Fuel 340 (2023) 127485

Contents lists available at ScienceDirect

Fuel

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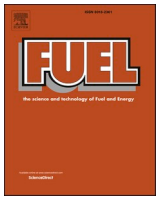

Full Length Article

New trends on crude glycerol purification: A review

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ARTICLE INFO

Keywords:
Crude glycerol
Purification
Glycerol market
Biodiesel
Pre-treatment

ABSTRACT

The increasing effort of the global community to reduce dependency on fossil fuels led to an increase in the production of biodiesel and therefore the oversupply of crude glycerol. Different steps are necessary to ensure this oversupply of highly impure, waste-based crude glycerol (approximately 680,000 tonnes by 2024) can be made suitable for applications. This review paper aims to give an overview of the recent developments of the global glycerol market and discusses advanced crude glycerol purification technologies (as compared to physio-chemical treatments). The market overview involves information on the relevance of the global glycerol market and the different grades of glycerol which are produced. Additionally, different application areas for glycerol are detailed; including current industrial solutions, challenges, and outlooks. The second part reports newly proposed crude glycerol purification technologies from industry and recent research since 2014, their advantages and disadvantages, and feasibility in terms of industrial implementation at scale. The results of this review suggest that pressure-, thermally- and electrochemically-driven membrane-based separation technologies could solve the issue of expensive large scale vacuum distillation columns lowering capital and operating expenditures reaching > 99 % of glycerol purity. However, the increase of lower quality glycerol generated resulting from 2nd generation bio-diesel plants presents challenges due to the increasing ash and matter organic non-glycerol (MONG) impurities (due to the use of waste-based feedstocks in biodiesel production). As result, hybrid solutions may be needed since advanced purification technologies cannot be used as stand-alone solutions but need to be accompanied by a proper pre-treatment.

1. Introduction

As the world population increases, the need for sustainable development in economic, environmental, and social terms is necessary [1]. Biofuels are pillars of a sustainable society and will play a significant role in the coming decades and will ultimately supersede conventional fossil fuels. The EU implemented the Renewable Energy Directive EC/2009/28, which mandates a level of 10 % for renewable energy use in transport for 2020 [2]. This number will increase to 14 % by the year 2030 [3]. Increasing the sustainability of how biofuels are produced will play a critical role as the target increases. Advanced biofuels are considered the same product as first-generation biofuels but utilise waste-based, non-edible feedstocks [4]. In biodiesel production, this has led to a shift of using waste-feedstocks such as tallow or used cooking oil instead of crop-based vegetable oils [5]. Biodiesel production involves a transesterification reaction, which yields crude glycerol as a by-product. In the case of waste-based biodiesel feedstock, glycerol purity drops drastically. This has led to an excess supply of highly impure crude glycerol during the last decade, which is mainly incinerated [6], used for cattle feed [7,8], biogas generation [9,10], or even transferred to landfill [11].

Glycerol ($C_3H_8O_3$), also known as Propane-1,2,3-triol, is a major component in many products used in our daily lives. It is a major component in the personal care and pharmaceutical industry due to its mildly antimicrobial and antiviral properties, used as a sweetener in the food industry. The use of crude glycerol has been considered also for applications such as gasification for the production of hydrogen and other products [12]. Some of the properties of glycerol are listed in Table 1.

Early in the 20th century, glycerol was produced primarily as a by-product of the saponification of fats (Fig. 1) and was used as a raw material to produce nitro-glycerine. During the 1st world war, glycerol became a strategic resource, and therefore the demand exceeded the supply, leading to the first synthetic plants to produce glycerol by microbial sugar fermentation. Furthermore, the replacement of natural soaps with synthetic washing detergents has led to an increase in glycerol demand which accelerated the shift towards competitive

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https://doi.org/10.1016/j.fuel.2023.127485
Received 28 August 2022; Received in revised form 26 November 2022; Accepted 8 January 2023
Available online 31 January 2023

Nomenclature

ABP	Animal by-product
AC	Activated Carbon
AEM	Anion exchange membrane
AGMD	Air gap membrane distillation
BED	Bipolar Electrodialysis
CAT	Category
CAGR	Compound annual growth rate
CEM	Cation exchange membrane
CEMD	Continuous-effect membrane distillation
CG	Crude glycerol
DCMD	Direct contact membrane distillation
ED	Electrodialysis
FCC	Food Chemical Codex
FFA	Free fatty acids
FOGS	Fats, oils and greases (mainly waste-water treatment based)
GMO	Genetically modified organism
GOR	Gain output ratio
HVO	Hydrogenated Vegetable Oils
HZD	Hydrated zirconium dioxide
ICP	Inductively coupled plasma
LCD	Limiting current density
MD	Membrane distillation
MOF	Metal organic frameworks
MONG	Matter organic non-glycerol
MT	Metric ton
MWCO	Molecular weight cut-off
RSM	Response Surface Methodology
PTFE	Polytetrafluirethylene
PVDF	Polyvinylidene fluoride
SGMD	Sweeping gas membrane distillation
TAG	Triacylglyceride
TEOS	Tetraethylorthosilicat
TFC	Thin Film Composite
TMP	Trans-membrane pressure
UCO	Used cooking oil
USP	United States Pharmacopeia
VMD	Vacuum membrane distillation
ZHP	Zirconium hydrophosphate

Greek letters

η_D	Refractive Index

Table 1
Main properties of glycerol at room temperature [13].

Properties	
Chemical formula	$C_3H_8O_3$
Molar mass [g/mol]	92.094
Appearance	Colourless hygroscopic liquid
Odour	Odourless
Density [g/cm^3]	1.261
Melting point [°C]	17.8
Boiling point [°C]	290
Solubility in water	miscible
Lower heating value [MJ/kg]	24
Refractive Index (η_D)	1.4746
Viscosity [Pa•s]	1.412

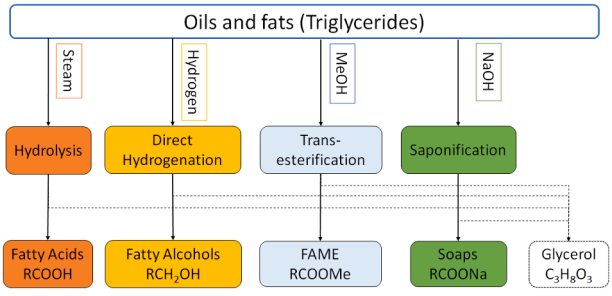


Fig. 1. Conventional reactions of oils and fats in the oleochemical sector yielding glycerol as by-product. The reaction mechanisms are given in Appendix A. Figure adapted from reference [14].

Table 2
Average crude glycerol composition by different production processes [22].

Component	Transesterification [%]	Saponification [%]	Hydrolysis [%]
Glycerol	30–60	83–84	88–90
Ash	10–19	8.5–9.5	0.7–1.0
Water	≤10	6–7	8–9
MONG	≤40	3–4	0.7–1.0

petrochemical (synthetic) production routes. The company I.G. Farben used high-temperature chlorination of propene to allyl chloride process to produce synthetic glycerol [14]. About 25 % of the global glycerol demand was met by petrochemical synthesis from propylene before the acceleration of the biodiesel market in the early 1990s. The other 75 % was obtained by the saponification of fats [15].

With the development of the biodiesel industry, crude glycerol has been produced as a by-product from bio-diesel production using vegetable oils as well as waste animal fats, UCO (used cooking oil) and other waste fat as feedstocks [16]. During the transesterification reaction of triglycerides with methanol, approximately 10 wt% of glycerol is produced as a by-product [17].

Since most of the crude glycerol cannot be utilized due to major impurities [18], this paper seeks to review conventional, recent, and novel purification methods which can improve the quality further to provide the global glycerol market with a feedstock with suitable purity.

Glycerol is produced as a by-product in four main reactions, which are depicted in Fig. 1. All these reactions involve different chemicals and produce different products and by-products, which influence its final composition. This final composition has a significant effect on the purification effort, which must be delivered to valorise the crude glycerol and subsequently convert it into higher-value chemicals. In Table 2, the average glycerol compositions generated by three main reactions are depicted. Typical impurities in crude glycerol are water (also moisture), ashes (i.e., inorganic salts containing potassium, phosphorous, sodium, iron, and others), and MONG (matter organic non-glycerol), which usually consists of FFAs (free fatty acids), FAME (fatty acid methyl esters), glycerides (mono-, di- and triglycerides), alcohols such as methanol or ethanol and soaps (saponified fatty acids, i.e., fatty acid salts) [19] and other organic compounds (e.g. Aldehydes) [20]. In the case of direct hydrogenation, it is not possible to determine the composition of the crude glycerol due to the decomposition of the material. Hence, this process is not commercially implemented [21].

The lowest purity of glycerol is obtained by the transesterification reaction (in biodiesel production), which also yields the highest amounts of ashes due to alkali-based catalysts. This is highly problematic since the inorganic ashes act as major inhibitors in many biotechnological applications [23] and often poison the heterogeneous catalysts of downstream chemical conversion units [24]. Furthermore, high MONG content is being generated due to partially reacted glycerides,

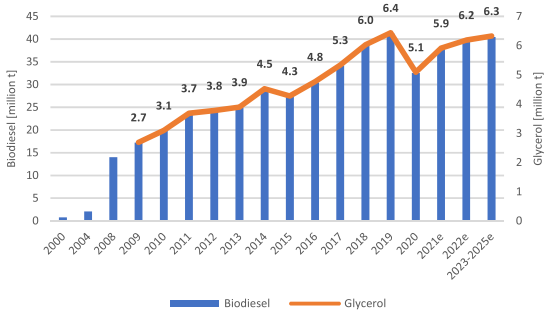


Fig. 2. Global biodiesel and glycerol production Biodiesel values for 2020–2025 are calculated based on a density of 880 kg/m^3 (density at 25 °C). Glycerol values are based on 10 wt% of the production of biodiesel. The total production is deduced from the assumption/simplification that from 2009 to 2025 biodiesel supplies 64 % of the entire glycerol market. Data taken from reference [34,35].

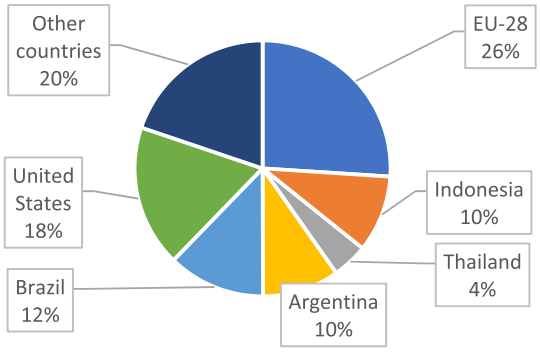


Fig. 3. Major biodiesel-producing countries (2016) in %. Data taken from reference [25] and adapted.

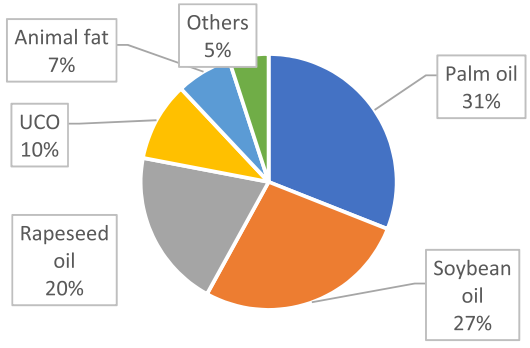


Fig. 4. Feedstocks used in world biodiesel production (2016) in %. Data taken from reference [51] and adapted.

residual FAME, fatty alcohol, or fatty acids which are used in the transesterification reaction reducing the glycerol content even further. The usual pH value of crude glycerol in the transesterification lies above 7 due to the usage of alkali catalysts such as sodium hydroxide, potassium hydroxide, or sodium methoxide [25] but can also be acidic if a neutralisation step of the crude glycerol takes place.

The quality of crude glycerol from biodiesel industry varies considerably (Table 2). Usually, the crude glycerol produced from biodiesel refineries using edible oils or purified used cooking oils yields crude glycerol with acceptable purities (60–80 %) [27]. However, there is a trend among producers to utilize waste-based feedstocks due to their cheapness, availability, abundance and sustainability (as it does not compete with food prices such as edible oils) [26]. Particularly, the use of low-cost, waste-based feedstocks such as sewage sludge, FOGs (fats, oils and greases), animal fats and tallow are interesting due to their high oil content. Their use does not just reduce the cost of feedstock but alters the usually acceptable purity of the by-product of crude glycerol as it decreases its purity down to 30 % wt. as reported by industrial examples.[1] To improve the environmental and economic performance, crude glycerol valorisation through proper purification methods has been proposed and is currently under consideration by research and industry.

This paper reviews the current and recent global glycerol market (section 2) and particularly focuses on novel purification methods (section 3) discussed in the recent scientific literature sources. A special focus is set on new technologies recently proposed in 2014 mostly focused on pressure-, thermal- and electrochemical-driven processes which were not compared comprehensively before. This work provides the foreground and industrial guidance to implement develop and scale up new technologies which could reduce costs and technical challenges for the bio-diesel industry.

2. Market overview

2.1. Global biodiesel and glycerol production

The global glycerol market had a market volume of $2,500 million in 2018 and it is expected to increase to $3,300 million by 2023 [28], having a CAGR of 5.7 %. Due to the versatility of glycerol and its application in the personal hygiene sector, this demand is likely to be maintained. Most of the glycerol that is supplied on the market is derived from the biodiesel industry. As can be seen in Fig. 2, the biodiesel market has grown dramatically in the last 30 years since its market introduction (early 1990s [29]). This is largely influenced by governments wanting to continuously increase the uptake of renewable fuels and fulfil their sustainability goals [30]. In 2009, approximately 64 % of the glycerol was supplied by the biodiesel industry compared to the original 9 % in 1999 [15]. This number did not change significantly and remained high at 63 % in 2018 [28]. The remaining glycerol is supplied mostly by the soap or fatty acid industries, available already at high purity. The major biodiesel producers such as Indonesia [31] planned to increase their biodiesel mandate up to B40 (which is equal to 40 vol-% of biodiesel mixed with conventional diesel). The cost associated with fuel blending has led to a failure or delay in similar plans in Malaysia [32] and Brazil [33]. The biodiesel market experienced a downturn in 2020 due to the COVID-19 pandemic, but it is expected to reach 40 million tonnes per year in the next 3 years (Fig. 2). As a result, about 6.3 million tonnes of crude glycerol will be produced by 2025.

The European Union is the biggest single contributor to the biodiesel market with 26 %, followed by the United States and Brazil (Fig. 3). At the same time, the EU has the highest cost of production with 0.82 USD/litre compared to 0.47 USD/litre in the United States [36]. Generally, biodiesel producers are differentiated based on the feedstocks used for the transesterification process. First-generation biodiesel producers use edible oil feedstocks [37] such as palm oil or rapeseed oil, while second-generation biodiesel producers use waste-based feedstocks [38] such as animal fats, tallow, UCO, or sewage material such as FOGs [39]. Currently, research is being undertaken for algae utilization to become the third generation of biodiesel [40] and GMOs to become the fourth generation feedstocks for biofuels [41].

The high cost of production and feedstock/commodity, as well as environmental pressure to refrain from edible oils such as palm oil as feedstocks, has led to an increase in waste-based feedstocks to produce biodiesel [42] (Fig. 3). Currently, animal fat and UCO account for 17 % of the entire feedstock, Fig. 4, which means that from the 4.04 million tonnes of bio-glycerol which will be produced by the end of 2025 (64 %

[1] Argent Energy glycerol purity available from 30% to 70% depending on the feedstock.

Table 3
Different grades of glycerol, after [52].

Grades of glycerol	Glycerol content [wt.%]
Crude glycerol	30–90
Technical grade	95.5
United States Pharmacopeia (USP)	96 (tallow-based) 96–99 (vegetable-based)
Food Chemical Codex (FCC)	99.5 USP/FCC-Kosher 99.7 USP/FCC-Kosher

Table 4
Animal by-products (ABP) categories [55].

ABP categories	Risk	Content
Cat 1	High risk	• Carcasses of (wild) animals suspected of being infected with TSE or other diseases that humans/animals could contract • Zoo/circus animals • Animals used in experiments
Cat 2	High risk	• Carcasses containing residues from authorised treatments, of animals killed for disease control purposes, of dead livestock • Manure • Digestive tract content
Cat 3	Low risk	• Carcasses passed fit for humans to eat at a slaughterhouse • Products/Foods of animal origin originally meant for human consumption but withdrawn for commercial reasons • Domestic catering waste • Hides/skins from slaughterhouses • Eggs and egg by-products

Table 5
Refined and crude glycerol prices for different relevant global areas (June/December 2020).

Product	USA [€/tonne]	Europe [€/tonne]	China [€/tonne]
Refined glycerol (99.7 %, kosher grade)	705	650	565
Refined glycerol (99.5 %, technical grade)	660	520	505
Crude glycerol (80 %, vegetable-based)	200–280	395	295
Crude glycerol (75 %, non-vegetable-based)	180–240	150–250	145–175

of entire glycerol production), approximately 680,000 tonnes of crude glycerol (17 % of the bio-glycerol production) will be with a maximum purity of 76.6 % [27] and cannot be used for personal care, food or other traditional glycerol application sectors. This amount likely increases further in the future due to legislative issues as well as deforestation concerns [43] and the competition for food [44], which are inherent when using edible oils as feedstocks [45]. On the other hand, crude glycerol consumption from 2010 to 2019 in the North America and EU market combined have been on average 450,000 tonnes annually [46] and global glycerol consumption is expected to reach 4 million tonnes by 2024 [47] outstripping the supply by over 2 million tonnes.

However, the crude glycerol market will change significantly within the next two decades, especially in the regions of Europe, the US, and China as electric cars are replacing internal combustion engines. Additionally, pressure is being created by competing technologies such as renewable diesel, which does not produce glycerol within their supply chain [48]. These factors are pressuring the biodiesel industry, and it remains unclear whether the market will favour HVO (hydrogenated vegetable oil) or biodiesel in the long term. While in general the market is expected to grow during the next decade due to an increasing trend to replace fossil fuels with biofuels [49], renewable diesel could partially slow down the total production. The further shift towards waste-based biodiesel production, especially in Europe and other developed countries, will increase the need for suitable vegetable-based crude glycerol supply which can be used in the refined glycerol market for hygiene applications, and it may even be possible, though unlikely, for chemical companies to re-enter the market again to produce synthetic glycerol to sustain the demand for refined glycerol as DOW chemical did in 2008 [50].

It can be concluded that the excessive development of the biodiesel industry led to an excess supply of mostly impure (bio-)glycerol. This excess supply of crude glycerol consequently led to an imbalance in supply and demand, potentially leaving a much higher supply in 2025 of approximately 6.33 million tonnes, from which 680 kilo-tonnes are highly impure, to a much lower demand of 4 million tonnes in 2025, making supply and demand effectively independent from each other. The consequences are very low prices for impure crude glycerol with the probability of it becoming even a waste stream.

2.2. Glycerol grades

The industry distinguishes between different grades of glycerol, based on its purity (by wt.%). An overview of the different grades is given in Table 3.

Glycerol grades for non-food applications are termed technical grade and the maximum purity reaches 95 %wt. USP grade glycerol has a purity of 96–99 % wt. and is used for food and pharmaceutical applications. The highest purity has the FCC grade with a purity of 99.5–99.7 % wt. The application area for this glycerol is mainly in kosher foods. The high range of crude glycerol is due to the different feedstocks which can be used to produce biodiesel. Biodiesel producers using waste feedstocks such as ABP (Animal by-products) have legal problems to sell their glycerol to the pharmaceutical and hygiene industries [53]. ABP can be considered as parts of the animal which are not meant for human consumption, mainly consisting of abattoir waste. ABP is categorised in three different ways, which are listed in Table 4. The price per ton decreases with lower categories due to the limited applications of by-product glycerol which can only be used to make compost, biogas, or other low-value products. In many cases, the crude glycerol must be disposed, thus resulting in a net cost such as in Brazil where incineration is 15 $/tonne [54]. Nevertheless, there is no regulation on the usage of ABP categories (Table 4) such as Cat 1 and Cat 2 to produce energy or high value intermediate chemicals, making them an interesting alternative (green) feedstock for these applications.

2.3. The US, European, and China glycerol market

The global glycerol market is highly fragmented due to the various grades that exist. As depicted in Fig. 3, the most relevant areas in the biodiesel market and consequently also in the glycerol market are the US, the European Union, and other international countries. In case of glycerol, China is the biggest country to consume glycerol [56]. Generally, different spot prices (intended as market prices) are available for refined, technical, and crude glycerol for different regions in the world. The historical price development of kosher grade glycerol with a purity of 99.7 % for the period of 1995 to 2020 in the US and EU markets show that spikes in both markets are synchronized, and the prices follow the same trend ranging between 400 and 800 €/tonne [57]. The entire market surged during 2020, especially due to the COVID-19 pandemic, where many countries required high-grade glycerol for the pharmaceutical and health industries [58]. Refined and crude glycerol prices for the year 2020 and different areas are listed in Table 5 [59,56]. It also shows why the valorisation of crude glycerol to refined technical glycerol is economically reasonable despite the existing cost of purification and refining. It is important to mention that crude glycerol from processing plants using feedstocks from ABP has a much lower value and reaches a negative value [60].

The glycerol market, in general, is highly volatile and subject to

Table 6
Research on crude glycerol valorisation to valued-added chemicals (2019–2021). The references next to the authors are referring to the academic papers.

Author	Year	Research Focus	Product	Price [US $/kg]
Kumar et al. [70]	2021	Chemical Industry	Polyhydroxybutyrate (PHB)	4.75 [71]
Hassan et al. [72]	2019	Biotechnology	Hydrogen	0.79 [73]
			ButanolPolyhydroxyalkanoate (PHA)	0.89 [74]
				2.40 [75]
Almuharef et al. [76]	2019	Biotechnology	2,3-butanediol	10–50 [77]
			Acetoin	10–30 [77]
Veiga et al. [78]	2020	Energy	Hydrogen	0.79 [79]
Zahid et al. [80]	2021	Chemical Industry	Solketal	3 [81]
Sittijunda et al. [82]	2020	Biotechnology	Hydrogen	0.79 [79]
			1,3-propanediol	1.45 [83]
			Ethanol	1.06 [84]
Genieva et al. [85]	2020	Chemical Industry	Alkyd Paints	–
Yao et al. [86]	2020	Biotechnology	β-farnesene	8.6×10^{6} 1) [87]
Wang et al. [88]	2020	Chemical Industry	Alanine	–
Tian et al. [89]	2020	Biotechnology	Lipase	–
Shahrin et al. [90]	2019	Biotechnology	Monolaurin	1.55×10^{6} 1)
Abd Rahim et al. [91]	2019	Biotechnology	Lovastatin	$6. \times 10^{6}$ 1) [92]
			(+)-geodin	810×10^{6} 1) [93]
			Sulochrin	145×10^{6} 1) [94]
Wu et al. [95]	2019	Biotechnology	Levoglucosan	150×10^{6} 1) [96]
Wang et al. [97]	2019	Biotechnology	Polysaccharide production	–
Rodrigues et al. [98]	2020	Energy	Hydrogen	0.79 [79]

1) Prices are related to small quantities (100 mg), here recalculated to kg.

constant change. For the European market in the second half of 2020, crude glycerol (80 %) for kosher applications experienced a fall from approximately 500 €/tonne$_{Gly}$ to 400 €/tonne$_{Gly}$ while crude glycerol of 80 % purity increased from 160 €/tonne$_{Gly}$ to almost 250 €/tonne$_{Gly}$. The same trend can be observed with refined glycerol. Prices plummeted for kosher grade glycerol from 825 €/tonne$_{Gly}$ to almost 550 €/tonne$_{Gly}$ and recovered by the end of 2020 to a price of slightly below 700 €/tonne$_{Gly}$. A similar course showed the technical grade glycerol, which started at 650 €/tonne$_{Gly}$ in the second half and plummeted to 475 €/tonne$_{Gly}$, reaching a value of 625 €/tonne$_{Gly}$ at the end of 2020 [46].

2.4. Application areas of glycerol

Glycerol can be sold by producers as a refined commodity on the global market as well as be used in various other applications. Current market applications which exist and have large-scale use (pharma and personal care 42%, Alkyd resins 13%, Food and Beverage 14%, Polyether polyols 10%, tobacco 9.5%, others 11.5%) [28]. Pharmaceuticals and personal care are overwhelmingly the largest area for refined high-grade glycerol with a share of over 40 % where glycerol is used due to its antimicrobial and antiviral properties [61], followed by the alkyd resin market, which uses technical grade glycerol [62], the food industry where glycerol is used as a humectant, solvent and even sweetener [63]. In the tobacco industry, glycerol is used to preserve the tobacco and keep it moisturized [64]. Other application areas include cattle feed, incineration for energy generation, or anaerobic digestion [65], especially for waste-based biodiesel feedstocks (ABP feedstocks). Additionally to the above uses, glycerol is already used or subject to research to produce important chemicals such as epichlorohydrin [66], propylene glycol [67], or bio-methanol [68]. New routes for the production of chemicals such as acrylic acid are being investigated as well [69]. Especially, crude glycerol has been the focus of many different research papers during the last years. Due to the excess supply and its low price, researchers all over the world try to develop novel methods to valorise and subsequently convert crude glycerol into very high-value chemicals via (bio-) chemical routes.

Research is mainly taking place in the areas of biotechnology, chemical, and energy industries. While in the chemical and energy industries, the focus is to convert it into bulk chemicals, in the area of biotechnology, the focus lies on speciality chemicals, which are sold in the ranges of milligrams but have a very high price per unit mass as shown in Table 6.

3. Advanced glycerol purification techniques

The problems associated with crude glycerol derived from biodiesel are the significant amounts of impurities it contains, such as methanol, salts, and a high MONG content, namely soaps, FFAs and esters. Since the purification of crude glycerol is costly and often not economical for small and medium-sized biodiesel plants [99], crude glycerol is disposed at cost [100]. Several techniques are available for the purification of crude glycerol. Depending on the scale and composition of the crude glycerol, a combination of different purification routes is applied. A big problem in crude glycerol purification remains the volatility of the crude glycerol composition, making it complicated to find a standardized method of purification. Purification techniques include sequential physio-chemical treatments such as saponification, acidification, phase separation, neutralization and anti-solvent treatment with a solvent [101–103]. Furthermore, advanced refining technologies are applied to purify crude glycerol, such as vacuum distillation [104], ion exchange [105], membrane separation [22], adsorption [106], electrodialysis [107] and membrane distillation [108].

Conventionally, four refining steps are necessary to purify the glycerol [52]:

1. Reduction of MONG and salt content through saponification, acidification, and subsequent neutralization [22,101,102,109]
2. Anti-solvent treatment with a solvent/alcohol [110]
3. Evaporation of solvent/alcohol and water to concentrate the solute [111]
4. Adsorption with activated carbon to remove colour and odour [112,113]

A comprehensive review of physio-chemical treatments up to 2014 has been conducted by Ardi et al. [52] and appendix B presents an overview of purification experiments which have been conducted by various authors after 2014, providing information on the purification

Table 7
Overview of adsorbents used by different authors for the purification of crude glycerol.

Adsorbent/Source	Year	BET surface area [m^2/g]	Pore size [nm]	Micro-pore volume [cm^3/g]	Optimal Ratio/ Dosage	Contact time [h]	Operating Temperature [°C]	Comment	Ref.
Bentonite	2018	n/a	n/a	n/a	12 %	1.25	60	Particle size: 60 mesh (0.2 mm)	[115]
Tea Waste	2018	n/a	n/a	n/a	12 %	1.5	60	Particle size: 180 μm	[116]
Reactivated spent bleaching earth/Solid waste from palm oil refinery	2021	73.1	n/a	0.164	10 wt%	1	50	Removal rate: 93 % (FFA, cartenoid, chlorophyll removed)	[118]
Activated Charcoal/Acrocomia aculeate endocarp	2020	627	2.5	0.09	10 g/L	2	25	Column packed with activated carbon (h = 15 cm, d = 1 cm, mAC = 10 g)	[120]
Activated Carbon/Wastewater treatment sludge	2017	107	n/a	0.09	67 g/L	2	30	AC adsorption followed Langmuir isotherm	[102]
Activated Carbon	2016	n/a	n/a	n/a	0.933 g / 10 mL	2	n/a	Bleaching Earth used as comparison to AC	[122]
Organo-bentonite and activated carbon	2011	n/a	n/a	n/a	1 % + 1 %	1	50	Organoclays have limited efficiencies in the removal of colour, only useable as co-adsorbents	[117]
Dead yeast cells immobilized on chitosan/Saccharomycess cereviceae, chitosan-based biosorbent	2014	n/a	n/a	n/a	10 g/L	0.67	n/a	Use of microwave irradiation using a microwave oven at 2.56 GHz	[119]
Electrospun chitosan/poly (ethylene oxide) nanofibers/ chitosan-based biosorbent	2018	n/a	n/a	n/a	n/a	n/a	n/a	Relative high adsorption capacity compared with chitosan powders/films (120/ g)	[114]
Activated Charcoal	2019	n/a	n/a	n/a	n/a	n/a	60	Equilibrium, thermodynamic and kinetic study on the use of AC	[123]
Activated Carbon/Oil palm empty fruit bunch (OPEFB)	2021	26	80.13	0.17	2.5 wt%	1	n/a	Colour removal: >89 %	[100]

route and the final purities of all relevant components such as glycerol, water, ash, and MONG.

Recently, the focus has shifted to more advanced purification technologies to achieve a more economically feasible purification of industrial waste-based crude glycerol. Advanced glycerol purification techniques are usually applied in combination with a physio-chemical pre-treatment [22,111].

3.1. Adsorption using waste-based biogenic materials

Adsorption is preferably used as a final step after other separation techniques to reduce the colour as well as the odour by removing mainly smaller fatty acids from the glycerol mixture [114]. Usually, a porous material is used, such as commercially activated carbon, but the focus shifted during the last years more towards waste adsorbents such as bentonite [115] or tea waste [116]. An important step for the utilization of waste-based adsorbents is the proper chemical or physical activation. With ultraviolet–visible spectroscopy, the colour reduction and transparency of (crude) glycerol can be measured at a wavelength of 200–800 nm [109]. Pure glycerol has a low absorbance rate compared to crude glycerol, which is one variable to determine the degree of purity in the glycerol mixture. Variables which are investigated in adsorption experiments are the contact time, the temperature, type of adsorbent, (re-)activation as well as activated carbon loading.

Anzar et al. [115] used bentonite, which was activated with 1.5 M sulphuric acid after acidification. Therefore, 100 g of crude glycerol was mixed with 12 g of bentonite. The mixture was investigated at different stirring rates (30–90 min), bentonite concentrations (3–15 % wt. based on crude glycerol weight), and temperatures (30–70 °C). The optimum conditions of adsorption were stirring at 75 min, 12 % wt. bentonite concentration, and a temperature of 60 °C, leading to a glycerol purity of 89.5 % wt. Organo-bentonites were also used by Kocak et al. [117] to replace fresh activated carbon with the result that a mixture of 1 % of activated carbon and 1 % of microwave dried organoclay is as effective as 3 % of fresh activated carbon when conducted at 50 °C and 1 h contact time. Hence, a reduction of 60 % in material usage could be shown with the usage of organo-bentonites as co-adsorbents. Isalmi Aziz et al. [116] used tea waste as an adsorbent which was activated by 0.05 M sodium hydroxide and varied the contact time (30–120 min), the adsorption temperature (30–75 °C), the bio-sorbent concentration (6–18 %), and bio-sorbent particle size (180–630 μm). Before this, the crude glycerol mixture was acidified with phosphoric acid. The highest glycerol purity of 95.95 % wt. was achieved by setting the contact time to 90 min, adsorption temperature to 60 °C, bio-sorbent concentration at 12 %, and particle size at 180 μm. A different bio-sorbent was used by Hunsom et al. [113]. A wastewater treatment sludge-derived KOH-activated carbon was used with various KOH:char ratios (1–6 w/w), KOH soaking times (5–25 h) and activation temperatures (500–900 °C) used to prepare the material. The best material was obtained by using a KOH:char ratio of 5 with a soaking time of 25 h and an activation temperature of 800 °C which was used to upgrade glycerol to a purity of 93 wt% when used at a dose of 67 g/L for a contact time of 2 h and stirred at 250 rpm. Hunsom et al. [112] published earlier similar experiments by investigating the influence of different chemical activating agents such as phosphoric acid, potassium carbonate and potassium hydroxide but came to similar results as in the previous paper that using KOH as reactivating agent yields the best surface properties. Different materials were used by other authors such as spent bleaching earth [113,118] or spent activated carbon [106] after reactivation, bio-sorbent synthesized from dead yeast cells immobilized on chitosan [119], activated carbon from Acrocomia culueata endocarp [120] or from oil palm biomass [121] and synthetically produced electrospun chitosan/poly(ethylene oxide) nanofibers [114]. Table 7 gives a general overview of adsorbents used by different authors as well as the optimal conditions that were used.

The general shift to waste-based adsorbents involves different

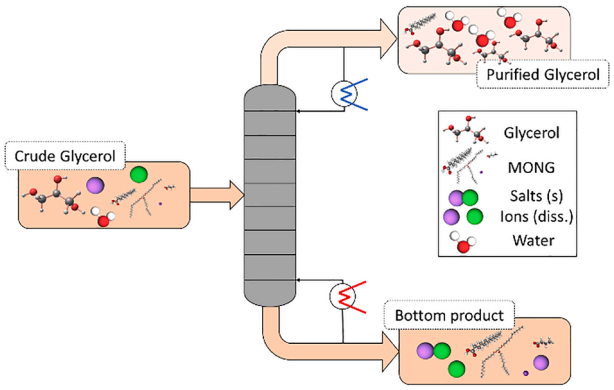


Fig. 5. Working principle of vacuum distillation for crude glycerol purification.

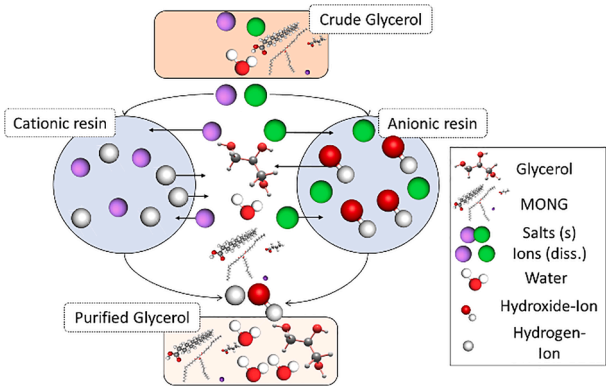


Fig. 6. Working principle of ion-exchange resins for the purification of crude glycerol.

positive and negative aspects which must be considered for the purification process. The material is abundantly available and cheap. Nevertheless, its preparation requires the addition of external chemicals which generate additional wastes, which must be considered during the purification step. Furthermore, their reactivation requires the addition of solvents which must be treated subsequently as well [113].

3.2. Vacuum distillation

Crude glycerol can be purified by vacuum distillation as depicted in Fig. 5 due to its sensitivity and preference for undesirable reactions at high temperature. Three possible unwanted side reactions can take place. At high pH values, polymerization of glycerol to polyglycerol can take place if an excess of sodium hydroxide is used and the temperature is higher than 200 °C [124]. At low pH values, glycerol can dehydrate into acrolein [125].

Furthermore, it can oxidize to glycerose, which is a mixture of glyceraldehyde and dihydroxyacetone [104]. Nevertheless, vacuum distillation is effective at recovering glycerol from crude glycerol in the presence of high salt and MONG content. A big disadvantage is the high energy input for vaporization, maintaining a high vacuum, and high capital expenditure, making the process uneconomical for small and medium-sized plants [52]. Furthermore, the use of vacuum distillation for highly impure crude glycerol is questionable due to the low yield and the possible clogging of the bottom. The most thorough analysis of crude glycerol purification via vacuum distillation was done by Ooi et al. almost 20 years ago [104]. 1 kg of crude glycerol was used for vacuum distillation at 120–126 °C and pressure of 0.4 – 0.04 mbar and obtained 141.8 g of glycerol with a purity of 97 %. The entire one-step purification was done at a pH smaller than 5 to avoid any foaming. The bottom of the column contained mainly salts, high boiling point MONGs, and some glycerol. Overall, the entire process has been seen as a simple way of purifying crude glycerol, albeit with a very high vacuum applied. Isahak et al. [126] used the same configuration but with prior pre-treatment to achieve a purity of 96.6 % wt. at an optimum pH of smaller than 5 to avoid foaming just as with Ooi et al. [104]. Their work also clarified that at high temperatures, free sodium hydroxide reacts with the fatty acids to form short and medium chained soaps and that higher pH levels intensify this reaction. The same configuration was used by Yong et al. [104], which yielded the same purity at a pH of 3.5. Pitt et al. [11] used a vacuum distillation step at 120 °C to remove water and alcohol fraction after neutralization and vacuum filtration and prior to the adsorption step. According to the experiment, the distillation step provided the greatest increase in density due to the removal of lower density components which increased the density from 1.1243 g/cm^3 to 1.2460 g/cm^3.

Vacuum distillation has proven itself as the only suitable industrial purification method to treat comparably pure, crude glycerol. It can be applied as a single purification step (if sweet water containing 10–20 % wt. of glycerol is used as feedstock) or within different purification steps. Nevertheless, vacuums applied in the research experiments are far too low to be applied in real-life applications – e.g., crude oil vacuum distillation works at a very high vacuum of 10–30 mbar [127]. Furthermore, highly impure crude glycerol containing high MONG and ash contents require different pre-treatments to increase the glycerol purity which will increase the operating costs of vacuum distillation.

3.3. Ion-exchange resins

Ion-exchange resins are mostly used as an additional step for refining in the purification route. Ion-exchange resins are mainly used to remove low amounts of salts from aqueous solutions [128]. The principle of ion exchange is depicted in Fig. 6: the cations and anions of the crude glycerol solution are exchanged by the cationic and anionic ions in the resin resulting in the formation of water which must be subsequently removed from the purified glycerol solution. The process is not energy intensive, and the resins can be regenerated [13]. Typical parameters which are varied are the bed height, residence time or operating temperature. Table 8 gives an overview of different ion-exchange resins which have been used for the purification of crude glycerol by different authors.

Abdul Raman et al. [12] used as a pre-treatment step acidification and subsequent ion-exchange resin to purify crude glycerol from an initial purity of 35.6 % wt. to 98.20 % wt. Therefore, a cation exchange H + resin was used (Amberlyst 15), and the optimal operating conditions were determined as 40 g of resin, a flow rate of 15 mL/min, and 60 % of solvent. Isahak et al. [126] used Amberlite IRN-78 and Amberlite 200C to remove free ions from crude glycerol after neutralization and microfiltration. Furthermore, silica beads were added to reduce the moisture content. After the treatment, the resin was regenerated by washing with diluted sodium hydroxide for Amberlite IRN-78 and diluted sodium chloride for Amberlite 200C. The purity of the initial 77.4 wt% could be increased to 99.4 wt% and subsequently reduce the amount of ash by 99.9 % wt. An increase of 59.3 % wt. crude glycerol to 85 % wt. of ion-exchange treated glycerol was achieved by Lopes et al. [20] by applying a three-step ion exchange method consisting of a cationic step followed by two anionic steps. Priya et al. [105] used ion-exchange resins in a column to purify 18 % crude glycerol up to 40 % (crude) glycerol by using a bed height of 6 cm at 40 °C.

A more fundamental study was conducted by Carmona et al. [128]. The aim was to obtain the equilibrium and kinetic data for an ion exchange process using 0.5 L of a glycerol-water mixture (90 % wt. glycerol and 10 % wt. water) with 0.1 mol/l sodium chloride by applying a strong acid Amberlite-252 resin. Therefore, the equilibria were studied at three different temperatures (303 K, 318 K, 333 K), and the effective diffusion coefficient of sodium in the resin was studied to obtain the kinetic data. The equilibrium results showed that selectivity for sodium

Table 8
Overview of ion-exchange resins used by different authors for the purification of crude glycerol.

Cation Exchange Resin	Anion Exchange Resin	Year	Temperature [°C]	Amount of resin [g]	Flow rate [mL/min]	Amount of solvent [%]	Mode	Comment	Ref.
Amberlite 252	n/a	2009	60	n/a	n/a	n/a	n/a	Investigation of equilibrium, kinetic data for removal of sodium ions	[128]
Amberlyst 15	n/a	2019	22	40	15	60	Column	Flow rate most important variable	[125]
Amberlite IRA 120Na	Amberlite IRA 410Cl	2019	n/a	n/a	n/a	n/a	n/a	Use of one cationic exchange step followed by two anionic exchange steps	[20]
Amberlite 200C	Amberlite IRN-78	2016	n/a	2.5	n/a	n/a	Column	Regeneration with diluted NaOH for Amberlite IRN-78, NaCl for Amberlite 200C	[126]
n/a	n/a	2019	40	n/a	n/a	n/a	Column	Ion-exchange resin produced by Thermochem Corp PVT. ltd RT Nagar; Optimum bed height: 6 cm	[105]

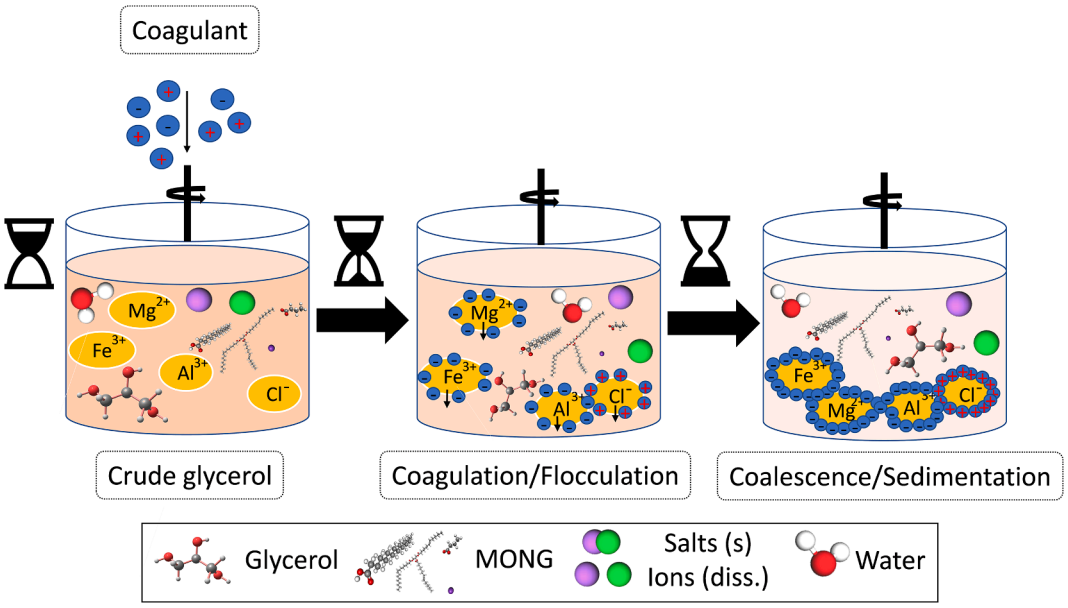


Fig. 7. Working principle of coagulation and flocculation for the purification of crude glycerol.

uptake is favoured at lower temperatures (303 K instead of 333 K) and experimental data can be described satisfactorily with the Langmuir model or mass action laws. The kinetic study showed that higher temperatures favour the ion-exchange process and a kinetic model based on homogeneous reaction allows to obtain the diffusion coefficients at each temperature. The study concluded that Amberlite-252 is a good choice to remove sodium ions from glycerol-water solutions with high salt concentrations. Despite concentrations and volumes used to conduct the experiment were quite low compared to usual glycerol solutions.

Ion exchange resins remain an interesting option for the purification of crude glycerol, especially for the treatment of solutions with low salt contents [129]. It is already being applied in the production of deionised water [130] and even on very large scales for cane sugar decolourization [131]. Nevertheless, high salt contents of the glycerol solution make the process uneconomical due to the chemical regeneration cost [111], especially when glycerol contains >5–7 % wt. salt [132].

3.4. Coagulation and flocculation

Coagulation and flocculation can be used as purification methods to destabilize and aggregate (charged) colloidal particles in a suspension through the interaction between the coagulants and the colloids (coagulation) and their subsequent sedimentation via flocculation (Fig. 7). This method is interesting for the removal of ions in crude glycerol but has not been fully investigated. Lopes et al. [20] used, in a pre-treatment step, a cationic condensed tannin polymer derivative as a coagulant agent to treat crude glycerol from a biodiesel process using frying oil to a purity of 77.3 % wt. The step can successfully replace routes such as acidification, bleaching, deodorization, or salting-out by reducing ions such as chloride, iron, aluminium, and magnesium.

3.5. Membrane separation technologies

Membranes belong to the emerging technologies in the purification of crude glycerol. They are highly interesting due to their low energy requirement compared to conventional vacuum distillation and the avoidance of additional chemicals [129]. Currently, most of the research is being undertaken around pressure-driven membrane technologies.

A relatively new technique for crude glycerol is based on thermally driven membranes such as membrane distillation (MD). MD generates different temperatures on both sides of the membrane, making the vapour pressure the driving force of this process. In general, four different MD processes have been established: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD), and vacuum membrane distillation (VMD).

Table 9
Overview of membranes used by different authors for the purification of crude glycerol.

Membrane Mode	Year	Membrane Type	Material	Glycerol purity [wt. %]	Comment	Ref.
Cross-flow filtration (Semi-continuous)	2018	Ultrafiltration tubular membrane Manufacturer: Tami Industries	Ceramic composed of ZuO2-TiO2 with TiO2 support	93.7	Optimal conditions: MWCO = 5 kDA T = 50 °C p = 700 kPa V = 50 mL/min	[22]
Dead-end filtration	2016	Ultrafiltration/Fine Ultrafiltration Manufacturer: Tami Industries	Ceramic composed of ZrO2ATiO2 with TiO2 support	97.5	Optimal conditions: MWCO = 1 kDA T = 60 °C p = 350 kPa	[111]
Vacuum Membrane Distillation	2016	Flat sheet hydrophobic	PVDF	n/a	Glycerol rejection: 99.9 %	[13]
Vacuum filtration	2016	Manufacturer: Sartorius Stedim Biotech S.A.	Cellulose acetate	90.4	Optimal conditions: pH = 3.26 mAC = 0.933 g Phosphoric acid	[122]
Dead-end filtration	2013	Hybride membrane with thin film composite	Polyvinyl alcohol Polyethylene glycol Polysulfone resin Tetraethylorthosilicate	n/a	NaCl rejection: 43.98 %	[133]
Electrodialysis	2017	Composite membranes CMI 7000 and AMI7000 Manufacturer: Membrane International	Heterogeneous Polymer membranes, modification with Hydrated zirconium dioxide (HZD) and Amorphous zirconium hydrophosphate (ZHP)	n/a	Decrease of salt concentration by 100 times; modification increases stability against fouling	[140]
Electrodialysis	2017	Composite membranes CMI 7000 and AMI7000 Manufacturer: Membrane International	Heterogeneous Polymer membranes, modification with Hydrated zirconium dioxide (HZD) and Amorphous zirconium hydrophosphate (ZHP)	n/a	90 % desalination of solution	[139]
Sweeping gas membrane distillation	2014	Microporous flat-sheet membrane Manufacturer: Millipore	PTFE	n/a	Solute rejection: 99 %	[108]
Continuous-membrane distillation	2015	Hollow fibre air-gab membrane (AGMD) Manufacturer: Accurel Membrana, Chembrane Engineering and Technology	Polypropylene	n/a	Glycerol rejection efficiency: 99.9 %	[136]
Bipolar Electrodialysis (BED)	2003	Bipolar membranes BP-1 ACM anionic membrane CMB cationic membrane Manufacturer: Tokuyama Soda	n/a	95	80 % demineralization of a 65 % glycerol solution	[107]

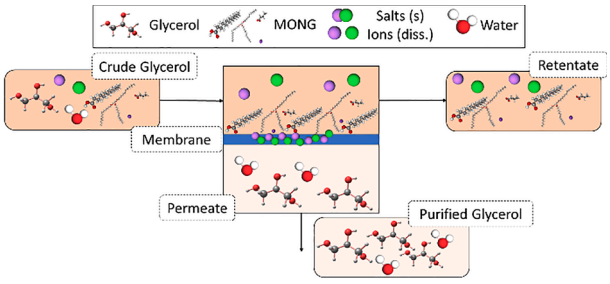


Fig. 8. Working principle of a dead-end membrane filtration module for the purification of crude glycerol.

Lastly, Electrodialysis (ED) is a membrane-based electrochemical process consisting of a stack of different, alternating cationic exchange and anionic exchange membranes, which separate the cations and anions of the incoming crude or pre-treated glycerol solution due to an applied external power source. This leads to alternating chambers which consist of desalinated glycerol and concentrated chambers consisting of anions or cations. An overview of different membrane modules and types which have been used to purify crude glycerol is given in Table 9.

3.5.1. *Membrane separation (pressure-driven)*

The working principle of a dead-end filtration module for the purification of crude glycerol is depicted in Fig. 8. The main factors studied in membrane separation are the type of membrane (polymeric, ceramic or hybrid), temperature, tans-membrane pressure (TMP), MWCO, rejection and permeate fluxes.

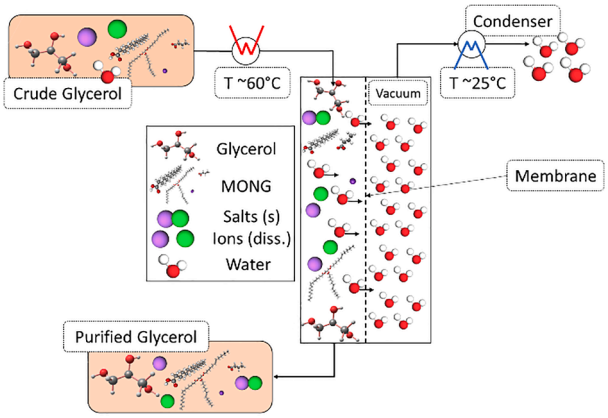


Fig. 9. Working principle of a membrane vacuum distillation for the purification of crude glycerol.

Dhabhai et al. [111] used the membrane separation step as a subsequent step to a physio-chemical treatment. Ceramic membranes such as a dead-end filtration with by-pass composed of ZrO_2-TiO_2 with TiO_2 support with a molecular weight cut-off (MWCO) of 1–15 kDa were used. The membranes were cleaned with methanol periodically. In their experiments, the effect of temperature (25–60 °C), transmembrane pressure difference (50–350 kPa), and MWCO (1–15 kDa) were investigated. The results showed that the highest glycerol purity was achieved at 60 °C (equal to 97.5 % wt.) due to the lower viscosity and a MWCO of 1 kDa, which lead to greater glycerol enrichment than greater MWCO. This would result in incomplete filtration due to the increased pore size leading to impurities in the filtrate. Concerning the TMP, it was shown that at 100 kPa, generally a higher glycerol content was obtained than at 350 kPa for any membrane, except for a 1 kDa membrane where the glycerol content increased with pressure. An increased MWCO at fixed pressure shows a lower purity to the impurities which can pass the membrane.

Chol et al. [22] used a 5 kDa ultrafiltration ceramic tubular membrane made of the same material as above and investigated temperature (25–50 °C), TMP (345–1380 kPa), and flow rate (50–200 mL/min). Compared to Dhabhai et al. [111], a cross-flow filtration in semi-continuous mode was used achieving similar results. The optimum was found at 50 °C, a TMP of 700 kPa, and a flow rate of 50 mL/min yielding a purity of 93.7 % wt. Ceramic membranes have many advantages, such as resistance to chemical, mechanical and thermal degradation, combined with higher permeability rates and easier cleaning compared to polymer membranes. Furthermore, a techno-economic analysis was conducted with the unit cost and revenue of crude glycerol purification of 50.85 USD/kg and 80.36 USD/kg, respectively.

A different trend in membrane purification has been seen in hybrid membranes reported in Shaari et al. [133]. The advantage of hybrid membranes is their higher mechanical and thermal stability in combination with enhanced hydrophilicity associated with permeation of water-soluble material. In this study, a thin film composite (TFC) was used with three different hybrid membrane formulations (consisting of polyvinyl alcohol, polyethylene glycol, tetraethylorthosilicate (TEOS)) as a barrier layer and studied the effects of flux rate measurement, percentage glycerol permeated and NaCl rejection to increase NaCl rejection and increase recovery of glycerol while maintaining a sufficiently high flux. For the third membrane glycerol was incorporated to see any relevant changes. The results showed a >40 % NaCl rejection when glycerol was incorporated into the membrane as it increased the porosity and thermal stability of the barrier layer.

A more fundamental study was undertaken by Mah et al. [134] about filtration modes using reverse osmosis (RO) membranes investigating the glycerol rejection and water permeability in dead-end and crossflow filtration. The results showed a higher rejection and permeability of crossflow filtration. Reverse osmosis membrane with high surface roughness, high negative charge in glycerol solution, low water contact angle, high water affinity and small pore radius showed better performance. The highest rejection and permeation were achieved at temperatures of 40 °C by crossflow membrane with TFC-HR membranes (consisting of proprietary thin film composite polyamide material) with a rejection of 99.81 %, having a permeate flux of 11.86 kg/m^2•h compared to dead-end filtration with a separation of 96.37 % and permeate flux of 4.93 kg/m^2•h.

In general, membranes are an interesting alternative to the conventional purification route. While ceramic ultra-filtration membranes are efficient and offer ease of separation and robustness, polymeric membranes show excellent behaviour towards permeability and selectivity for water [135]. Lower energy consumption with less capital expenditure compared to a vacuum column makes this option attractive for small and medium-sized plants. A major drawback of membranes

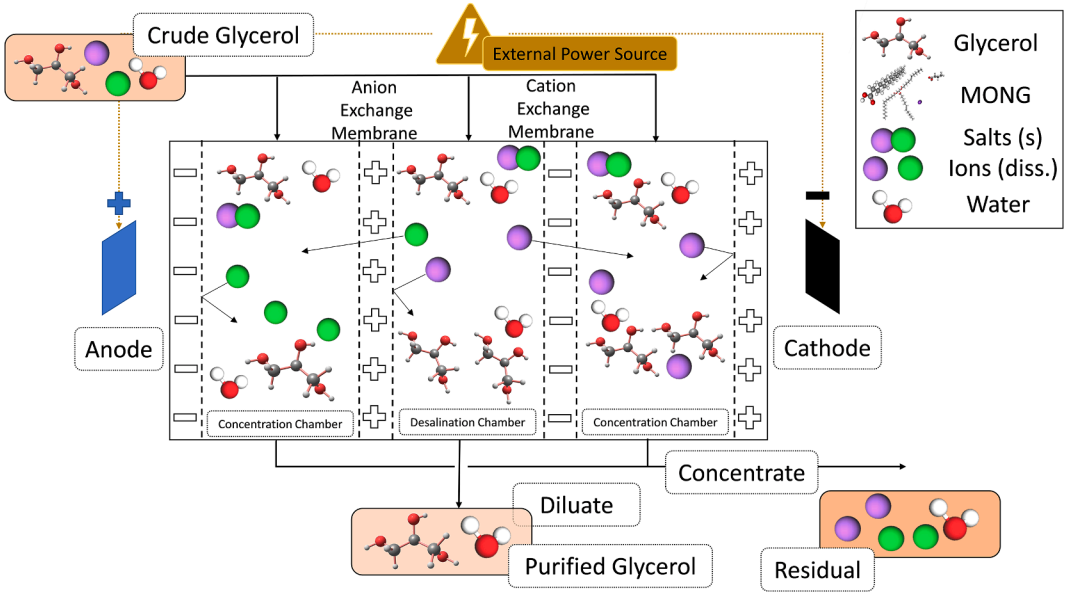


Fig. 10. Working principle of electrodialysis for the purification of crude glycerol.

Table 10
Advantages and disadvantages of various crude glycerol purification routes.

Techniques	Advantages	Disadvantages
Vacuum Distillation	• Established way of industrial glycerol purification [141] • Very high glycerol purity [145] • No pre-treatments are required [104] • Good for high content of salt and MONG [104]	• High CAPEX [15] • High OPEX (energy intensive) [15] • Not suitable for small and medium size plants [15]
Adsorption with activated carbon	• Decolourization [102] • Removal of odour [109]	• Removal of loaded adsorbent requires additional steps such as filtration [146] • Inefficient for other impurities smaller than glycerol [102] • Used as the final polishing step [52]
Ion-Exchange	• Effective removal of ions [128] • Reliable industrial implementation [132] • Low energy consumption [133]	• Regeneration of resins necessary [132] • Waste stream produced is not recoverable [52] • Only economical for low salt content material <5-7 wt.% [132]
Electrodialysis	• Effective removal of ions [140] • Continuous process [147] • High yields possible [139]	• Industrially implemented only for aqueous systems [148] • Pre-treatment is necessary [137] • Issues associated with membranes such as concentration polarization, water splitting on monopolar membranes, and scale-up [148]
Membrane (Thermally-driven)	• High purities are achievable [135] • Lower heat loss through membrane matrix [13] • Lower operating pressure and temperature compared to pressure-driven membrane processes [135] • Required equipment for MD can be much smaller [108] • Use of energy sources such as waste thermal energy in industrial plants, solar, wind or geothermal energies can be used to operate MD [108]	• Pore wetting [13] • Heat recovery is negligible [13]
Membrane (Pressure-driven)	• High rate of flux [13] • Economically feasible [22]	• MONG content can cause fouling [52] • High-pressure operation [13] • Disposal problem [13] • Pre-treatment step necessary [22] • The membrane must be flushed with solvent to avoid MONG [22]
Coagulation	• One-step removal of charged colloids [20] • Mild treatment conditions [20]	• Considerable quantities of coagulant are needed to achieve an appropriate level of flocculation [149] • Some quantity of sludge formed must be processed externally [149]

remains fouling behaviour which can reduce the filtration area and hence the performance of the membrane [22]. Therefore, a pressure-driven membrane separation needs a pre-treatment step as well, to reduce the MONG content as much as possible. Furthermore, the periodical exchange of the membranes and their cleaning with methanol adds additional costs which must be considered.

3.5.2. Membrane separation (thermally-driven)

The working principle of a vacuum membrane distillation (VMD) for the purification of crude glycerol can be seen in Fig. 9. Possible variables which are studied for membrane distillation are the feed temperature, feed inlet concentration and feed circulation rate and vacuum.

Pal et al. [13] used a vacuum membrane distillation process to purify a glycerol-water mixture using flat sheet PVDF membranes which were prepared in the lab. Therefore, membrane rejection which is the ability of the membrane to retain the desired component was investigated. Within a feed concentration of 10–90 % glycerol and water mixture, a membrane rejection of 99.9 % of glycerol was achieved with feed temperature between 25 and 30 °C and permeate side vacuum pressure of 0.007 bar. The glycerol concentration in the permeate stream was 0.07 vol% yielding a highly pure permeate side consisting mainly of water.

A different process was reported by Shirazi et al. [108] using sweep gas membrane distillation (SGMD). The purpose of this experiment was to concentrate diluted glycerol from wastewater (dewatering). Therefore, a microporous hydrophobic flat-sheet PTFE membrane was used, and operating parameters such as feed temperature, glycerol concentration in the aqueous phase, feed and sweep gas flow rate were studied. The optimal results have been achieved at 65 °C, 400 mL/min, 1 % wt. of glycerol and 0.453 Nm^3/h, and the process is particularly low cost in terms of energy, making it interesting for further investigation.

A similar study was conducted by Zhang et al. [136] to concentrate aqueous glycerol solution by using continuous-effect membrane distillation (CEMD) which enables higher energy efficiency and lower operating cost compared to other MD solutions. A hollow fibre air gap membrane distillation (AGMD) module was used (using two different types of porous hollow fibres and dense-wall hollow fibres made from polypropylene) to concentrate a feed of 10 g/L up to about 400 g/L with a rejection efficiency of >99.9 %, a *trans*-membrane flux of 5.7 L/m^2h and a maximum value of gain output ratio (GOR: a measure of how much thermal energy is consumed in a desalination process) of 16.2 which is 33 % higher compared to conventional seven-effect evaporation (which is a type of multiple-effect evaporators). Nevertheless, the system provided a comparable GOR for concentrations of up to 350 g/L (GOR = 5.3) with a *trans*-membrane flux of 3.1 L/m^2•h. Problems started at an increasing glycerol concentration of 300 g/L as the viscosity started to increase and subsequently the vapour pressure of water to decrease. The process showed high selectivity to separate aqueous solution of non-volatile solutes such as glycerol leading to a distillate which was consisting almost purely of water and results indicated that the more porous membrane exhibited better features due to the reduction of heat loss by conduction and reduction of mass transfer resistance. Furthermore, a long-term test of 60 days showed good stability of the process.

Membrane distillation seems to be an interesting application for the dewatering of crude glycerol which usually requires more energy. The process features lower energy consumption compared to conventional distillation and lower operating temperature than phase separation by evaporation [135]. It can't be compared directly to pressure-driven membrane processes as the permeate (product) produced usually consists entirely of water and other volatile matter which could pass the membrane. Hence, MD leaves a retentate behind consisting of glycerol, non-volatile MONG and ashes. Currently, the application of membrane distillation in academia is solely focusing on concentrating dilute aqueous glycerol mixtures and not addressing any ash or MONG separation, making them unsuitable for the purification of highly impure crude glycerol [108].

3.5.3. Electrodialysis

The schematic of electrodialysis applied to glycerol purification is depicted in Fig. 10. Different relevant factors which are investigated in ED purification are the limiting current density (LCD), different

Table 11
Appendix B.

Main Separation Route	Year	Glyt = 0 [wt. %]	Glyt = 1 [wt. %]	Asht = 0 [wt. %]	Asht = 1 [wt. %]	MONGt = 0 [wt. %]	MONGt = 1 [wt. %]	Watert = 0 [wt. %]	Watert = 1 [wt. %]	Comments	Ref.
Neutralization Adsorption	2018	67.7	89.5	17.85	3.6	n/a	n/a	38.6	4.3	Use of bentonite as adsorbent	[115]
Acidification Extraction	2019	74.72	92.04	12	8	11.31	1.14	1.98	0.2183	Use of ethylene glycol as solvent	[153]
Acidification Adsorption	2018	67	96	11.6	0.3	5.2	0.7	16.2	3	Use of tea waste as adsorbent	[116]
Acidification Neutralization Evaporation Anti-solvent treatment Adsorption	2014	13	96	5.6	1.04	70.2	1.09	9.2	1.30	Decreasing trend of ASH and MONG contents with decreasing pH	[109]
Acidification Adsorption Distillation	2020	61	79.64	n/a	n/a	n/a	n/a	n/a	n/a	Acetylation process after glycerol purification	[154]
Neutralization Distillation Anti-solvent treatment Adsorption Distillation	2016	35.66	97.37	4.08	1.1	47.86	n/a	12.4	n/a	Glycerol from a UCO biodiesel plant	[146]
Extraction Adsorption	2015	74	99.2	n/a	n/a	12.5	0.3	13.5	0.5	Use of Petroleum ether and Toluene as solvents (hazard)	[155]
Saponification Acidification Anti-solvent treatment Membrane Adsorption	2018	40	98.07	4.90	1.2	55.91	0.17	5	3	Use of ceramic membranes	[22]
Electrodialysis	2019	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	Fundamental study on different membranes used for electrodialysis	[138]
Electrodialysis	2015	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	Novel process with 95 % salt removal after removal of MeOH, Soaps	[137]
Acidification Neutralization Ion-Exchange	2019	35.6	98.2	4.73	0.39	50.29	0.78	9.38	0.63	Optimization of experiment by Taguchi method	[125]
Anti-solvent treatment / Extraction	2019	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	Purification of salts by different solvents investigated	[156]
Coagulation/ Flocculation Ion-Exchange Evaporation	2019	53.9	94.5	n/a	n/a	n/a	n/a	n/a	n/a	Flocculation as alternative for acidfication; very efficient to remove metal content	[20]
Saponification Acidification Neutralization Membrane Adsorption	2016	40	97.5	4.9	n/a	55	0.3	5	2.2	Viscosity must be high during membrane step / high Glycerol purity of 88.6 wt% after physiochemical treatment	[111]
Neutralization Evaporation	2020	22.88	98.5	3.52	0.21	73.6	1.23	0	0.01	Citric Acid use inefficient / Use of “Green Metrics” to assess ecological factor	[157]
Vacuum Distillation Adsorption	2019	51.88	78.72	n/a	n/a	n/a	n/a	n/a	n/a	Distillation is best purification step	[11]
Neutralization Ion-Exchange	2016	77.4	99.4	2.4	0.002	17.7	0.3	2.5	0.25	Silica beads enabled reduction of moisture	[126]
Acidification Reaction Vacuum distillation Adsorption	2013	n/a	98.1	n/a	0.0002	n/a	n/a	n/a	n/a	Complex reaction conducted to remove further impurities	[158]
Saponification Acidification Anti-solvent treatment Adsorption	2021	40.7	98.2	5.4	0.4	45.22	≪1	5.3	0.8	Synthetic Crude Glycerol AC from oil palm empty fruit bunch	[100]
Adsorption	2021	96.79	98.67	0.10	0.08	1.37	0.69	1.62	0.42	Use of reactivated spent bleaching earth from palm oil refineries as adsorbents	[118]
Saponification Acidification	2018	n/a	n/a	n/a	Nil	n/a	n/a	n/a	0.02	Generated sodium phosphates used in biodiesel production	[159]

(*continued on next page*)

Table 11 (*continued*)

Main Separation Route	Year	Glyt = 0 [wt. %]	Glyt = 1 [wt. %]	Asht = 0 [wt. %]	Asht = 1 [wt. %]	MONGt = 0 [wt. %]	MONGt = 1 [wt. %]	Watert = 0 [wt. %]	Watert = 1 [wt. %]	Comments	Ref.
Neutralization Anti-solvent treatment Adsorption											
Acidification Neutralization Anti-solvent treatment Evaporation	2021	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	Purified glycerol used as carbon source for microbial oil production	[160]
Acidification Neutralization Anti-solvent treatment Adsorption Membrane	2016	51.68	93.89	5.76	0.23	12.9	5.22	29.4	0.15	Synthetic Crude Glycerol RSM used to optimize the purification process Membrane used as final purification stage	[122]
Acidification Neutralized Anti-solvent treatment Adsorption Evaporation	2020	n/a	95.99	n/a	n/a	n/a	n/a	n/a	4.01	Synthetic Crude Glycerol Paper has main focus on adsorption and preparation of adsorbent	[120]
Physio-chemical pre-treatment (according to Manosak et al.) Adsorption	2017	27.2	93	36.2	7	n/a	n/a	n/a	n/a	Optimum condition: AC dose: 67 g/L Contact time: 2 h Shaking rate: 250 rpm Sludge-derived KOH-activated carbon	[113]
Neutralization Extraction	2020	54.8	98.4	residual	n/a	43.8	residual	residual	residual	Use of microreactor	[161]
Electrodialysis	2017	n/a	n/a	n/a	n/a	8	n/a	10	n/a	Current efficiency of 95–98 % 1000 mol/m^3 NaCl	[140]
Acidification Neutralization Adsorption	2018	20	n/a	6.4	0.1	n/a	n/a	10.2	0	Crude glycerol refined up to pharmaceutical grade	[162]
Electrodialysis	2017	90	n/a	n/a	n/a	8	n/a	10	n/a	90 % desalination of solution First a glycerol-water mixture was added based on this impurities were added, 1000 mol/m^3 NaCl	[139]
Membrane Distillation	2014	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	Solute rejection of 99 %	[108]
Membrane Distillation	2015	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	Glycerol rejection efficiency: 99.9 % Feed of 10 g/L successfully concentrated to about 400 g/L	[136]
Microwave Irradiation Acidification Neutralization Adsorption	2014	35.4	94.2	3.3	0.002	53.5	0.001	12.3	0.01	Bio-adsorbent synthesized from dead yeast cells immobilized on chitosan	[119]
Neutralization Anti-solvent treatment Neutralization Drying	2020	80–90	n/a	4.82	0.74	4.27	2.62	n/a	n/a	Optimum dosage of 20 g/L FFAs removed by physisorption and chemisorption by the reaction with –OH attached on carbon surface	[106]
Adsorption	2018	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	Use of Electrospun chitosan/poly(ethylene oxide) nanofibers as adsorbents	[114]
Adsorption	2019	n/a	n/a	5.68	5.67	n/a	n/a	13.48	n/a	Kinetics and thermodynamics of glycerol adsorption	[123]
Membrane Distillation	2019	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	Rejection of glycerol: 99.9 %	[13]
Ion-exchange	2019	18	40	n/a	n/a	n/a	n/a	n/a	n/a	Optimum condition: Bed height: 6 cm Temperature: 40 °C	[105]

membrane types and feed compositions.

Vadthya et al. [137] used electrodialysis to desalinate a synthetic solution of crude glycerol containing a specific amount of sodium sulfate and water to desalinate it with commercial AMI-7001 and CMI-7000 ion exchange membranes. Different water-glycerol and sodium sulfate salts ratios were prepared. It was determined that a higher salt content at constant water and glycerol ratios leads to longer operating times due to the increasing numbers of ions that migrate. Furthermore, the decrease in conductivity is much steeper when higher salt concentrations are used. An increase in water content led to a decrease in operating time. The results showed >95 % separation of the target salts.

A more fundamental study was conducted by Schepper et al. [138] using various ion-exchange membranes to compare their performance with respect to glycerol desalination. A synthetic crude glycerol solution containing sodium chloride was prepared to study the salt, glycerol, and water transport and derive model coefficients to evaluate the transport. In this work, desalination of 92 % after 3.2 h and 9.5 h with Q380 (pilot stack) and ED100 (small stack) stacks were reached respectively. Q380 is therefore the preferable set up due to its higher membrane surface. Being a technology based on membranes, fouling could reduce dramatically the performance, therefore a pre-treatment step such as with the other membrane-based processes is required.

Schaffner et al. [107] used bipolar electrodialysis (BED) to desalinate a 65 % glycerol solution from diester plants which contain 0.35 mol/L sodium sulphates by 80 %. The purified glycerol contained 95 % glycerol with less than 2 % mineral content. Lower mineral contents affected the faradaic efficiency. During the process, approximately 2.5 % glycerol loss occurred of which half of it could be recovered via the acid recycling loop. The study concluded that an increase in the current density leads to a smaller membrane area but also an increase in the cost because the faradaic efficiency decreases.

The trend of composite membranes can be found in ED applications as well. Rozhdestvenskaya et al. [139] investigated the NaCl removal from a highly concentrated glycerol-water and artificial impurities mixture (90 % wt. glycerol and 10 % wt. water with 1000 mol/m^3 NaCl and 8 % wt. organic impurities) using composite membranes. Therefore, modification of heterogeneous polymer cation and anion-exchange membranes with nanoparticles of zirconium hydrophosphate (ZHP used as modifier for cation-exchange membrane CEM) and hydrated zirconium dioxide (HZD used as modifier of anion-exchange membrane AEM) were obtained. The results showed a decrease in salt concentration by 90 %, a current efficiency of 95–98 % for 70 h and that the modified membranes showed improved stability against fouling compared to pristine membranes. Furthermore, it was detected that organic additives remained in the desalinated glycerol-water mixture. A similar study was undertaken by the same research group by Dzyako et al. [140] using the same membranes but focusing more on the characterization of the membranes.

Electrodialysis remains an interesting option, especially to remove ions which could otherwise harm a catalyst in a subsequent reaction step. However, the same limitations as with pressure-driven processes remain such as the problem with fouling. Potentially, this could be resolved by adding a pre-treatment step to reduce the MONG content in the crude glycerol. Whether such a process is economically and technically feasible using real waste-based crude glycerol requires further studies.

4. Industrial glycerol purification techniques

Industrial glycerol purification technologies were developed by many different companies. Currently, plants with large outputs use vacuum distillation as the most common purification technique due to its reliability. The drawbacks of vacuum distillation are its high energy consumption responsible for about 50 % of plant operating costs, and high investment costs.

Air Liquide's technology [141] offers the production of pharmaceutical-grade glycerol (purity of 99.7 %) with a by-product of technical grade glycerol (purity of 85–90 %). Vacuum distillation is used where the mixture is pre-heated to 175 °C to separate the glycerol from organic components and salts. The residue is treated in a post-distillation still to increase glycerol yield, and the salt is decanted. Adsorption with activated carbon in a fixed bed is used as a final step; the product is bleached to achieve a purity of 99.7 %. Air Liquide's technology can process 10 tons per day to 600 tons per day with an operating expenditure of 35 USD/tonne.

A more complex purification route that can also be found in academia is proposed by KVT technology [142]. Their glycerol purification technology is based on neutralization and drying, methanol rectification, distillation, rectification, and MONG desalination yielding a glycerol purity of 99.7 %, leading to pharmaceutical grade. Other possible solutions are offered by GE with their electrodialysis module for efficient salt removal [143] or Lanxess with their commercial LEWATIT resins which are available for different applications [144].

The industry offers a broad range of solutions for the purification of crude glycerol for large-scale processes. Nevertheless, cost-competitive technologies are not available for small and medium-sized biodiesel companies, especially for glycerol derived from 2nd generation biodiesel plants which present high levels of impurities.

5. Challenges in the glycerol industry and future research focus

Many problems and challenges remain in the crude glycerol purification industry. As the amount of highly impure crude glycerol from waste-based biodiesel is increasing, new and more cost-effective solutions are being considered also because many other oleochemical-based waste streams require similar purification. A lot of research has been done on this topic, given the relevance, the growing market and applications of glycerol for food, pharmaceutical and chemical industries. However, as this crude glycerol is derived from waste, it cannot be used in the traditionally high-profit segments such as pharma and food but only for technical applications such as raw chemicals from gasification or biogas. The design of a purification process is relevant to reach accommodate the requirements of the downstream processes. Simultaneously, the glycerol recovery has to be maintained high to avoid an economic loss through the purification. Acidification and neutralization are proven processes at laboratory scale, but they require many steps, the addition and handling of hazardous chemicals, and the importance of corrosive-resistant material have hindered their implementation at industrial scale. A modular unit with membranes could be the answer to the existing challenge for small and medium scale glycerol purification technologies with limited energy consumption and without the addition of hazardous chemicals. The risk of fouling may be circumvented by reducing the MONG content in the glycerol upstream by physiochemical means. A list of the advantages and disadvantages of each process can be found in Table 10.

Since crude glycerol is a by-product and, in many cases, a waste-stream, industry is often reluctant to invest on its purification. This will change in the future as more existing and new producers of biodiesel will shift towards the use of exclusively waste-based feedstocks. This shift will not just yield an avalanche of highly impure crude glycerol but also add costs to the final price of bio-diesel. The current gold standard for the purification of crude glycerol is vacuum distillation [52]. However, this will change as soon as the vacuum distillation becomes less profitable at higher impurity content such as in the case of short- and long-chained organic molecules in the MONG content leading to high operating costs. Adsorption using biogenic materials will remain a finisher step in the future and should only be used to remove residual matter which has already been reduced significantly by prior treatment. Io-exchange resins are useful for the reduction of ash contents but only for mixtures containing less than 10 wt% otherwise the regeneration costs make the process not profitable. Ion-exchange resins and all membrane-based processes share the same problem with the handling of

the high MONG content which deactivates the resins or it generates fouling. However, pressure-driven membranes have shown in lab trials the ability to obtain high purity glycerol whether this can be converted to industrial scale remains subject to research. Electrodialysis has also shown its efficiency in removing selectively ions from crude glycerol. Whether ED can be used to remove ions for industrial waste-based crude glycerol has not been yet demonstrated. Membrane distillation could replace vacuum distillation in the future making the permeate even purer through the selective membrane and reducing the CAPEX significantly.

Coagulation can remove charged particles, making it possibly useful for the removal of ashes and soaps. However, non-charged MONG content will not be affected by this. In the future, the issue of high MONG and ash content with simultaneously the requirement to achieve a high glycerol purity and recovery can potentially only be resolved by using a combination of conventional and advanced purification methods.

In the far future, other possible promising solutions which have been currently at the level of conceptualisation include advanced adsorbents such as MOFs (Metal-Organic Frameworks) [150] as well as hybrid processes such as MOF-aided membranes, graphene-based membranes [151] or nanomaterials [152] which are currently employed in water desalination.

6. Conclusion

From the market study, it is expected that by the year 2024, 6 million tonnes of crude glycerol will be produced from which 4 million tonnes are derived from the biodiesel industry (bio-glycerol). Furthermore, it can be expected that approximately 680,000 tonnes of this glycerol are highly impure and not suitable for typical glycerol applications such as food and pharma products. Hence, waste-based crude glycerol purification and valorisation remain important research area for the industry. In terms of purification, vacuum distillation is still the most dominant way of industrial crude glycerol purification given its use. The scale-up of physio-chemical treatments is hampered by the application and handling of hazardous and corrosive chemicals, making the process comparably unsafe and expensive in terms of CAPEX and OPEX. Advanced purification technologies such as pressure-driven membrane separation, ion-exchange, electrodialysis or membrane-distillation have proven to work although their technology development requires more effort to reduce inherent problems such as fouling or high cost of resin regeneration. Hence, finding a cost-competitive environmentally friendly alternative to purifying highly impure crude glycerol remains a technical and commercial challenge which must be addressed in the future considering the amount of crude glycerol provided to the market.

CRediT authorship contribution statement

Taha Attarbachi: Conceptualization, Methodology, Investigation. **Martin D. Kingsley:** Conceptualization, Methodology. **Vincenzo Spallina:** Supervision, Project administration, Conceptualization, Methodology, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

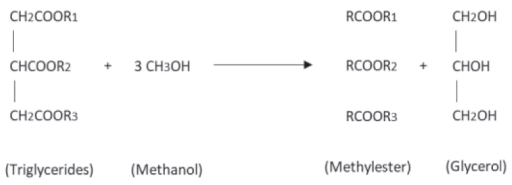
Data availability

Data will be made available on request.

Acknowledgements

This work is part of the GLAMOUR project which is supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No 884197. The authors would like to thank Dr Christopher De Leeuwe for his constructive criticism of the manuscript.

Appendix A



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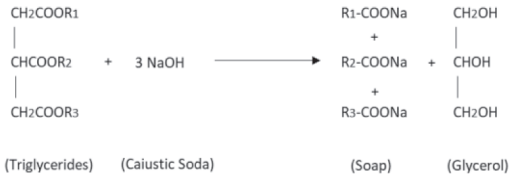
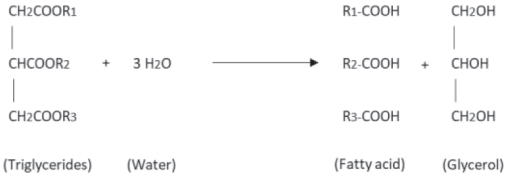
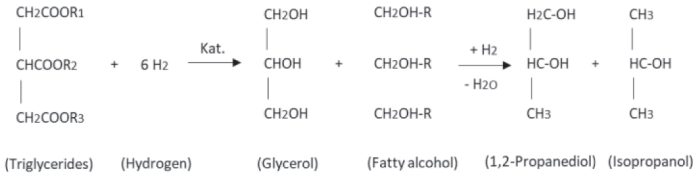


Saponification



Hydrolysis



Direct Hydrogenation

Appendix B

Table B1

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