable oil and fossil diesel, are mixed in specific ratios to form a homogeneous mixture without altering the chemical structure.[1] Fuel blends produced by this simple and inexpensive method are susceptible to microbial contamination, often causes engine corrosion, and issues related to its high viscosity. Microemulsification[13] combines renewable feedstocks with organic solvents such as methanol or ethanol in the presence of emulsifiers, resulting in a stable colloidal emulsion with reduced viscosity and droplet sizes between 1 and 150 nm. However, incomplete combustion and coke formation are common drawbacks. Pyrolysis, a thermal cracking process conducted in the absence of oxygen, converts organic materials into lower-viscosity products similar to those from petroleum refining. Despite its potential to produce liquid fuels, pyrolysis is costly and can yield numerous unwanted by-products depending on process conditions and feedstock composition.[14,15]

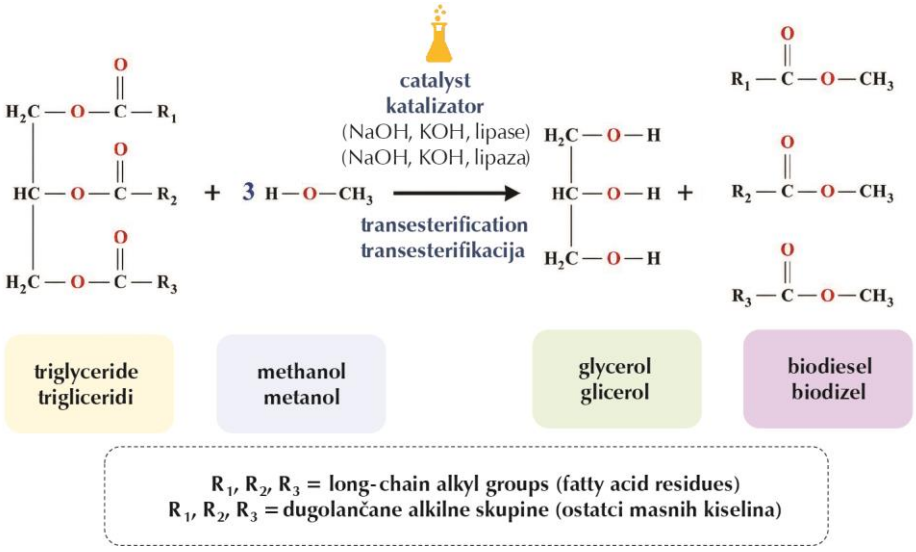


Fig. 2 – Transesterification of triglycerides with methanol
Slika 2 – Transesterifikacija triglicerida s metanolom

Among all available methods, transesterification is the most widely applied and efficient route for biodiesel production. It is a chemical reaction involving the exchange of alkyl groups between triglycerides and alcohols, with or without a catalyst, producing biodiesel and glycerol as the main products.[16]

Several transesterification routes have been developed to improve biodiesel production efficiency, each characterised by specific operating conditions, advantages, and limitations. Supercritical transesterification[17–19] is carried out at elevated temperatures and pressures, using a large excess of alcohol. This method enables rapid reaction rates and high process efficiency but requires significant energy input and may cause thermal degradation of methyl esters. Acid-catalysed transesterification[20] operates at lower temperatures and atmospheric pressure and is suitable for feedstocks with high free fatty acid content, which require pretreatment. However, it requires a high methanol-to-oil ratio, is inhibited by water, and involves difficult product separation and catalyst neutralisation. In contrast, base-catalysed transesterification[21,22] also occurs under mild conditions and requires a lower methanol-to-oil ratio but is limited to purified feedstocks with low free fatty acid content. Product separation and catalyst removal remain challenging in this method as well. Enzymatic transesterification[23,24], which uses lipases as biocatalysts, offers several advantages, including mild operating conditions, easy product separation, and the potential reuse of glycerol, a valuable by-product. Despite these benefits, the process is hindered by long reaction times, enzyme deactivation, and high enzyme costs.[6] Additionally, feedstock selection dominates process economics, as the cost of oils and fats can account for approximately 75 % of total production costs, making feedstock availability and price pivotal to competitiveness.[3] Biodiesel feedstocks are commonly grouped by generation: first-generation from edible vegetable oils, second-generation from lignocellulosic residues and waste oils or greases, and third-generation from microalgae and other advanced biomass sources.[4] Because biodiesel is produced from biodegradable resources, it is itself readily biodegradable and tends to break down naturally, offering an environmental advantage over fossil diesel, which can persist and cause long-term pollution after spills.[1]

Chemically, biodiesel is a mixture of fatty acid alkyl esters (FAME if methanol is used) produced by transesterification of triglycerides (vegetable oils or animal fats) (Fig. 2) with short-chain alcohols, most commonly methanol, in the presence of a catalyst, typically alkaline KOH/NaOH or lipase.[25] As shown in Fig. 2, glycerol is formed as the main by-product of the reaction along with biodiesel, and must be removed from the biodiesel mixture.[26] In addition to glycerol, other contaminants that can affect biodiesel performance include residual alcohol, soap, water, catalyst, glycerides, and free fatty acids.[26,27]

2.2 Methods of biodiesel purification

Glycerol is the main by-product of transesterification, and crude biodiesel contains it as free glycerol (water-soluble glycerol dispersed or dissolved in the ester phase) and as bound glycerol within residual mono-, di-, and triacylglycerides. Complete conversion of triglycerides and alcohol produces free glycerol, which largely separates from the ester phase, while incomplete conversion leaves glyceride intermediates that increase the total glycerol content. Both free

and bound glycerol must be minimised to meet fuel specifications, as residuals can increase viscosity, foul injectors, form deposits and plug filters.[28]

Methanol is the most commonly used alcohol for transesterification because it is inexpensive, has high reactivity, and is easier to recover than other alcohols. However, residual methanol in biodiesel can cause various environmental and safety problems, as it is toxic and corrosive. Excess methanol can also make biodiesel more flammable and more dangerous to transport and storage.[29] In addition, the water content in biodiesel fuel must meet standards, as it can cause engine corrosion,[30] and promote the growth of various organisms, leading to sludge formation and blockage of engine lines.[31] The presence of water can also induce hydrolysis reactions, converting FAME to free fatty acids, and cause phase separation when blended with fossil fuels.[32] Oils and fats used as biodiesel feedstocks may contain free fatty acids (FFAs), which react with alkaline catalysts to form soaps. This reaction consumes the catalyst, lowers effective conversion and ester yield, and promotes stable emulsions that hinder clean phase separation of glycerol from biodiesel, complicating purification.[29]

For all the aforementioned reasons, biodiesel must comply with quality standards EN 14214 (Europe) and ASTM D6751 (USA), which, among other parameters (such as density at 15 °C, viscosity, and oxidation stability), limit free glycerol to 0.02 % (m/m), methanol to 0.2 % (m/m), sodium and potassium to $\leq$ 5.0 mg kg^{-1} (EN 14214) or water and sediment to $\leq$ 5.0 ppm (ASTM D6751). EN 14214 limits water content to 500 mg kg^{-1}, whereas (ASTM D6751). ASTM D6751 limits the combined water and sediment content to 0.050 % (v/v). These limits are critical, as exceeding them can damage engines. Therefore, downstream purification and quality control are required to deliver biodiesel that protects engines and can be legally and safely sold as a transportation fuel.[33] To remove these contaminants and produce fuel that meets EN/ASTM standards, several purification methods are used. The first step is typically the use of a decanter. However, a certain amount of free glycerol and other impurities often remains in the biodiesel after this step, making further downstream purification processes necessary to achieve the required fuel quality. The most common techniques include wet washing, dry washing, membrane separation, and distillation.[27] Wet washing is the most widely used method for removing polar contaminants, especially glycerol and methanol, which are highly water-soluble, from crude biodiesel. In this process, water is added and gently mixed with the ester phase to minimise emulsion formation. The phases are allowed to separate, and the wash is repeated until clear wash water is obtained. The biodiesel is then dried. However, this approach has notable drawbacks as it consumes large volumes of water (up to 10 l of water *per* 1 l of biodiesel),[34] generates wastewater that requires treatment, lengthens cycle time, and demands significant energy for post-wash drying. In the presence of soaps, washing can also promote stable emulsions, reducing yield and complicating phase separation.[34] Another widely used biodiesel purification method is dry washing, which replaces water with solid adsorbents, typically magnesium silicate (Magnesol), ion-exchange resins (*e.g.*, Amberlite, Purolite), silica, activated alumina, or activated carbon, to remove polar impurities directly from crude biodiesel.[9] Compared with wet washing, dry washing is faster as it does not require multi-stage water washes or lengthy settling and drying, and it reduces operating costs by eliminating water purchase and wastewater treatment. Because no water is introduced, meeting water-content specifications is simpler, and disposal and compliance costs decrease accordingly.[34] The main limitation is the finite capacity of the adsorbent; once saturated, the medium loses removal efficiency and contaminants break through into the product.[17] In addition, dry washing cannot effectively remove residual methanol or water, so separate alcohol recovery and drying steps are still required to meet fuel specifications.[35] Other purification methods used include distillation and liquid-liquid extraction (ionic liquids, deep eutectic solvents (DES)) (Table 1).

Comparative analysis of biodiesel purification technologies indicates that UF provides the most favourable balance between environmental sustainability and purification efficiency, particularly due to its negligible water consumption and minimal waste generation. However, its industrial competitiveness still depends on improvements in membrane lifetime, fouling resistance, and process economics.

3 Principles of UF in the biodiesel processing

Over the past decade, membrane technology has attracted increasing attention as an effective alternative for biodiesel purification. Studies have shown that membrane-based separation can significantly reduce water consumption during the purification stage, thereby lowering overall process costs.[12,38,39] In addition to producing high-quality fuel, membrane systems offer several operational advantages, including mild temperature and pressure conditions, enhanced safety, low energy requirements, elimination of

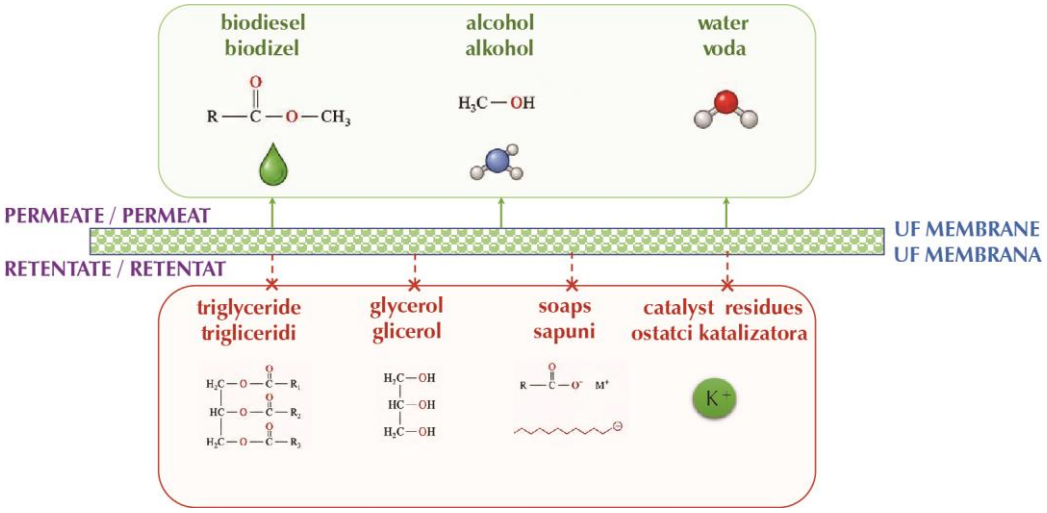


Fig. 3 – Biodiesel purification using UF

Slika 3 – Pročišćavanje biodizela primjenom ultrafiltracije (UF)

wastewater treatment, excellent mechanical, thermal, and chemical stability, and a reduction in the number of processing steps.[40] These factors have contributed to their growing adoption in biodiesel production. In principle, membranes act as semi-permeable barriers that selectively allow certain components of a mixture to pass through while retaining others. The most commonly used membrane processes are microfiltration (MF, 0.1–10 μm nominal pore size), UF (0.01–0.1 μm nominal pore size), nanofiltration (NF, 0.001–0.01 μm nominal pore size), and reverse osmosis (RO, 0.0001–0.001 μm nominal pore size). UF is a widely used membrane filtration method that enables the selective retention and passage of certain components through a semi-permeable membrane. Biodiesel passes through the membrane as permeate, while dispersed glycerol-rich droplets, aggregates, and other retained impurities are concentrated in the retentate (Fig. 3).[41]

The choice of membrane material is crucial for successful UF in biodiesel processing, with membrane materials generally classified as polymeric (organic) or ceramic (inorganic) membranes.[41] These membranes can be configured as hollow-fibre, spiral or tubular configurations.[42] Ceramic membranes are generally preferred over polymeric membranes due to their stability in organic solvents,[1,43] well-defined pore structures, high chemical and thermal resistance (up to 500 °C), strong mechanical strength, and excellent hydrophilic properties, which together enhance durability, fouling resistance, and ease of cleaning.[1,41] They are most commonly used on an alpha-alumina support structure coated with titanium oxide or zirconium oxide.[43] However, their high capital cost limits widespread adoption.[1] To address this cost barrier, various polymeric membranes have been investigated for biodiesel purification.[1] Polymeric UF membranes used in biodiesel purification are often made from materials such as polyethersulfone (PES), polysulfone (PS), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), cellulose acetate or other regenerated celluloses, and polyamide, among others,[43] while ceramic membranes can be made of Al_2O_3, TiO_2, ZrO_2 or SiC. These polymers exhibit enhanced resistance to microbial and chemical degradation.[41] Organic membranes are also categorised according to their hydrophobic or hydrophilic nature. Hydrophilic membranes are more sensitive to changes in pH and temperature but are less prone to fouling because of their water affinity. In contrast, hydrophobic membranes are generally preferred for oil separation processes.[43] The main disadvantage of using polymeric membranes is swelling, which can cause pore-size changes, compromise separation performance, and ultimately reduce membrane lifetime.[41]

Among organic membranes, PVDF membranes exhibited higher flux (10.5 l m^{-2} h^{-1}) and better glycerol retention (67 %) than PSF membranes (7.4 l m^{-2} h^{-1}, 48 %), along with good chemical and thermal stability.[39] However, PSF membranes may undergo physical degradation over time. Comparative studies have shown that PSF can outperform PAN membranes (98.5 *vs.* 98.0 % glycerol retention), although other research has reported that PAN membranes achieved even higher retention (99.99 %) under specific conditions.[40,44,45] All these studies used dead-end filtration configurations.[1] The variability in reported glycerol retention among PSF, PVDF, and PAN membranes suggests that membrane material alone is insufficient to predict separation performance. Operating conditions, feed composition, membrane fouling behaviour, and filtration mode strongly influence process efficiency, making direct comparison between studies difficult.

Table 1 – Comparison of conventional and emerging biodiesel purification methods: principles, performance, and sustainability assessment[1,7–12,26,30]

Tablica 1 – Usporedba konvencionalnih i novih metoda pročišćavanja biodizela: principi rada, učinkovitost i procjena održivosti[1,7–12,26,30]

Purification method Metoda pročišćavanja	Principle Princip rada	Advantages Prednosti	Disadvantages Nedostatci	Water consumption Potrošnja vode	Energy demand Energetski zahtjevi	Waste generation Nastanak otpada	Removal efficiency Učinkovitost uklanjanja	Industrial maturity Industrijska razvijenost	Sustainability assessment Procjena održivosti
Wet washing Mokro pranje	Washing crude biodiesel with water to remove soaps, catalysts, methanol, and glycerol Ispiranje sirovog biodizela vodom radi uklanjanja sapuna, katalizatora, metanola i glicerola	Excellent removal of polar impurities Izrazito učinkovito uklanjanje polarnih nečistoća	Large water demand and wastewater treatment required Velika potrošnja vode i potreba za obradom otpadnih voda	Very high Vrlo visoka	Moderate to high Umjereni do visoki	High wastewater production Velika količina otpadnih voda	Excellent Izrazito učinkovito	Industrially established Industrijski dobro uspostavljeno	Moderate Umjerena
Dry washing Suho pranje	Adsorptive removal of impurities using solid materials Uklanjanje nečistoća adsorpcijom na čvrste materijale	Low water use, efficient soap/catalyst removal Niska potrošnja vode, dobra učinkovitost uklanjanja sapuna i katalizatora	Limited adsorbent capacity, adsorbent disposal Ograničen kapacitet adsorbensa i zbrinjavanje otpadnog adsorbensa	Low Niska	Low to moderate Niski do umjereni	Spent adsorbent waste Otpadni zasićeni adsorbens	Good Dobra	Industrially established Industrijski dobro uspostavljeno	Moderate to high Umjerena do visoka
Distillation Destilacija	Removes water, methanol, glycerol, and catalysts based on volatility Uklanjanje vode, metanola, glicerola i katalizatora na temelju različitih temperatura vrelišta	Efficient, high purity Učinkovita, visoka čistoća proizvoda	High operational costs and energy consumption Visoki operativni troškovi i potrošnja energije	Very low Izrazito niska	Very high Izrazito visoki	Low Mala količina otpada	Excellent Izrazito učinkovita	Industrially established Industrijski dobro uspostavljena	Moderate Umjerena

Table 1 – (continued)
Tablica 1 – (nastavak)

Purification method Metoda pročišćavanja	Principle Princip rada	Advantages Prednosti	Disadvantages Nedostatci	Water consumption Potrošnja vode	Energy demand Energetski zahtjevi	Waste generation Nastanak otpada	Removal efficiency Učinkovitost uklanjanja	Industrial maturity Industrijska razvijenost	Sustainability assessment Procjena održivosti
Liquid-liquid extraction (water) Ekstrakcija kapljevina–kapljevina (voda)	Extraction of impurities into water Ekstrakcija nečistoća iz sirovog biodizela u vodu	Robust, broad impurity removal Robusna metoda, uklanja širok raspon nečistoća	High water consumption Visoka potrošnja vode	High Visoka	Moderate Umjereni	Wastewater generation Nastanak otpadnih voda	Good Dobra	Limited industrial application Ograničena industrijska primjena	Moderate Umjerena
Liquid-liquid extraction (ionic liquids) Ekstrakcija kapljevina–kapljevina (ionske kapljevine)	Extraction of impurities into ionic liquids Ekstrakcija nečistoća u ionske kapljevine	Non-flammable, non-volatile ionic liquids Nezapaljive i nehlapljive ionske kapljevine	High cost, solvent recovery required Visoka cijena i potreba za regeneracijom otapala	Low Niska	Moderate Umjereni	Solvent management required Potrebno zbrinjavanje i regeneracija otapala	Good Dobra	Limited industrial application Ograničena industrijska primjena	Moderate Umjerena
Liquid-liquid extraction (DESs) Ekstrakcija kapljevina–kapljevina (DES)	Extraction of impurities into DES Ekstrakcija nečistoća u DES	DES - low cost, biodegradable, non-toxic, non-reactive with water DES – niska cijena, biorazgradivost, netoksičnost, nereaktivnost s vodom	Total glycerol/glycerides may remain above limits Ukupni glicerol i gliceridi mogu ostati iznad granica propisanih standardima	Low Niska	Moderate Umjereni	Solvent regeneration required Potrebna regeneracija otapala	Good Dobra	Emerging technology Tehnologija u razvoju	High Visoka
Ultrafiltration Ultrafiltracija	Separation through semipermeable membranes Separacija pomoću polupropusnih membrana	High glycerol and soap removal, low water demand Visoka učinkovitost uklanjanja glicerola i sapuna, niska potrošnja vode	Membrane fouling and membrane cost Čepljenje i cijena membrana	Very low Vrlo niska	Low to moderate Niski do umjereni	Minimal Minimalan nastanak otpada	High Visoka	Emerging technology Tehnologija u razvoju	High Visoka

UF offers several clear advantages over traditional biodiesel purification methods such as wet or dry washing. Firstly, UF removes glycerol with minimal or no added water, eliminates the settling/decantation step, and avoids solid waste from spent adsorbents.[40,41,46] These benefits allow UF to replace both the decanter and the aqueous wash, purifying crude biodiesel in a single, compact step.[12,41,46] In practice, UF typically requires less energy and time to achieve on-spec fuel, it can reliably reach free-glycerol levels below the standard limit, and is naturally suited to continuous operation.[1,12,40] Environmentally, UF is attractive because it uses negligible water and produces no wastewater, compared with approximately 1–10 l of wastewater *per* l of biodiesel in wet washing.[26] However, trade-offs do exist. Wet washing relies on simple, widely used equipment at industrial scale, whereas UF requires pumps, valves, membrane modules, and mild heating, thus increasing system complexity.[40] Moreover, UF is less effective than wet washing at removing some dissolved, low-molecular-weight species (such as acids, certain divalent ions, small organics, and minerals), so a separate polishing step may still be required.[1] Even so, UF generally provides higher overall efficiency and lower waste burdens than typical wet-washing and dry-washing approaches, which depend on consumable adsorbents and generate solid waste.[40] Although membranes are effective in separating biodiesel from other impurities, membrane fouling remains one of the most significant technical challenges, as it causes flux decline and necessitates membrane cleaning.[12]

Our previous studies[12] in this area have specifically investigated UF as an environmentally friendly purification strategy for biodiesel produced by enzymatic transesterification, including membrane selection, fouling behaviour, and membrane blocking mechanisms. These experimental findings complement the broader literature overview presented here and provide practical insight into the applicability of UF under realistic biodiesel purification conditions.

4 UF process configurations

Two UF modes are central to controlling flux in biodiesel purification: dead-end and cross-flow (Fig. 4). Dead-end operation (Fig. 4a) is a simpler, more common laboratory setup in which flux is driven perpendicularly through the membrane at low pressure, requiring low energy and modest operating costs. Its drawback is rapid fouling, *i.e.*, cake layer formation, which causes flux decline (Fig. 5a) and requires frequent cleaning.[47] In the cross-flow configuration (Fig. 4b), the flow moves tangentially along the membrane, constantly sweeping the membrane surface and limiting cake layer build-up (Fig. 5b). These systems are more complex and energy-intensive, but can reduce fouling and maintain a more stable permeate flux than dead-end filtration.[40,48]

Building on the choice of configuration, operating parameters further determine performance and scale-up potential.[37] Careful control of transmembrane pressure (TMP), temperature, flow rate and feed composition is essential for achieving the target fuel quality and assessing economic feasibility. The UF membrane process offers continuous operation under moderate pressures (1–3 bar), temperatures (30–50 °C), and flows between 60 and 150 l min^{-1}.[41]

TMP is defined as the pressure difference between the retentate and permeate sides of the membrane.[48] Membrane systems are classified into two groups based on their operating TMP: high-pressure membranes (> 200 kPa) and low-pressure membranes (100–200 kPa), with UF in the latter category. As high-pressure systems result in greater energy consumption and higher operating costs, low-pressure systems are generally preferred.[49] An overview of UF studies on biodiesel purification is shown in Table 2. In practical implementation, *Gomes et al.* achieved 99.6 % glycerol retention using tubular ceramic membranes with a 0.2 μm pore size at 2.0 bar, and demonstrated that pressures above 2 bar did not increase glycerol retention.[50] Higher feed temperature lowers the viscosity of crude biodiesel and increases flux. *Rodriguez et al.* reported that permeate flux doubles with a 10 °C increase in temperature,[51] and a similar effect was described by *Tran et al.*[52] Feed composition is another critical determinant of UF performance in biodiesel purification. Crude streams enriched in glycerol and soaps foul rapidly; glycerol promotes rapid cake layer formation on the membrane, reducing flux, while soaps stabilise emulsions that further hinder permeation and cause flux decline.[53]

Although UF shows significant potential for biodiesel purification, the literature reveals[12,39,41,45,46,49–51] considerable variability in reported process performance, indicating that membrane efficiency depends strongly on operating conditions, feed composition, membrane properties, and process configuration. Reported glycerol retention values vary substantially even for similar membrane materials, suggesting that membrane composition alone is insufficient for predicting separation efficiency. Instead, membrane fouling behaviour, transmembrane pressure, filtration mode, and biodiesel composition collectively determine overall process performance.

One of the most significant limitations preventing wider industrial implementation of UF is membrane fouling. The accumulation of glycerol, soaps, catalyst residues, phospholipids, and unreacted glycerides on the membrane surface progressively reduces permeate flux and increases operational instability. Although cross-flow configurations partially mitigate fouling through tangential flow and reduced cake layer formation, they require higher energy input and more complex system design than dead-end systems.

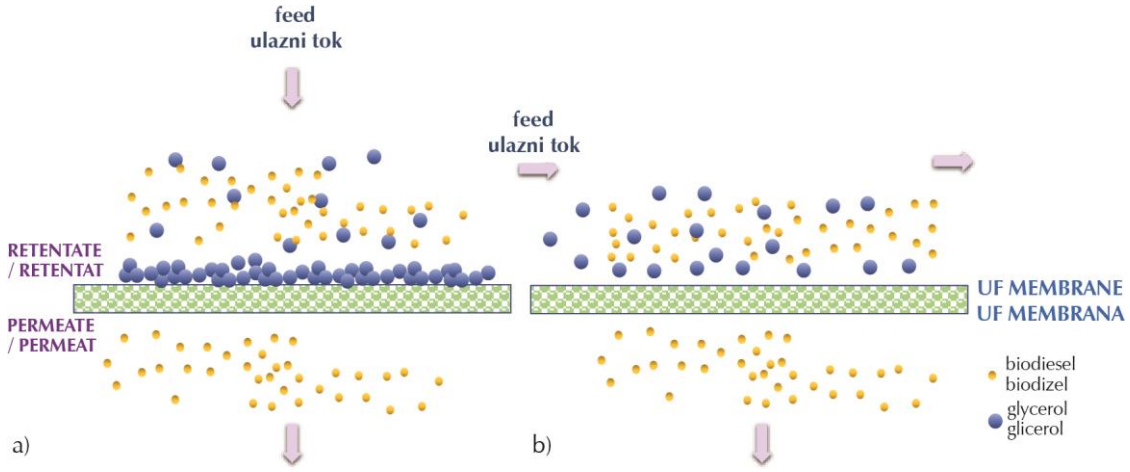


Fig. 4 – Filtration modes: a) dead-end, and b) cross-flow
Slika 4 – Načini provedbe filtracije: a) poprečna i b) uzdužna

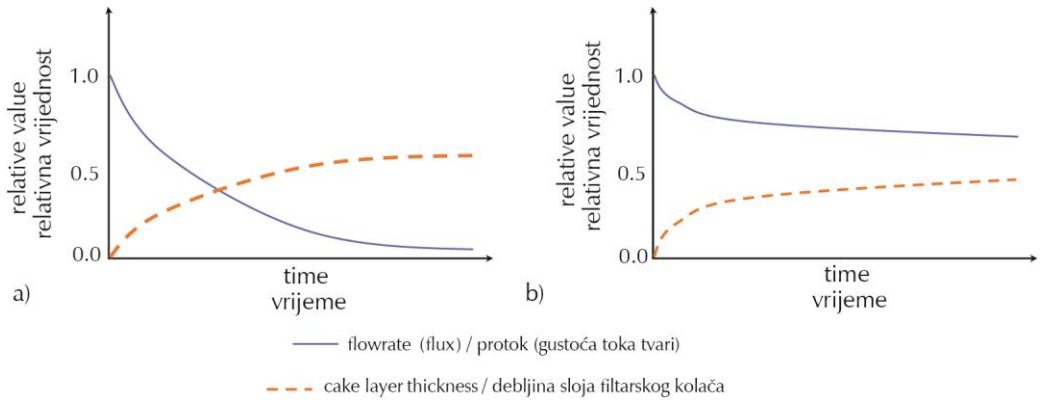


Fig. 5 – Cake layer formation and flux decline in a) dead-end, and b) cross-flow filtration
Slika 5 – Formiranje sloja filtarskog kolača i pad gustoće toka tvari kod a) poprečne i b) uzdužne filtracije

Consequently, there is a trade-off between process simplicity and long-term operational stability. The literature[12,39,41,45,46,49–51] also indicates that direct comparison between published UF studies is difficult due to the lack of standardised operating conditions. Different studies use various feedstocks, catalyst systems, alcohols, membrane materials, pore sizes, operating temperatures, and pressures, often preventing objective comparison of membrane performance. As a result, glycerol retention and flux data should be interpreted with caution. From a sustainability perspective, UF offers clear environmental advantages over conventional wet-washing because it substantially reduces or eliminates water consumption and wastewater generation. This characteristic is particularly important due to the increasing global pressure to reduce industrial water use and wastewater treatment demands. In addition, membrane systems operate under relatively mild temperature and pressure conditions, which can potentially lower energy consumption compared with thermal purification methods such as distillation.

However, despite these advantages, UF cannot yet be considered a universal replacement for conventional biodiesel purification methods. Wet washing remains attractive due to its operational simplicity, established industrial use, and relatively low capital cost. Dry washing is also competitive because of its rapid operation and straightforward integration into existing biodiesel plants. In contrast, UF still faces challenges related to membrane cost and replacement frequency, fouling control, and long-term process stability. Economic factors further complicate industrial implementation. Ceramic membranes offer superior chemical and thermal resistance and generally provide better long-term

durability, but their high capital cost remains a major barrier to widespread industrial adoption. Polymeric membranes are significantly less expensive and easier to manufacture, but are more susceptible to swelling, solvent-induced degradation, and have a shorter operational lifetime. Consequently, the choice between ceramic and polymeric membranes often involves a compromise between process performance and economic feasibility. Another important limitation is scale-up since most published investigations remain confined to laboratory-scale experiments conducted under controlled conditions, whereas industrial biodiesel production involves highly variable feed compositions and continuous operation over extended periods. Therefore, further pilot-scale validation is necessary before UF can be reliably implemented as a primary industrial purification technology.

Overall, the available evidence suggests that UF is currently one of the most promising environmentally friendly purification technologies for biodiesel production. However, its future industrial role will likely depend on continued improvements in membrane durability, fouling resistance, process integration, and economic optimisation. According to current literature, UF appears particularly promising as an integrated polishing or hybrid purification technology rather than as a complete standalone replacement for all conventional purification methods.

5 Future perspective

As global pressure intensifies to decarbonise the transport sector and reduce dependence on fossil fuels, biodiesel is expected to play an increasingly important transitional role, particularly in hard-to-electrify sectors such as heavy-duty transport, agriculture, and maritime applications. However, the long-term competitiveness and sustainability of biodiesel will depend not only on feedstock availability and conversion efficiency, but also on advances in downstream purification technologies that reduce cost, energy consumption, and environmental impact. Among emerging purification strategies, membrane-based UF is set to become a key enabling technology. Future research is likely to focus on improving membrane performance, durability, and affordability to overcome current technical and economic barriers. In particular, the development of next-generation polymeric membranes with enhanced resistance to organic solvents, reduced swelling, and tailored surface properties represents a promising direction. Surface modification techniques, such as grafting hydrophilic or anti-fouling layers, incorporating nanoparticles, or blending polymers, may significantly reduce fouling caused by glycerol, soaps, and residual catalysts, thereby extending membrane lifetime and stabilising flux. Ceramic membranes, despite their high capital cost, may see wider industrial adoption as manufacturing processes become more scalable and cost-effective. Advances in low-cost ceramic supports, alternative oxide materials, and additive manufacturing could reduce initial investment and make ceramic membranes economically viable for medium- and large-scale biodiesel plants. Hybrid membrane systems combining ceramic and polymeric modules may also offer a practical compromise between performance and cost.

Process integration is another important future trend. UF is well suited to continuous operation and could be increasingly integrated with upstream transesterification and downstream polishing steps to create compact, intensified biodiesel production lines. Coupling UF with alcohol recovery units, adsorption polishing, or nanofiltration may enable complete removal of low-molecular-weight contaminants that UF alone cannot fully eliminate, ensuring consistent compliance with EN 14214 and ASTM D6751 standards. Process modelling and techno-economic assessments will be critical for identifying optimal configurations and operating windows for industrial deployment. From a sustainability perspective, membrane-based purification aligns well with circular economy principles. The near-elimination of water use and wastewater generation directly addresses one of the major environmental drawbacks of conventional wet washing. As environmental regulations become more stringent and water scarcity intensifies in many regions, these advantages are likely to drive regulatory and market incentives for membrane adoption. Additionally, improved purification efficiency may facilitate the use of lower-quality, second- and third-generation feedstocks by better handling higher impurity loads, further enhancing the overall sustainability of biodiesel production.

Finally, digitalisation and process control are expected to play an increasing role in future biodiesel purification systems. Real-time monitoring of membrane performance, fouling behaviour, and fuel quality using sensors and data-driven control strategies could enable predictive maintenance and adaptive operation, reducing downtime and operating costs. These technological advances position UF not merely as an alternative purification method, but as a cornerstone of next-generation biodiesel production systems that are cleaner, more efficient, and economically resilient.

5.1 Research gaps and future research needs

A critical analysis of the available literature reveals several significant knowledge gaps that currently limit the wider industrial implementation of UF for biodiesel purification. Firstly, there is a lack of standardised experimental conditions for evaluating membrane performance.

Table 2 – Overview of studies on the application of UF in biodiesel purification
Tablica 2 – Pregled istraživanja primjene UF kod pročišćavanja biodizela

Membrane type / Vrsta membrane	Membrane material / pore size Materijal izrade membrane / veličina pore	Filtration mode Tip filtracije	Feedstock / Biodiesel source Sirovina / porijeklo biodizela	Main result Glavni rezultat	Key limitation Ključno ograničenje	Ref. Ref.
Polymeric membrane Polimerne membrane	PP, PES, PAN, RC 0.2 μm PP, PES, PAN, RC 0,2 μm	Dead-end Poprečna filtracija	Biodiesel from lipase-catalysed transesterification of sunflower oil and methanol Biodizel proizveden enzimski kataliziranom transesterifikacijom suncokretova ulja i metanola	Membrane selection and blocking mechanisms analysed; effective purification demonstrated Analizirani odabir membrana i mehanizmi čepljenja; potvrđeno učinkovito pročišćavanje	Membrane fouling major operational challenge Čepljenje membrane glavni procesni izazov	12
Polymeric membranes Polimerne membrane	PVDF, PSF ~ 4.0–4.4 nm PVDF, PSF ~ 4,0 – 4,4 nm	Dead-end Poprečna filtracija	Biodiesel produced by transesterification of semi-refined soybean oil with ethanol Biodizel proizveden transesterifikacijom polurafiniranog ulja soje uz etanol	PVDF membrane showed higher flux (10.5 $l m^{-2} h^{-1}$) and glycerol retention (67 %) than PSF membrane Primjena PVDF membrana rezultira većom gustoćom toka tvari (10,5 $l m^{-2} h^{-1}$) i zadržavanjem glicerola (67 %) u odnosu na PSF membrane	Membrane fouling and limited long-term stability Čepljenje membrane i ograničena dugotrajna stabilnost	39
Ceramic Keramika	Al_2O_3/TiO_2 0.05–0.20 μm Al_2O_3/TiO_2 0,05 – 0,20 μm	Cross-flow Uzdužna filtracija	Crude biodiesel from alkaline transesterification of palm oil with methanol Sirovi biodizel dobiven alkalnom transesterifikacijom palminog ulja i metanola	Efficient glycerol and soap removal; biodiesel met fuel standards Učinkovito uklanjanje glicerola i sapuna; biodizel zadovoljava standarde kvalitete goriva	Higher capital cost of ceramic membranes Visoki investicijski troškovi keramičkih membrana	41
Polymeric membranes Polimerne membrane	PSF, PAN ~ 10.0–20.0 nm PSF, PAN ~ 10,0 – 20,0 nm	Dead-end Poprečna filtracija	Crude biodiesel produced by transesterification of canola oil with methanol Sirovi biodizel proizveden transesterifikacijom ulja uljane repice s metanolom	High glycerol removal efficiency (up to 99.99 % under optimised conditions) Visoka učinkovitost uklanjanja glicerola (do 99,99 % pri optimalnim procesnim uvjetima)	Flux decline due to fouling Pad gustoće toka tvari uslijed čepljenja membrane	45
Ceramic Keramika	α-Al_2O_3/TiO_2 0.05 μm α-Al_2O_3/TiO_2 0,05 μm	Cross-flow Uzdužna filtracija	Biodiesel produced by transesterification of vegetable oils (degummed soybean oil, crude canola oil, commercial refined soybean and canola oil) with ethanol Biodizel proizveden transesterifikacijom biljnih ulja (degumirano sojino ulje, sirovo ulje uljane repice te komercijalno rafinirano sojino ulje i ulje uljane repice) s etanolom	Achieved 99.6 % glycerol retention at 2 bar Postignuto 99,6 % zadržavanje glicerola pri 2 bara	No major retention improvement above 2 bar Nije uočeno znatno povećanje zadržavanja glicerola pri tlakovima većim od 2 bara	46

Abbreviations: PVDF – polyvinylidene fluoride; PSF – polysulfone; PAN – polyacrylonitrile; PP – polypropylene; PES – polyethersulfone; RC – regenerated cellulose; PTFE – polytetrafluoroethylene; FAME – fatty acid methyl esters.

Kratice: PVDF – poliviniliden fluorid; PSF – polisulfon; PAN – poliakrilonitril; PP – polipropilen; PES – polietersulfon; RC – regenerirana celuloza; PTFE – politetrafluoretilen; FAME – metilni esteri masnih kiselina.

Table 2 – (continued)
Tablica 2 – (nastavak)

Membrane type / Vrsta membrane	Membrane material / pore size Materijal izrade membrane / veličina pore	Filtration mode Tip filtracije	Feedstock / Biodiesel source Sirovina / porijeklo biodizela	Main result Glavni rezultat	Key limitation Ključno ograničenje	Ref. Ref.
Polymeric membrane Polimerne membrane	PES 0.2 µm PTFE 0.05 µm PES 0,2 µm PTFE 0,05 µm	Dead-end Poprečna filtracija	Biodiesel produced by enzymatic hydroesterification of soapstock splitting products from chemical refining of vegetable oils, and olein obtained from glyceride splitting of mixed vegetable oils Biodizel proizveden enzimskom hidroesterifikacijom proizvoda cijepanja sapunastog taloga nastalog tijekom kemijske rafinacije biljnih ulja te oleina dobivenog cijepanjem glicerida iz smjese biljnih ulja	Effective dry polishing of biodiesel with reduced downstream steps Učinkovito suho pranje biodizela uz smanjenje broja koraka pročišćavanja	Sensitivity to operating conditions and membrane fouling Osjetljivost na procesne uvjete i čepljenje membrana	49
Ceramic Keramika	Al_2O_3/TiO_2 0.2, 0.4, 0.8 µm Al_2O_3/TiO_2 0,2, 0,4, 0,8 µm	Cross-flow Uzdužna filtracija	Biodiesel produced by transesterification of soybean oil with ethanol Biodizel proizveden transesterifikacijom ulja soje uz etanol	99.4–99.6 % glycerol retention achieved using 0.2 µm ceramic membrane; membrane microfiltration proved effective for biodiesel purification. 99,4 – 99,6 % zadržavanja glicerola postignuto je keramičkom membranom od 0,2 µm; mikrofiltracija se pokazala učinkovitom za pročišćavanje biodizela	Process performance strongly depended on TMP and ethanol content; higher pressures increased fouling and reduced glycerol retention Uspješnost procesa snažno je ovisila o TMP i udjelu etanola; viši tlakovi povećavali su čepljenje membrane i smanjivali zadržavanje glicerola	50
Polymeric membranes Polimerne membrane	Composite PVDF membrane containing sulfonated carbon 17.8 nm Kompozitna PVDF membrana sa sulfoniranim ugljikom 17,8 nm	Dead-end Poprečna filtracija	Synthetic mixture simulating transesterification products (biodiesel, glycerol, ethanol and catalyst residues) Sintetska smjesa koja simulira produkte transesterifikacije (biodizel, glicerol, etanol i ostaci katalizatora)	Efficient biodiesel purification without decantation; maximum permeate flux of 12.6 $l m^{-2} h^{-1}$ achieved at 60 °C and 8 bar. Učinkovito pročišćavanje biodizela bez dekantacije; maksimalni permeatni tok od 12,6 $l m^{-2} h^{-1}$ postignut pri 60 °C i 8 bar	Process performance strongly depended on temperature and TMP Učinkovitost procesa snažno je ovisila o temperaturi i TMP	51

Abbreviations: PVDF – polyvinylidene fluoride; PSF – polysulfone; PAN – polyacrylonitrile; PP – polypropylene; PES – polyethersulfone; RC – regenerated cellulose; PTFE – polytetrafluoroethylene; FAME – fatty acid methyl esters.

Kratice: PVDF – poliviniliden fluorid; PSF – polisulfon; PAN – poliakrilonitril; PP – polipropilen; PES – polietersulfon; RC – regenerirana celuloza; PTFE – politetrafluoretilen; FAME – metilni esteri masnih kiselina.

Published studies employ different feedstocks, catalyst systems, membrane materials, pore sizes, temperatures, and operating pressures, making direct comparison between studies challenging.[12,39,41,45,46,49–51]

Future research should therefore focus on developing standardised evaluation methodologies to enable more reliable comparison of membrane performance and fouling behaviour. Secondly, although many studies report glycerol retention and permeate flux values, relatively few examine long-term membrane stability and operational durability under realistic industrial conditions. Long-duration experiments and pilot-scale studies remain limited, particularly for continuous biodiesel production systems. Thirdly, membrane fouling mechanisms are still insufficiently understood, especially in complex biodiesel mixtures containing soaps, phospholipids, residual catalysts, free fatty acids, and unreacted glycerides. More detailed mechanistic studies that combine membrane characterisation, fouling analysis, and process modelling are needed to improve membrane design and cleaning strategies.

Another significant research gap concerns techno-economic analysis. Although UF is often described as environmentally friendly and cost-effective, comprehensive economic assessments comparing membrane systems with conventional purification technologies remain relatively scarce. Future studies should include detailed analyses of membrane replacement costs, cleaning requirements, energy consumption, and overall process economics. Furthermore, only a limited number of studies investigate the integration of UF with enzymatic biodiesel production, despite the strong compatibility between enzyme-catalysed processes and membrane-based purification technologies. Integrating reaction and purification steps may represent an important direction for future process intensification. Finally, relatively few studies evaluate UF from a broader sustainability perspective using life-cycle assessment (LCA), carbon footprint analysis, or circular economy criteria. Such analyses will become increasingly important as environmental regulations become more stringent and sustainable fuel production gains strategic importance worldwide.

6 Conclusion

This overview evaluated current biodiesel purification technologies, with particular emphasis on UF as a sustainable alternative to conventional downstream purification methods. Analysis of the available literature confirmed that biodiesel purification remains a crucial step for achieving compliance with international fuel standards such as EN 14214 and ASTM D6751, particularly regarding the removal of glycerol, methanol, water, catalyst residues, and soap. Conventional purification technologies, including wet washing, dry washing, distillation, and extraction methods, remain effective but are associated with significant environmental and operational limitations such as high water consumption, wastewater generation, adsorbent disposal, and elevated energy demand. In comparison, UF offers several significant advantages, including reduced water consumption, elimination of wastewater generation, relatively mild operating conditions, and compatibility with continuous processing. Critical assessment of published studies demonstrated that UF performance strongly depends on membrane material, operating conditions, feed composition, and filtration mode. Ceramic membranes generally provide superior chemical and thermal stability, whereas polymeric membranes offer lower cost and easier processing but are more susceptible to swelling and degradation. Despite numerous successful laboratory-scale studies reporting high glycerol retention and satisfactory biodiesel quality, membrane fouling remains the major technical limitation restricting long-term operational stability and wider industrial implementation. The analysis further indicated that direct comparison between published UF studies is difficult because of non-standardised operating conditions and differences in feedstock composition, membrane characteristics, and process parameters. In addition, the limited number of pilot-scale and long-term industrial investigations highlights the need for further research focused on process scale-up, techno-economic analysis, membrane durability, and process integration. Overall, UF represents one of the most promising environmentally friendly technologies for sustainable biodiesel purification. However, based on currently available evidence, UF is most realistically positioned as an integrated polishing or hybrid purification technology rather than a complete standalone replacement for all conventional purification methods. Continued advances in membrane materials, anti-fouling strategies, process integration, and industrial optimisation will be essential for broader industrial adoption and long-term commercial viability.

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SAŽETAK

Održivo pročišćavanje biodizela ultrafiltracijom. 1. dio – Pregled proizvodnih postupaka, načela i načina rada

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Ubrzano iscrpljivanje zaliha fosilnih goriva, porast troškova energije i rastuća zabrinutost za okoliš intenzivirali su interes za održiva biogoriva, pri čemu se biodizel ističe kao jedna od najvažnijih alternativa dizelskom gorivu nastalom preradom nafte. Sirovi biodizel dobiven transesterifikacijom sadrži zaostali glicerol, metanol, sapune, katalizatore, vodu i gliceride koje je potrebno ukloniti da bi se zadovoljili međunarodni standardi kvalitete goriva EN 14214 i ASTM D6751. Konvencionalne metode pročišćavanja sirovog biodizela, poput mokrog i suhog pranja, destilacije te ekstrakcije kapljevina-kapljevina, često su povezane s velikom potrošnjom vode i energije, nastankom otpadnih tokova, ponajprije otpadnih voda, i procesnom složenošću.

Cilj ovog rada bio je pružiti pregled tehnologija pročišćavanja biodizela s posebnim naglaskom na ultrafiltraciju (UF) kao održivu alternativu za pročišćavanje sirovog biodizela. U radu su prikazana načela UF-e, materijali za izradu membrana, konfiguracije membranskih modula, načini filtracije, procesni parametri te problemi povezani s čepljenjem membrana i procesnim ograničenjima relevantnim za industrijsku primjenu UF-e. Analiza dostupne literature pokazala je da je UF-a, u odnosu na konvencionalne metode pročišćavanja biodizela, okolišno prihvatljiva tehnologija, ponajprije zahvaljujući smanjenoj potrošnji vode, izostanku nastajanja otpadnih voda i mogućnosti kontinuirane provedbe procesa. Uspješnost provođenja procesa UF-e pri pročišćavanju biodizela u najvećoj mjeri ovisi o materijalu od kojeg je membrana napravljena. Tako keramičke membrane općenito pokazuju bolju toplinsku i kemijsku stabilnost, dok je primjena polimernih membrana ekonomičnija, ali su te membrane osjetljivije na bubrenje i čepljenje. Prethodno navedeno upućuje na to da UF-a predstavlja jednu od najperspektivnijih okolišno prihvatljivih tehnologija za održivo pročišćavanje sirovog biodizela, no daljnji razvoj materijala za izradu membrana i optimizacija uvjeta provedbe procesa nužni su za njezinu širu industrijsku primjenu.

Ključne riječi

Pročišćavanje biodizela, ultrafiltracijske membrane, transesterifikacija, uklanjanje glicerola, obnovljiva goriva

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