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Review

Current and Future Trends for Crude Glycerol Upgrading to High Value-Added Products

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Abstract: Crude glycerol is the main byproduct of biodiesel manufacturing from oleaginous crops and other biomass-derived oils. Approximately 10% crude glycerol is produced with every batch of biodiesel. Worldwide, there is a glut of glycerol and the price of it has decreased considerably. There are real opportunities for valorizing crude glycerol into higher value-added chemicals which can improve the economic viability of biodiesel production as an alternative fuel. Exploring new potential applications of glycerol in various sectors is needed such as in pharmaceuticals, food and beverages, cosmetics, and as a transportation fuel. However, crude glycerol produced directly from biodiesel often contains impurities that hinder its direct industrial usage and thus, a refining process is needed which is typically expensive. Hence, this review reports on current upgrading crude glycerol technologies—thermo-, bio-, physico-, and electrochemical approaches—that valorize it into higher value-added chemicals. Through comparison between those viable upgrading techniques, future research directions, challenges, and advantages/disadvantage of the technologies are described. Electrochemical technology, which is still underdeveloped in this field, is highlighted, due to its simplicity, low maintenance cost, and it working in ambient condition, as it shows promising potential to be applied as a major glycerol upgrading technique.

Keywords: crude glycerol; biodiesel; thermo-, electro-, and biochemical glycerol upgrading



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1. Introduction

Renewable energy is a rapidly developing industry in order to reduce the dependence on fossil fuels, oil, and natural gas as main resources for energy generation. In addition to energy savings, the shift to a civilization powered by renewable energy sources including waste, solar, wind, biomass, tidal, wave, and geothermal energy becomes an even more significant option in global use of energy. Based on the International Energy Agency (IEA) [1] report at the COP26 Climate Change Conference, it is anticipated that between 2021 and 2026, there will be a 50% increase in renewable capacity compared to the period between 2015 and 2020 which is due to aggressive support from government policies towards clean energy goals and the replacement of non-renewable fossil fuels. Renewable energy sources are anticipated to increase at the quickest rate of all energy sources according to the World Energy Outlook [2]. Furthermore, this type of energy is also expected to dominate two-thirds of the total global primary energy supply in 2050 based on the REmap Case, held in Abu Dhabi [3]. Municipal solid waste (MSW), including biomass and plastic waste, is the only energy source in this spectrum that is based on carbon. Figure 1 illustrates a breakdown of renewables in the energy sector, where the key role of bioenergy (30%) [3] comprised of biomass industry, biomass buildings, liquid biofuels and biogas as well as biomass power, which is mainly sourced from biomass and waste. Hence, there is much potential for further analysis for green energy development.

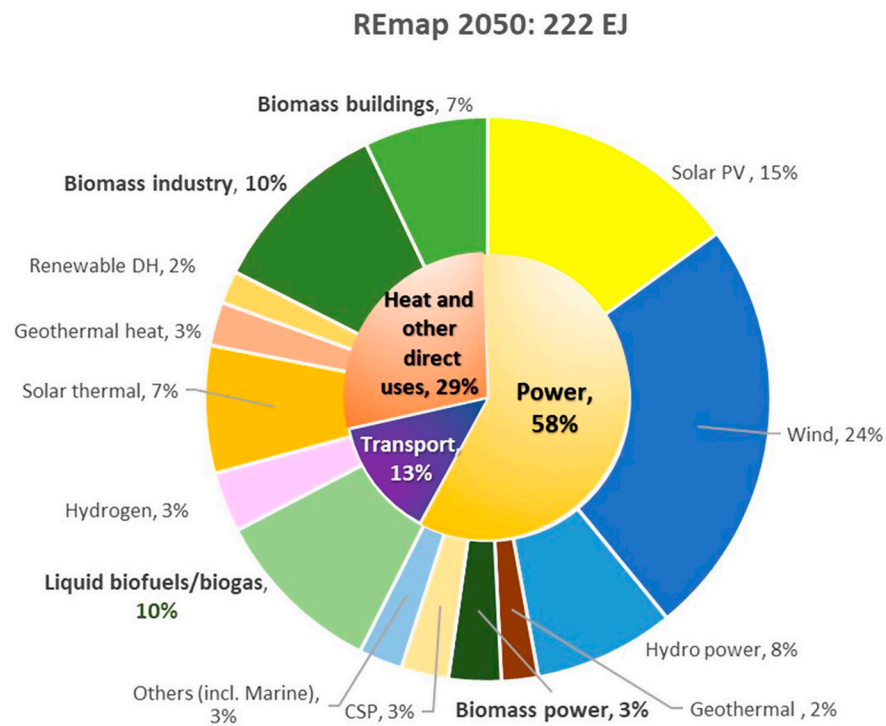


Figure 1. Percentage of total final energy consumption by renewables, according to the IRENA's Remap CASE 2050 (%). Note: Excludes non-energy use. DH refers to district heat. CSP refers to concentrated solar power. PV refers to photovoltaic. Source: [3].

Crude glycerol, which is widely produced as a byproduct of biodiesel production, has become of particular interest as a potential feedstock to convert into value-added biofuels, e.g., bio ethanol [4,5], green methanol [6], bio propane [7], and hydrogen [8,9]. Several publications report that glycerol yield is between 10 and 20% of the overall amount of biodiesel synthesized. In other words, for every 100 kg of biodiesel produced, roughly 10 kg of glycerol is also generated [10]. According to the most recent figures available, European Union (EU) countries recorded annual biodiesel production increased from 3.7 million tons of oil in 2006 to approximately 11 million tons of oil in 2015 and forecasted to increase slightly by 2050 [11]. This level of production will yield more than 1.2 million tons of crude glycerol as the main co-product. Given that crude glycerol exhibits poor characteristics including low heating value (16–22 MJ/kg), high oxygen content (52 wt.%), and poor combustion performance, the expanding biodiesel production in the future will undoubtedly result in an increasing supply and disposal problem. When disposed without proper treatment, there will be social and environmental problems, as along with glycerol, biodiesel washing wastewaters, methanol, and solid byproducts are also generated [12]. According to Nitayavardhana and Khanal [13], large scale biodiesel producers mainly valorized the solid bio-residues as compost or animal food whereas the crude glycerol was refined into pure form and utilized for commercial uses. However, the refinement process of crude glycerol is expensive and economically unviable [13]; as a result, many studies have been reported on crude glycerol upgrading into various valuable byproducts. Thus, researchers and industrialists believe that this approach will improve the economics of biodiesel by reducing its manufacturing costs.

Thus, there is a growing number of research papers to examine alternative technologies to improve crude glycerol into higher quality fuels with lower capital costs that are environmentally benign. Interest in this subject has been growing rapidly by the frequency of publications from 2010 to 2022 as shown in Figure 2. The number of publications of upgrading crude glycerol via biological approaches is the highest, more than 1152 studies. From previous studies, it is mentioned that this kind of technology is favored because

of cheap start-up and running costs as well as mild operating conditions. However, the longer reaction time, high solvent usage, and complexity in handling microorganisms which act as biocatalysts are the main drawbacks. Moreover, the number of studies using physicochemical methods was reported as more than 479 published articles. Works relating to esterification, transesterification, and etherification of crude glycerol were prominent techniques to emulsify blended fuels from crude glycerol which can be directly used as transportation fuels. However, several hindrances do affect their development including the challenges to scale up the methodologies as batch processes to an industrial scale. Additionally, due to the high oxygen concentration of feedstock and the time-consuming process [14,15], esterification and transesterification are still insufficient as a single process for upgrading crude glycerol.

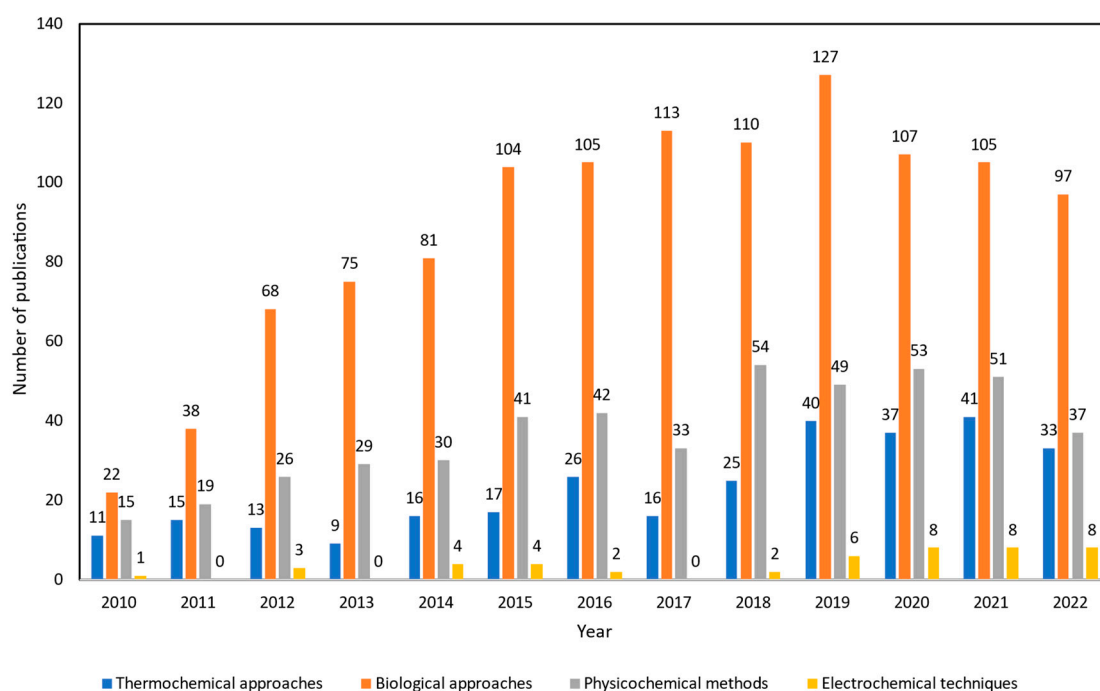


Figure 2. Number of publications about crude glycerol upgrading from 2010 to 2022. The Web of Science (WoS) search engine was used for the data collection by using specific key words. For thermochemical approaches, “(gasification OR pyrolysis OR supercritical water OR catalytic pyrolysis OR microwave assisted pyrolysis OR steam reforming OR aqueous phase reforming) AND crude glycerol” was applied. For biological approaches, “(fermentation OR microbial conversion) AND crude glycerol” was used. For physicochemical methods, “(emulsification OR esterification OR transesterification OR etherification) AND crude glycerol” was applied, and for electrochemical techniques, “(electrochemical OR electrocatalyst OR electrooxidation) AND crude glycerol” was utilized for the search.

Compared to other technologies, thermochemical technologies have been created and used conventionally. Almost 299 published studies have been recorded between 2010 and 2022 that investigate the efficiency of pyrolysis, gasification, supercritical water reforming, and aqueous phase reforming processes in valorizing waste/crude glycerol into various chemicals. Thermochemical approaches have been widely used in upgrading crude glycerol in industrial scale. However, its relatively high process temperature and pressure, increased manufacturing costs, and complex maintenance costs for long-term uses are the current knowledge gaps within this upgrading process. Plus, to some extent, there are needs for additional hydrogen external supply, microwave radiation heater, and use of expensive catalysts depending on intended end-products, which make it less favorable in terms of technoeconomic availability. On the other hand, electrochemical techniques are

currently being explored as the number of works are increasing, as observed in Figure 2. There are only around 46 literature studies that have been reported which is due to this electrochemical crude glycerol upgrading technology still being underdeveloped and facing various issues. Thus, there is significant need to further study and compare the applicability of each mechanism to be applied in the industrial scale of crude glycerol upgrading.

In this review, glycerol is first explained in terms of its properties and commercialized production methodologies. In the second part, the recent works on the various upgrading technologies of crude glycerol are discussed to present an overall view of the present state of available technologies—thermo-, bio-, physico-, and thermochemical approaches, their advantages and disadvantages, and pathways for improvements. Next, with the overview, the list of end-products produced via different approaches was also recorded and its further applications discussed. This review also aims to investigate and discuss the highly promising methodology of the electrochemical approach which is expected to successfully address the barriers to crude glycerol upgrading, according to the available research studies in the literature, via its low processing cost and ambient condition with high performance.

2. Glycerol and Its Properties

Referred to both as propane-1, 2, 3-triol and glycerin, glycerol is a basic trihydroxy sugar alcohol, shown in Figure 3, which was identified in 1779 by Swedish scientist Carl Wilhelm Scheele. Three hydrophilic hydroxyl groups bonded to carbon make up polyhydric alcohol glycerol, a feature that makes it stable, with diverse reactions and functions [16]. Glycerol is currently employed in the manufacturing of a variety of food and drink products, as a solvent for food flavors and colors, medical products, personal hygiene products, fuel additives, and anti-freeze chemicals.

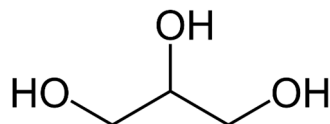


Figure 3. The structure of glycerol.

Table 1 displays physicochemical properties of glycerol as collected from numerous publications which shows glycerol has a high boiling point, is water-soluble, compatible with the majority of organic and inorganic chemicals, translucent, practically colorless, odorless, viscous, non-toxic, and hygroscopic. Additionally, glycerol has received a lot of interest as a “green solvent” in synthetic organic chemistry due to its remarkable physical and chemical properties.

Table 1. Physicochemical properties of glycerol [16–18].

Properties	Values
Form and color	Liquid and colorless
Formula weight (amu)	92.09
Density at 20 °C (g/cm ³)	1.26
Melting point (°C)	18
Boiling point (°C)	290
Thermal conductivity (W/m/K)	0.29
Ignition temperature/flash point (°C)	177
Calorific value (MJ/kg)	18

Glycerol can be found in three different forms: commercially produced glycerol, purified/refined glycerol, and crude/waste glycerol. The purity of refined and synthesized glycerol is higher than that of crude glycerol. While synthetic glycerol is produced in a separate way, often from propene, crude and pure glycerol are byproducts of the manufacturing

of biodiesel. According to Table 2, due to its lower degree of purity (60–80%), compared to refined and synthetic glycerol, crude glycerol cannot be utilized in delicate products such as food, medicine, and cosmetics [19]. Similarly, there may be significant amounts of ash, soap, and moisture in crude glycerol. Crude glycerol has a slightly higher acidity than the other types of glycerol. Its darker hue may be caused by the aforementioned quality as well as a few other small contaminants.

Table 2. Comparison of commercial, refined, and crude glycerol [19].

Composition	Commercial Glycerol	Refined Glycerol	Crude Glycerol
Glycerol content (%)	99.2–99.9	99.1–99.8	60–80
Moisture content (%)	0.14–0.29	0.1–0.8	1.5–6.5
Ash (%)	<0.002	0.054	1.5–2.5
Soap (%)	0.04–0.07	0.1–0.16	3.0–5.0
pH value (acidity level)	0.04–0.07	0.10–0.16	0.7–1.3
Color (APHA)	1.8–10.3	34–45	Dark

3. Various Glycerol Resources

As biodiesel production increases in the future, the glycerol surplus that emerges is being examined for potential uses. Today, however, a number of glycerol production pathways have been identified, including the saponification process (traditional soap manufacturing), obtained as a significant byproduct in the biodiesel process (the production of fatty acid ester), waste oil products, and biodiesel technology wastewater. Each of these pathways is produced through a different chemical reaction, as shown in Figure 4. In addition, glycerol can also be produced through glucose hydrogenolysis and biological fermentation, both of which are more practical and involve lower production costs [20]. The earlier synthetic glycerol manufacturing from propylene became economically unattractive as a result of these developments in glycerol production; in addition, rising crude oil prices also contributed to its demise [21].

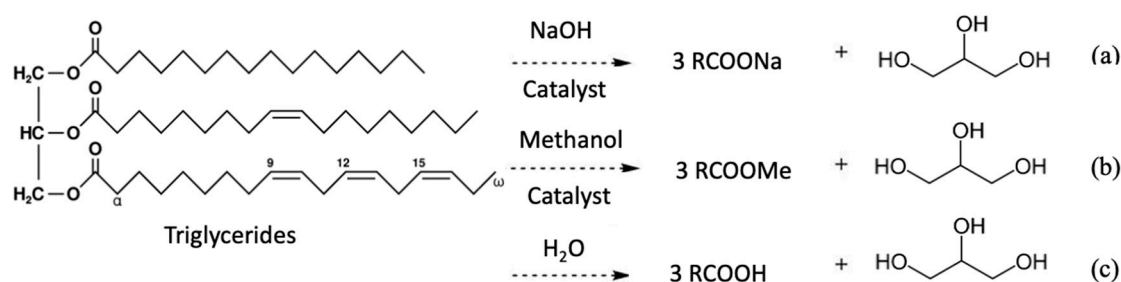


Figure 4. Glycerol production by (a) saponification process, (b) transesterification of biodiesel processes, and (c) hydrolysis of fat and oils.

3.1. Saponification of Soap Manufacturing

Crude glycerol has reportedly been found to contain glycerol, fatty acids, and salts during the reaction of saponification of triglycerides, including fats and oils. Within this reaction, the triglycerides are hydrolyzed with an alkali (sodium hydroxide (NaOH)) and produced two main products: salts of fatty acids (commonly known as soap) and glycerol [22]. The alkali breaks the ester bonds during the saponification reaction, generating soap of alkali metal (RCOONa) and glycerol. According to Figure 4a, one molecule of triglyceride interacts with three molecules of alkali to produce one molecule of glycerol while creating three molecules of soap. Caustic alkali spontaneously combines with free fatty acids in the presence of adequate mixing and agitation, instantly forming soap. A small amount of NaCl, precipitated impurities, free alkali, soluble soap, and 35% glycerol make up filtered soap.

Industrial soap-making method is based on this saponification mechanism, which also serves as the industry's cornerstone. Glycerol typically accounts for around 10% of the value of the soap produced during the manufacturing process of fats and oils [23]. Thus, to optimize the economics of large-scale soap manufacture, better reaction pathways and conditions are needed, along with effective glycerol purification.

3.2. Crude Glycerol from Transesterification of Biodiesel Production

Due to its plentiful supply and inexpensive market value of about \$312 (US) or ¥44,000 (JP) per ton, crude glycerol makes an intriguing substrate for bio-production. During the transesterification reaction within the biodiesel production, with the help of significant catalysts, one mole of triglyceride reacts with alcohol such as methanol to produce three moles of biodiesel and one mole of glycerol, as a byproduct. Both reactants are easily distinguished at the end of the transesterification reaction due to their different in density and polarity. The reaction stream separates into these two phases which are rich in glycerol (bottom layer) and biodiesel (top layer) [24].

3.3. Hydrolysis Reactions in Oleochemical Plants

Hydrolysis of fats and oils can produce the appropriate fatty acid and glycerol. Within this methodology, a fatty acid is liberated from the glycerol backbone of a triglyceride during the reversible process of hydrolysis, plus, glycerol compound also generated [25]. According to Gunstone [26], the hydrolysis reaction results in the production of a light phase made up of fatty acids and a heavy phase made up of glycerol and impurities. The glycerol byproduct needs to be continuously eliminated and collected for the reaction to end. The collected crude glycerol is mostly composed of glycerol, water, free fatty acids, and other impurities such undissolved triglycerides, organic and inorganic salts, and other organic materials. Therefore, in order to manufacture high grade glycerol, it is important to employ purification methods to eliminate impurities from the solution, following a similar scenario to crude glycerol yielded from saponification and transesterification process.

3.4. Biodiesel Technology Wastewater

According to Guo et al. [27], it is possible to produce glycerol from wastewater from enzymatic biodiesel technology. In this study, wastewater that included 5% glycerol underwent alkali treatment, vacuum distillation, and colloidal removal in order to collect glycerol that was up to 90.43% pure. Then, glycerol triacetate was produced using high purity glycerin and acetic acid. Glycerol and acetic acid combine to form glycerol triacetate assisted by catalyst phosphotungstic acid [27]. Thus, a yield of more than 90% glycerol triacetate is produced in 6 h. With this study, the issue of waste disposal during the production of biodiesel can be resolved, and high-value market items were also produced. Hence, this kind of effort can be a possible way to decrease the production cost of biodiesel and increase its techno economical value.

3.5. Synthetic Glycerol

Glycerol synthetically was manufactured from propylene in a number of ways, albeit typically not economical. The most crucial step is the epichlorohydrin procedure, which requires chlorinating propylene to produce allyl chloride, which is then oxidized with hypochlorite to produce dichlorohydrins, which are then reacted with a strong base to produce epichlorohydrin [17]. Glycerol is then produced by hydrolyzing this epichlorohydrin. The production of glycerol from acrolein and propylene oxide is one of the chlorine-free techniques using propylene [28]. Figure 5 shows the chemical reaction that happens within synthetic glycerol production.

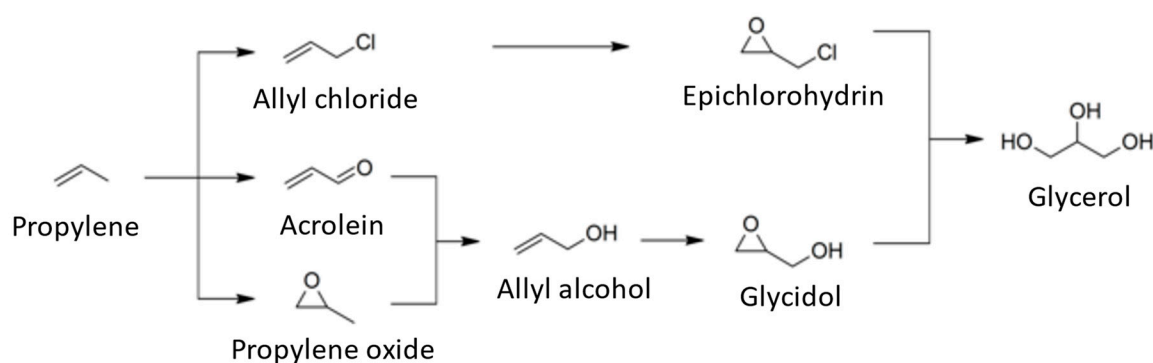


Figure 5. Reaction pathways for production of synthetic glycerol. Reproduced with permission of Ref. [17].

The market for synthetic glycerol is faltering as a result of the massive production of glycerol derived from fats and oils via aforementioned pathways [29,30]. Synthetic processes are therefore not profitable. Recently, glycerol derived from refined crude glycerol has been overproduced; hence efforts are being made to transform it into various high value-added chemicals and other chemical precursors.

4. Glycerol Upgrading

Since glycerol is available as a comparatively low-cost, high-volume biomass-derived waste, the valorization of crude glycerol which is underutilized is necessary for the economic viability of biodiesel manufacturing and waste fats/oil mass production. Due to its non-toxic, edible, biodegradable, and multifunctional qualities, glycerol is one of the top building block chemicals for organic synthesis from biomass [20]. The highly desirable molecule glycerol is utilized to make a wide range of beneficial chemical intermediates. Traditionally, one of the primary technologies for valorizing crude glycerol was through direct combustion approach. Such practice is inconvenient due to the production of acrolein, a hazardous combustion product of crude glycerol with low boiling point (53 °C) and high autoignition temperature (234 °C), and excess salt content [18]. When compared to other feedstocks, the volatile organic compound (VOC) emissions were notably greater, albeit with swirl refractory burners. Owing to its toxic potential, the acrolein produced throughout this technique has caused a lot of environmental concern [31]. Additionally, this technique of valorization falls short of utilizing full prospects of crude glycerol, which may be exploited through different high-end technologies.

In this regard, extensive research has been conducted over the past ten years on the chemical conversion of glycerol into specialized compounds with high added value [21]. Additionally, because glycerol has a high degree of functionalization, it can be used as a precursor for the production of a variety of common chemicals, including syngas, alkenes, alcohols, diols, ethers, acids, esters, acrylates, and even polyglycerols by the use of a variety of processes, involving thermochemical approaches of pyrolysis, biological techniques—fermentation and microbial conversion, physicochemical methods of etherification, trans- and esterification, electro oxidation, hydrogenolysis, dehydration, carboxylation, halogenation, polymerization, and glycerol acetalization [32], as depicted in Figure 6. Thus, in this section, existing glycerol upgrading technologies will be summarized and compared in terms of its state-of-the-art, intended end-products, conversion efficiency, and their process condition. Table 3 displays the summary of recent research and development for crude glycerol upgrading which will be further discussed.

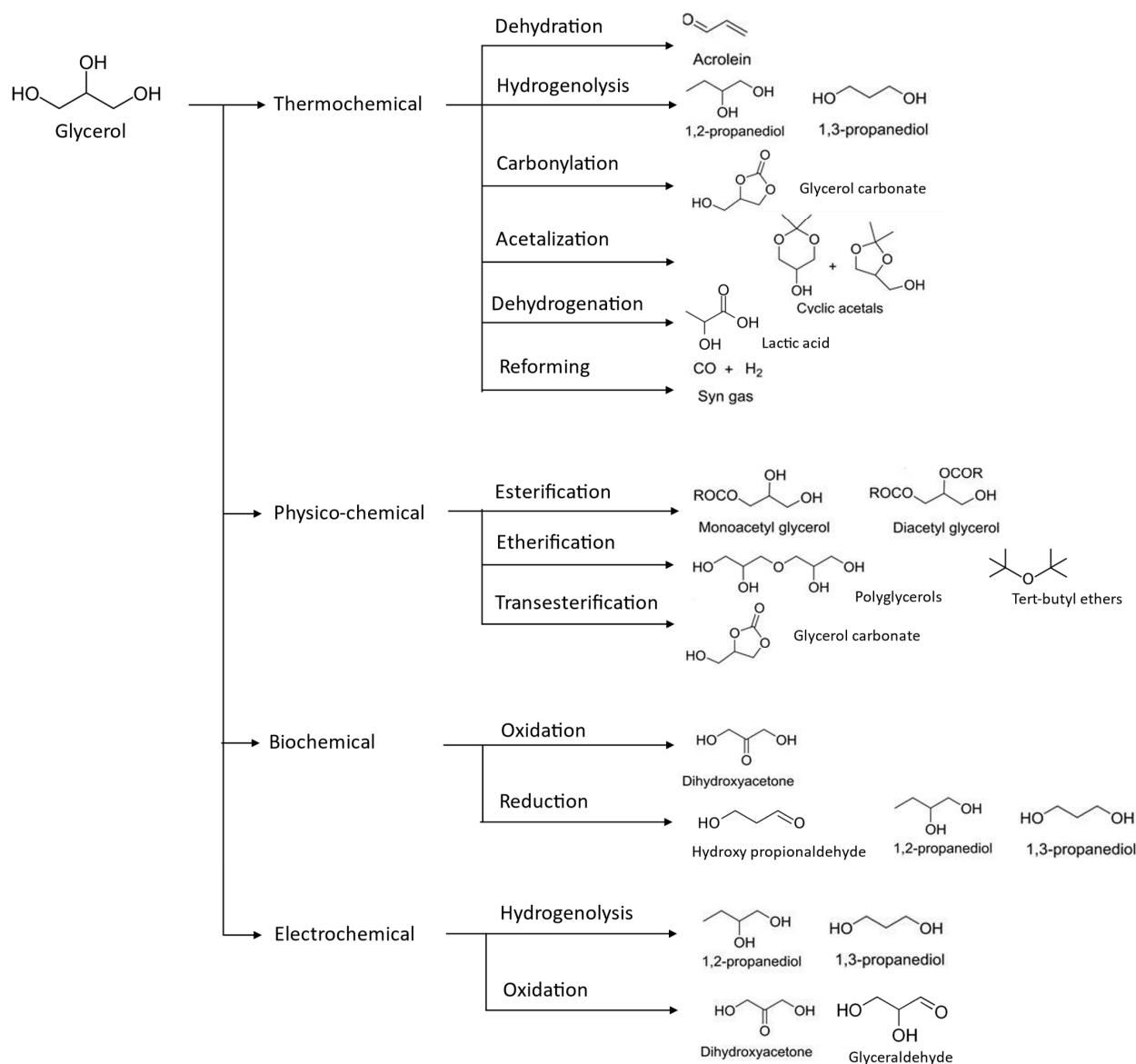


Figure 6. Valorization of glycerol compounds into various intended end-products through different chemical reaction.

Table 3. Summary of current approach for crude glycerol upgrading.

Upgrading Technique	Reaction Mechanism	End-Products	Process Condition	Process Efficiency		Ref.
				Advantages	Disadvantages	
Biochemical						
Microbial fermentation	Aerobic and anaerobically digestion	Bioethanol, diols—2,3-BDO, 1,3-PDO, DHA, LA, SA, PA, and H ₂	Enzymatic biocatalysts—yeast/fungi/modified strains/bacteria/microalgae, mild temperature (70–160 °C) and pressure, pH 5.5–7, stirring speed (200–400 rpm), process time (0.5–5 days)	High product selectivity (<70%), promotes biocatalyst, cheaper manufacturing cost	Complex microorganisms' preparation, longer reaction times (1–5 days), lower kinetic reaction, risks of working with pathogenic microbes	[33–42]

Table 3. Cont.

Upgrading Technique	Reaction Mechanism	End-Products	Process Condition	Process Efficiency		Ref.
				Advantages	Disadvantages	
Bio-electrochemical fermentation	Anaerobic reaction	1,3-PDO, 3-HPA, H ₂	Fed-batch mode in a H-cell reactor, biocathodes—bacteria/mixed microbial inoculum, mild temperature and pressure, time (1–10 days)	Higher production rate compared to non-EC fermentation	Using pure cultures, higher costs. Longer reaction times	[43–45]
Thermochemical						
Pyrolysis gasification	Dehydration	Acetaldehyde, acrolein, HA, and H ₂	Fixed bed reactor, temperature (650–850 °C); atmospheric pressure; catalyst (acid catalysts—metal-assisted zeolites, MMO); residence time (>7 s)	High temperature favors syngas/H ₂ (80%) Low temperature yields liquid products (70%) Shorter time	Produces CO	[46–48]
Fast pyrolysis	Hydrogenation, dehydration, decarboxylation, deoxygenation	Bio-BTX, diols, propylene glycol, syngas	Temperature (400–800 °C); absence of oxygen; residence time (0.5–3 s), external H ₂ supply (for hydrotreating), catalysts (modified zeolites, MMO, metal nitrides/phosphides, bifunctional catalysts)	High yield of HC compound	Coking issues, irreversible deactivation, high cost for hydrotreating process	[49,50]
Hydrothermal/supercritical fluids	Hydrocracking, dehydration	C _{2–4} HCs, H ₂ , CO ₂ , and other syngas	Batch reactor, temperature (>300 °C), time (1–4 h), pressure (10–30 MPa), solvent (deionized water, CO ₂)	No char formed, high H ₂ yields at 380 °C (90% of product gas)	Low selectivity (39%) and yield (40%), high cost of organic solvents	[9,51,52]
	Carbonylation	GC	Temperature (>150 °C), pressure (50 atm), solvent (methanol)	100% selectivity, high GC (90%),		[53,54]
	Dehydrogenation, keto-enol tautomerization, benzylic acid rearrangement	Lactic acid, propylene glycol	Temperature (>290 °C), pressure (50 atm), solvent (water), time (3 h), catalyst (CaO)	Other alternative for lactic acid production, high glycerol conversion (98%)	Low lactic acid yields	[55,56]
SR	Dehydrogenation, dehydration	H ₂ and other syngas	Fixed-bed reactor, catalyst (Ni and Pt-supported catalysts, Co, Cu, and Fe), temperature (350–800 °C)	Ni catalysts exhibit good catalytic behavior, high conversion rate (65–95%), high selectivity (50–82%)	Some setups take longer reaction time (8–20 h), requires proper catalysts	[57–60]

Table 3. Cont.

Upgrading Technique	Reaction Mechanism	End-Products	Process Condition	Process Efficiency		Ref.
				Advantages	Disadvantages	
APR	Dehydrogenation, hydrogenolysis	H ₂ , PDO, ethylene glycol	Ambient processing parameters (150–265 °C) at pressures (15–70 bar), catalysts (Pt/Ni-based γ -Al ₂ O ₃), time (1–56 h)	Low energy consumption. High glycerol conversion (70–80%), H ₂ yield (~20%)	Dramatical deactivation at high temperature. Longer reaction time for high conversion (>25 h)	[61–64]
Microwave-assisted pyrolysis	Gasification	Syngas (H ₂ , CO ₂)	Temperature (300–900 °C), carbonaceous catalysts (activated carbon), gas flow rates of 100–2000 mL/min	Higher production of syngas at low temperature	High-energy consumption	[65–67]
Physicochemical						
Emulsification	Microemulsion	GDM, emulsion fuel	Surfactants (RL, Span 80, Tween 80), cosurfactants (alkanols), temperature (45–65 °C), time (>12 h)	Direct use of fuel, improved pour, and cloud point	Longer reaction time and suitable with low concentration waste	[68–70]
Trans-esterification	Carbonylation	GC	Alkyl carbonates (DMC, DEC), catalysts (Ca-based catalysts, hydrotalcites, biochar), temperature (90–120 °C), time (1 h), low pressure (30–50 mbar)	High GC yield (90%), water removal, increasing heating value and stability	Low end-product yields	[14,71–73]
Catalytic etherification	Etherification, glycerol condensation	tert-butyl ethers, alkyl glycerol ethers, polyglycerols	Tert-butyl alcohol/isobutylene, batch mode, temperature (90–260 °C), catalysts (acid/base catalysts, zeolites, silica), time (2–24 h), pressure (0.1 MPa)	High GC (96%) at longer reaction time (24 h)	Complex system, low conversion (<30%)	[74–76]
Electrochemical						
Electrolysis	Electro oxidation, hydrogenation, and hydro deoxygenation	DHA, CO ₂ , glyceric acid, lactic acid, acetone, 1,2-PDO, isopropanol	Ambient temperature and pressure; electrocatalyst (CoOx, Au, Pt, AuPt NPs, Pt/C-Bi/Sb); electrolyte (alkaline, acidic medium), Ambient T, and t = 4 h	High selectivity (90–50%) and production rate, low processing cost	Low oxidation of secondary alcohol group, long electrolysis time (>5 h)	[77–83]

DHA—dihydroxyacetone; HA—hydroxyacetone; CoOx—cobalt oxide; 1,2-PDO—1,2-propanediol; 1,3-PDO—1,3-propanediol; APR—aqueous phase reforming, SR—steam reforming; GC—glycerol carbonate; DMC—dimethyl carbonate; DEC—diethyl carbonate; 2,3-BDO—2,3-butanediol; HDO—hydrodeoxygenation; HC—hydrocarbon; BTX—benzene, toluene and xylenes; RL—rhamnolipid; GDM—glycerol-in-diesel microemulsion; Span 80—sorbitan monooleate; Tween 80—sorbitan monooleate; MMO—mixed metal oxides; LA—lactic acid; SA—succinic acid; HPA—hydroxypropionic acid.

4.1. Biochemical Approaches

4.1.1. Microbial Fermentation—Anaerobic and Aerobic Digestion

Crude glycerol can also be converted biologically by fermenting with various microbial biocatalysts including yeast, fungi, bacteria, mixed culture from wastewater, and microalgae under aerobic or anaerobic conditions to produce valuable chemicals. Recent studies have concentrated on using crude glycerol as a carbon source in microbial fermentation to produce green compounds and other platform chemicals [40,69,84]. Thus, such bioconversions via biochemical approaches with the aid of microbes are a promising resource and subsequently enhances the techno economical value of the biodiesel industry. Some advantages of biological conversion via aerobic or anaerobic fermentation are due to their superior yield, selectivity, and product recovery [85]. However, due to factors including pathogenicity, stringent anaerobic conditions, contaminants in the substrate, and lower kinetic reaction which have resulted in longer reaction times may impair their growth and conversion rates. Plus, the capacity for these organisms to be manufactured at an industry scale may also hinder their further application. In this subsection, different microbial species used in upgrading crude glycerol into various high value-added products have been summarized as displayed in Table 4.

1. Bacteria

Clostridium, *Klebsiella*, *Komagataella*, *Lactobacillus*, *Lipomyces*, *Escherichia*, *Candida*, and *Raoultella* are a few often used glycerol-consuming species of bacteria used to manufacture valuable products either in aerobic, anaerobic, or microaerobic condition [85]. The oxidative and reductive metabolic pathways, which also result in the formation of organic acids and alcohols, are used to assimilate glycerol [86]. *Clostridium butyricum* [86–89] and *pasteurianam* [90–92], *Klebsiella oxytoca* [93,94] and *pneumonia* [38,95–98], *Citrobacter freundii* [99,100] and *werkmanii* [101], *Lactobacillus diolivorans* [102], *Enterobacter* sp. [39] as well as engineered *Escherichia coli* [103–105] have been widely utilized in glycerol conversion into 1,2- and 1,3-PDO. From the aforementioned previous studies of various bacteria, it can be summarized that high PDO yields have been recorded, approximately 0.62–1.09 mol/mol glycerol, with inconsistent process productivity of 0.92–10.3 g/L/h [87–90,106]. Tang et al. [105] have fabricated an engineered *E. coli* with additional genes for the production of 1,3-PDO, B12-independent glycerol dehydratase (DhaB1), and its activating factor (DhaB2) from *C. butyricum*. The final PDO yield, productivity, and conversion rate recorded were 1.09 mol/mol, 2.61 g/L/h and 90.2% (g/g), respectively. Johnson and Rehmann [91] investigated the effect of decreasing pH during fermentation of crude glycerol with *C. pasteurianum* which led to the decreased in cell growth rate, CO₂ production, and slower fermentations, thus resulting in higher butanol and PDO yields in a continuous process.

Table 4. Recent studies on microbial fermentation of crude glycerol into valuable products based on the type of microbes utilized.

Microbes	Strain	Outcomes		Ref.
		End-Products	Yield (mol/mol Glycerol)	
Bacteria				
	<i>Clostridium butyricum</i> VPI 1718	1,3-PDO	0.55	[87]
	<i>C. butyricum</i> VPI 3266	1,3-PDO	0.65	[88]
	<i>C. butyricum</i> DSM 10702	1,3-PDO	0.51	[86]
	<i>C. butyricum</i> AKR102a	1,3-PDO	0.52	[89]
	<i>C. pasteurianum</i>	1,3-PDO	0.17	[91]
	<i>C. pasteurianum</i>	Butanol	0.65	[92]
	<i>C. pasteurianum</i>	n-butanol	0.28	[90]
	<i>C. pasteurianum</i>	n-butanol	0.43	[106]
	<i>Clostridium</i> sp. Strain CT7	Butanol	0.40	[107]

Table 4. Cont.

Microbes	Strain	Outcomes		Ref.
		End-Products	Yield (mol/mol Glycerol)	
	<i>Klebsiella oxytoca</i>	1,3-PDO	0.47	[93]
	<i>K. oxytoca</i>	1,3-PDO	0.53	[94]
	<i>K. pneumonia</i> DSMZ 2026	1,3-PDO	0.42	[38]
	<i>K. pneumonia</i> mutant	1,3-PDO	0.53	[96]
	<i>K.pneumonia</i> ATCC 8724	1,3-PDO	0.73	[98]
	<i>K.pneumonia</i> M5a1	1,3-PDO	0.53	[95]
	<i>K. pneumonia</i>	2-butanol	0.01	[108]
	<i>Citrobacter freundii</i> AD970	1,3-PDO	0.49	[100]
	<i>C. freundii</i> FMCC-B294	1,3-PDO	0.48	[99]
	<i>C. werkmanii</i> DSM17579	1,3-PDO	0.62	[101]
	<i>Lactobacillus brevis</i> N1E9.3.3	1,3-PDO	0.89	[102]
	<i>L. reuteri</i> CH53	1,3-PDO	0.83	[109]
	<i>L. casei</i> NCIM 2125	Lactic acid	0.16	[110]
	<i>Enterobacter</i> sp. Strain MU-01	1,3-PDO	0.24	[39]
	<i>E. aerogenes</i> TISTR 1468	Ethanol	0.59	[5]
	<i>Escherichia coli</i>	1,2-PDO	0.21	[103]
	<i>E. coli</i> K-12 ER2925	1,3-PDO	0.90	[105]
	<i>E. coli</i>	n-butanol	0.35	[42]
	<i>E. coli</i>	D-lactic acid	0.85	[111]
	<i>E. coli</i>	L-lactic acid	0.93	[112]
	<i>E. coli</i> AC-521	Lactic acid	0.88	[113]
	<i>E. coli</i> SS1	Bioethanol	0.88	[37]
	<i>E. coli</i> SS1	Ethanol	1.0	[114]
Other bacteria and mixed culture				
	<i>Komagataella phaffii</i> Glpard	Lactic acid	0.67	[115]
	<i>Pachysolen tannophilus</i>	Ethanol	0.56	[36]
	<i>Rhodospseudomonas palustris</i> CGA009	H ₂	0.60	[116]
	<i>Paenibacillus macerans</i>	H ₂	0.81	[117]
	<i>Thermoanaerobacterium</i> sp.	H ₂	0.30	[8]
	Mixed culture	H ₂	0.52	[118]
	Mixed culture	H ₂	0.96	[41]
Fungi				
	<i>Lentinula edodes</i>	SCO	0.10	[84]
	<i>Aspergillus niger</i>	Oxalic acid	0.62	[84]
	<i>Galactomyces geotrichum</i>	SCO	0.44	[119]
	<i>Thamnidium elegans</i>	SCO	0.48	[87]
Yeast				
	<i>Saccharomyces cerevisiae</i>	D-lactic acid	0.80	[34]
	<i>S. cerevisiae</i>	Ethanol	0.12	[120]
	<i>Yarrowia lipolytica</i> NG40/UV7	Citric acid	0.90	[121]
	<i>Y. lipolytica</i> NG40/UV5	Citric acid	0.90	[122]
	<i>Y. lipolytica</i> A-101-1.22	Citric acid	0.64	[123]
	<i>Y. lipolytica</i>	Succinic acid	0.45	[124]
Microalgae	<i>Schizochytrium limacium</i> SR21	Docosahexanoic acid	0.23	[125]

For lactic acid generation, engineered *E. coli* has been widely used in converting crude glycerol as an alternative to nicotinamide adenine dinucleotide (NAD⁺) regeneration in the absence of external electron acceptors [112]. The biological route of crude glycerol upgrading to lactic acid assisted by microbes stimulates the development of one specific configuration of either D- or L-, because of the excellent selectivity of lactate dehydrogenase (LDH) [33]. Based on Mazumdar et al. [111,112], *E. coli* has been engineered to improve its efficiency towards the conversion of glycerol to D- and L-lactic acid under microaerobic and anaerobic conditions. The overall yield of 0.85 and 0.93 mol/mol glycerol has been recorded for D- and L-lactic acid, respectively, with 34 g/L and 50 g/L of each final concentration, whereas Hong et al. [126] utilized *E. coli* AC-521 to transform glycerol into lactic acid under the aerobic condition at optimized fermentation conditions of 42 °C, pH 6.5, and 0.85 min⁻¹ (K_LA). The overall lactic acid concentration and glycerol consumption peaked at 88 h of fermentation, resulting in 86.0 g/L lactic acid yield with 0.97 g/L/h productivity as well as a yield of 0.9 mol/mol glycerol. Other than *E. coli*, there are also studies relating to the utilization of *L. casei* NCIM 2125 [110], *K. phaffii* Glpard [115], and yeast *S. cerevisiae* [34] under fed-batch fermentation for lactic acid production.

The potential butanol producer, according to previous studies [90,106], *C. pasteurianam* under optimal condition can generate 0.43 mol/mol of butanol with 0.074 g/L/h of process productivity in 120 h using crude glycerol as a substrate. In a different study by Saini et al. [42], *E. coli* was used to assist the fermentation of crude glycerol into butanol with 0.35 mol/mol of butanol yield. Several type of bacteria were also utilized in the production of ethanol via fermentation of crude glycerol which includes *E. coli* SS1 [114], *E. aerogenes* TISTR 1468 [5], *Pachysolen tannophilus* [36], and engineered *K. pneumonia* [108] where they resulted in 1.00, 0.59, 0.56, and 0.89 mol/mol product yields, respectively. In addition, there is also a study of glycerol upgrading aided by *Saccharomyces cerevisiae* yeast [120] with an overall yield of 2.4 g/L ethanol recorded which proves the possibility of yeast in ethanol production.

2. Microbial mixed cultures and other bacteria

Mixed culture communities have also been studied for their potential to upgrade crude glycerol into other value-added products which include hydrogen gas and PHAs. According to the literature review, the production of H₂ was dominantly covered by fermentation of mixed culture extracted from wastewater or resulted from the mixing of rare strain types. Theoretically, crude glycerol fermentation provides a better capacity to generate hydrogen gas at the end of its reaction as compared to glucose fermentation due to it generating more NADH on a 3-carbon basis where one mole of hydrogen gas per mole of excess NADH. According to previous work, Mabutyana and Pott [116] extensively studied the homofermentative H₂ production via co-fermentation of glycerol with phenolic compounds assisted by *Rhodospseudomonas palustris* under anaerobic conditions at temperature of 35 °C equipped with tungsten light bulbs. According to Varrone et al. [118] and Chen et al. [41], the application of enriched activity sludge or microbial mixed culture efficiently enhanced the conversion of crude glycerol into H₂ with an approximate yield of 0.52–0.96 mol/mol glycerol, whereas *Paenibacillus macerans* [117] and *Thermoanaerobacterium* sp. [8], in another study, were also utilized in the fermentation of crude glycerol to produce H₂ which resulted in 0.81 and 0.30 mol/mol of yield. In addition, crude glycerol may be used as a substrate for anaerobic digestion to produce biogas. In the acidogenesis and acetogenesis phases, it is degraded to volatile fatty acids (VFAs), and in the final methanogenesis stage, methane is produced from either acetic acid, CO₂, or H₂ by the methanogenic community [127]. For further development, anaerobic process optimization to produce hydrogen from crude glycerol is very essential and needs to be explored thoroughly.

3. Fungi

Fungi are another promising biocatalyst to enhance the microbial conversion of crude glycerol into other specific valuable products such as single-cell oil (SCO). According to Chatzifragkou et al. [87], throughout the fermentation process, fungi tend to build up lipids

inside their mycelia. Andre et al. [84] studied the yield of SCO and oxalic acid from the fermentation of crude glycerol with *Lentinula edodes* strains and *Aspergillus niger* strains in carbon-limited and nitrogen-limited conditions, respectively. The maximum yield of lipid of 3.5 g/L and 0.1 g/g biomass was recorded. The SCO product was dominantly composed of oleic acids. *Galactomyces geotrichum* and *ascomycetous* fungus were utilized in SCO production of crude glycerol. Overall lipid yield of 0.44 g/g of dry biomass was accumulated, 4 times higher than pure glycerol control, with 38.0% of glycerol conversion throughout the process. A similar trend was also shown by Chatzifragkou et al. [87], who produced an improvement in lipid yield of 11.6 g/L with 70% of fat in biomass via application of eukaryotic microbes, *Thamnidium elegans*, for SCO production. In this study, acetic acid and mannitol were also generated as their side-products.

4. Yeast

Succinic, citric, itaconic, and malic acids may be generated from glycerol utilizing fungus of the genera *Rhizopus*, *Aspergillus*, and *Ustilago* [128,129]. However, recently, yeasts also exhibit the promising potential to catabolize crude glycerol via an aerobic route into citric and succinic acid. *Yarrowia lipolytica* exhibits the ability in upgrading crude glycerol into citric acid under the aerobic condition with optimal process parameters [121–123]. Li et al. [124] investigated the effect of co-fermentation of crude glycerol with various agro-residues into succinic acid under aerobic condition using *Y. lipolytica*. At the end of the process, 53.6 g/L of succinic acid concentration, process productivity of 1.5 g/L/h, and an overall yield of 0.5 mol/mol were produced.

4.1.2. Bio-Electrochemical Fermentation

Bio-electrochemical fermentation is one of the emerging metabolic pathways which combines both biochemical and electrochemical approaches in upgrading crude glycerol. This technology exploits microbes to catalyze redox reactions in an electrochemical reactor under mild processing conditions [130]. Microbial catalysts on the electrode have been utilized to enhance the electrochemical reaction as well as increase the rate and yields of glycerol conversion. In this approach, the electric current supplied was utilized to permit the fermentation of crude glycerol as the feedstock. By improving cells' capacity to regenerate NAD^+ into NADH, the cathodic current will stimulate microbial reduction processes and thus be able to change fermentation profiles. As mentioned in the previous study [44], a crucial NAD^+/NADH ratio greater than 4 has been linked to high PDO productivity and a high specific growth rate of *K. pneumoniae*. However, there are still a very small number of investigations using glycerol bio-electro fermentations within the cathode [43–45,130,131]. Zhou et al. [130] studied the carbon and electron fluxes during the bio-electro fermentation of crude glycerol using batch biocathodes and showed an increase in 1,3-PDO generation, while in the study by Choi et al. [132], *C. pasteurianum* was used and successfully demonstrated a shift in the microbial metabolism with improved PDO production when an electrical potential is applied. Recently, Xafenias et al. [43] reported a significant increase in PDO synthesis with aid of *Clostridiaceae*. High PDO concentrations of 42 g/L were recorded which shows the potential of this approach to be further studied.

4.2. Thermochemical Approaches

4.2.1. Gasification Pyrolysis

Pyrolysis is a simple method of upgrading glycerol, yet it is just as significant as other processes. This method involves pyrolyzing feedstocks under specific processing conditions—high temperature ($>600\text{ }^\circ\text{C}$), high pressure, in the deoxygenated environment inside a continuous or batch reactor [47,133], resulting from the thermochemical conversion of carbon contained in the feedstock of crude glycerol. The following processes take place to generate gaseous end-products [134]: (1) pyrolysis and devolatilization of feedstocks at relatively low temperature; (2) further degradation of the primary byproducts by continuous heating; and (3) coking gasification which leads to the production of high value-added syngas including carbon monoxide (CO), ethylene, methane, and hydrogen (H_2).

Dehydration and hydrogenation reactions dominantly happened throughout this approach. In the previous work of Skoulou and Zabaniotou [48], they used mixed crude glycerol, crude olive oil, and grains in a fixed bed reactor operating at 750–850 °C. Co-gasification attempts were made to increase the amount of hydrogen produced from the gas produced during the gasification process. According to the findings, combining crude glycerol with olive particles at a biomass weight ratio of 49% resulted in gas emissions of between 0.4 and 1.2 Nm³/kg [47,48]. In another work, based on Figure 7, Blass et al. [46] employed gasification pyrolysis of glycerol with H₂ in a reactor containing dehydration, hydrogenation and upgrading stages in series with help of HZSM-5 and Pd/α-Al₂O₃ catalysts at a temperature of 400 °C to produce a mixture of acetaldehyde, acrolein and hydroxypropanone, propanal, and olefins. Propanal condensed over Brønsted acid sites to produce C₄₋₅ olefins, which then underwent high conversion to produce C₂₋₃ olefins, which accounts for this. During this staged process, a C–C bond formed, and negligible carbon was dissipated as CO as a byproduct. Thus, due to environmental concerns of greenhouse gases production, industrial scaleup is limited.

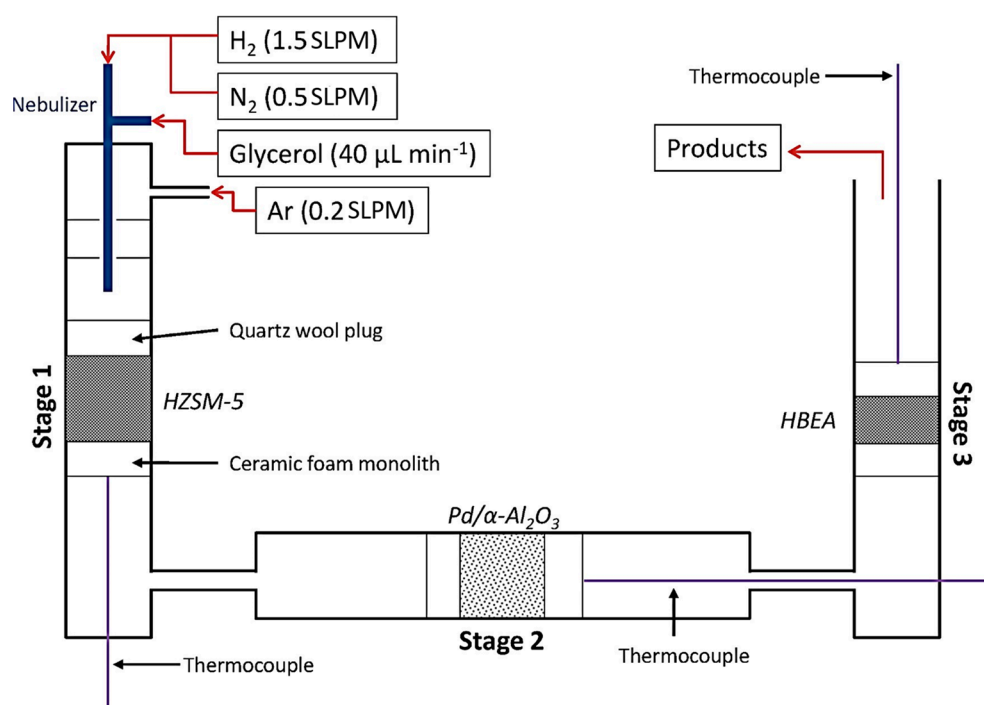


Figure 7. Schematic illustration of three staged reactor used for gasification pyrolysis of crude glycerol feed [46].

4.2.2. Fast Pyrolysis

Fast pyrolysis is a method that has been adopted to decompose biomass into essential chemical feedstocks and biofuels usually with presence of catalyst. For the manufacture of highly stable liquid fuels, the catalyst-assisted cracking process is executed at temperatures between 400 and 800 °C with a short residence time of between 0.5 and 3 s [48,49,133]. The yield and characteristics of the end-products of the process are also significantly influenced by different types of feedstocks, environment, and particularly catalyst species [135,136]. Hence, optimizing the parameters promotes enhanced byproducts yield such hydrocarbon oils with shorter chain (C₁₋₁₂), gases, and char [137,138]. Conventionally, hydrotreating of bio-oils and hydrocarbon wastes, derived from engine oil, transmission oil, and hydraulic oil, which fractured into high value-added products via thermal decomposition of pyrolysis and treated with external hydrogen gas has become a key technology in upgrading bio-oil into transportation fuels [139]. However, from the authors' knowledge, there are no works

on hydrotreating of crude glycerol which may be due to its high operating costs, and it is not worth it in waste upcycling, in term of its techno economic view.

There are several previous published works on upgrading crude glycerol via fast pyrolysis assisted with catalysts. He et al. [49] performed catalytic fast pyrolysis of crude glycerol into bio-based BTX in a tandem micro-reactor using ZSM-5/bentonite catalysts which operating at 520–536 °C. The study resulted in only 8.1 wt.% of bio-BTX yield (15% carbon yield) based on crude glycerol feed with fresh catalyst. In their work, the reduced end-product yields are mainly due to coking issues. The majority of the coke (10.5 wt.%) deposit was on the ZSM-5 planes, which not only reduced the number of Lewis and Brønsted acid sites but also clogged the pores, deactivating the catalyst. From previous published works, relatively poor BTX yields (2 wt.%) were also recorded, with different catalysts—Al₂O₃ [140] and Pd-Ru catalysts [141]. However, in other works [142,143], zeolites favored the production of acrolein (86%) from catalytic conversion of glycerol with higher glycerol conversion.

4.2.3. Supercritical Fluids

One of the alternative thermochemical conversion techniques for crude glycerol utilizes supercritical fluids, including water, ethanol, methanol, and CO₂, as the processing medium. This method has drawn a lot of interest recently and was demonstrated to be an appropriate reaction medium for biomass reforming. Either with or without the assistance of a catalyst, supercritical fluid reforming of crude glycerol and model compounds was already explored [9,51,52,144–146]. As an additional point, crude glycerol incorporates 6.5% of water content, as stated in Table 3; thus, the prior drying step can be neglected via this hydrothermal approach which reduced its processing cost.

Lighter weight liquid constituents and permanent gases, mixture of H₂, CO, CO₂, methane, and higher hydrocarbons will be produced during this glycerol upgrading process, with or without a catalyst. In addition, the rate of conversion, reaction selectivity, and the nature of the gas obtained are acknowledged to be impacted by the inclusion of a catalyst—homogenous catalysts (metal salt and acid catalysts lead to enhanced glycerol conversion and acrolein production). The utilization of various catalysts within this approach has been discussed in previous literature works by Markocic et al. [147] and Pavlovic et al. [148]. With the utilization of catalysts, the energy required for the procedure is reduced and it proceeds at lower operating temperatures and minimizes capital expenditures.

According to previous studies [52,144,147,149,150], it has been observed that the main solvent for crude glycerol upgrading via supercritical fluid reforming is water, while there are not many works utilizing CO₂ [51], and methanol [53]. According to Markocic et al. [147], utilization of water is due to the unique properties of supercritical water itself, when temperature and pressure of the normal water both reached its critical point (T_c = 373 °C, P_c = 22.1 MPa). As shown in Table 5, the essential physicochemical characteristics of sub/supercritical water are markedly different from those of water in ambient and vapor phase. The solubility of additional molecules of glycerol in water is thus improved by the decreasing dielectric constant, and supercritical water takes on the characteristics of a nonpolar solvent [151]. Other than that, reduced dynamic viscosity of supercritical water also leads to improved diffusion coefficients of dissolved substances. Therefore, polar, and ionic reactions as well as free radical reactions may occur at this state. In sub- and supercritical water, crude glycerol conversion proceeds quickly, and the high solubility of the intermediates in supercritical water prevents the development of tar and coke, and high product yields are produced at comparatively low temperatures [149,150].

Table 5. Physicochemical properties of water at different conditions [151].

Parameters	Water Phase or Status			
	Ambient	Steam	Subcritical	Supercritical
Temperature, T (°C)	25	100	250	373
Pressure, P (MPa)	0.1	0.1	5.0	22.1
Density, ρ (g/cm ³)	1	0.0003	0.80	0.17
Dielectric constant, ϵ	78.5	~1	27.1	5.9
Dynamic viscosity, η (mPas)	0.89	0.02	0.11	0.03
Heat capacity, c_p (kJ/kg/K)	4.22	2.1	4.86	13.0

4.2.4. Steam Reforming

Crude glycerol can be upgraded into H₂ using the steam reforming method. In steam reforming of crude glycerol, there are four main steps—feedstocks refinement, reforming, water-gas-shift (WGS) reaction, and end-product refining [152]. In the first step of raw material purification, sulfur and chloride impurities are removed. Then, in a fixed-bed reactor, the reforming process is commonly conducted. Thus, the raw material is brought into contact with steam while being catalyzed by a heterogeneous catalyst, resulting in the production of syngas and other gaseous byproducts. The catalytic WGS reactor collects this gas mixture, where the CO combines with the steam to produce more H₂. Finally, high purity H₂ is produced by purifying the resulting gas stream using various techniques, including pressure swing adsorption (PSA) and/or membrane systems. This strategy is suitable to prepare chemicals made of oxygenated hydrocarbons, including waste/bio-glycerol. These processes may be complemented by undesirable ones, which including methanation, dehydration, carbon precursor reactions, and dehydrogenation, depending on the operational circumstances.

Since scaling up the steam reforming strategy to an industrial level would not necessitate substantial changes to the present infrastructures used for natural gas reforming, this method can be regarded as one of the most promising glycerol upgrading technologies [153]. Industrial steam reforming exploits γ -Al₂O₃ supported Ni catalysts as its catalyst option due to their increased availability and lower cost compared to precious metal-based catalysts [58,154–157]. Furthermore, Ni-based catalytic systems are capable of cleaving C–C, O–H, and C–H bonds as well as the WGS reaction, with typical NiO contents of 10 to 25 wt.% [158]. WGS can eliminate the adsorbed CO from the surface of the catalyst by converting it into CO₂, the first three bonds must be broken in the reforming phase [58,156]. Due to its improved mechanical and chemical resistance, large surface area (S_{BET}), and favorable metal dispersion, the γ -Al₂O₃ support is also commonly employed. However, coke deposition and particle sintering cause some deactivation in these systems. The first occurrence is often attributed to the γ -Al₂O₃ acidic characteristic, whereas sintering is attributed, among other aspects, to metal phases and γ -Al₂O₃ hydrothermal disturbances [58,159]. Within steam reforming operation parameters, these changes are often connected to the transition of γ -Al₂O₃ into other stable phases.

4.2.5. Aqueous Phase Reforming

With a similar objective as steam reforming technology, the catalytic method of aqueous phase reforming was developed to convert oxygenated hydrocarbons generated from biomass into H₂-rich gas. However, when compared to other catalytic thermochemical approaches such as pyrolysis, gasification, or steam reforming, aqueous phase reforming exhibited various advantages [160,161]. Aqueous phase reforming chemically converts the liquid phase-feedstocks at ambient processing conditions, low temperature, around 150 to 300 °C, due to the partial evaporation of the water. Operating pressure, approximately 1.5–7 MPa, is used during the reformation of crude glycerol, such that ample pressure was exerted to allow the H₂-rich effluent to be in situ filtered via swing adsorption approach or, in some cases, using membrane technology which addresses its storage issue and ef-

efficiently isolated CO₂ from the main products. With extremely low CO concentrations (100–1000 ppm), it is possible to generate H₂ gas in a batch reactor assisted with metal catalysts, produced higher amount of H₂ as compared to the existing steam reforming technique. In conclusion, this approach functions at minimal pressure, at a low temperature, and with less costly technology [152]. Additionally, they are simple to integrate into safe, environmentally friendly energy production systems.

4.2.6. Microwave-Assisted Pyrolysis

The microwave-assisted pyrolysis process uses a distinct technology of microwave radiation, as an indirect heat source, to pyrolyze waste materials and/or biomass as shown in Figure 8 [136,137]. The microwave absorbent must be capable of absorbing microwave energy and heat to the requisite temperature in order to pyrolyze waste [162]. Based on a study by Leong et al. [66], using a carbonaceous catalyst and temperatures between 300–800 °C, a microwave heating technique utilized to convert crude glycerol collected from biodiesel plants into biofuels. The product yields in each phase of such a process is determined by the processing conditions including residence time, process temperature, and type of catalysts employed during the reaction, all of which affect the reaction system and relative activation energy. From previous studies [65–67,162], it is observed that there was a decreased total mass of gaseous products due to the catalyst's inclination toward hydrogen gas selectivity. Other than that, temperature reduction and longer residence times increased the overall energy production. The findings demonstrated that crude glycerol has the potential to produce syngas and bio-oil for use in bioenergy [67].

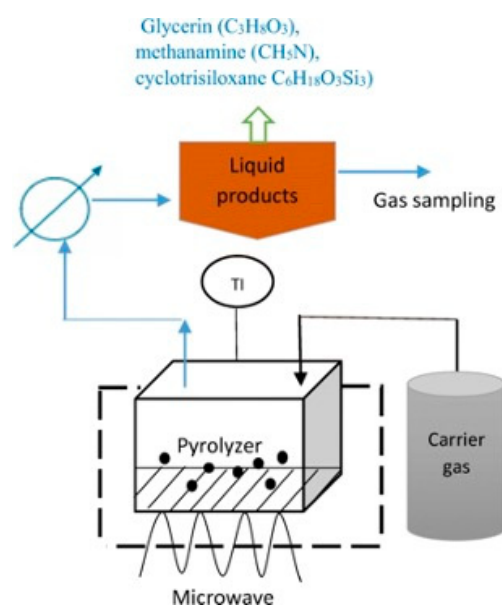


Figure 8. Microwave-assisted pyrolysis of crude glycerol by magnetron microwave in a quartz reactor with the presence of activated carbon as catalyst. Extracted with permission from Ref. [136].

4.3. Physicochemical Techniques

4.3.1. Esterification

Esterification is a reversible chemical reaction, thus adding an excess of one reagent might tip the balance in favor of the desired products through acetylation reaction. The acetylation, as shown in Figure 9, is another potential method for converting biodiesel-derived glycerol [54,163–165]. The mono-, di-, and triacetyl esters that are produced have several industrial uses. The mono- and diacetylated esters, or mono- and diacetin, are employed as fuel additives in diesel engines cryogenics, and as fuel sources to synthesize biodegradable polyesters, whereas triacetin, a triacetylated derivative, is primarily uti-

lized in various sectors including food and beverages, cosmetics, as fuel additives and in pharmaceutical applications.

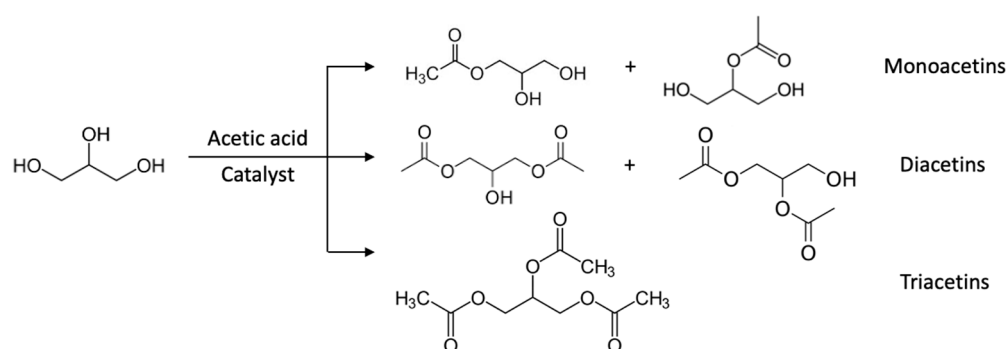


Figure 9. Chemical pathways of acetylation of crude glycerol by esterification method [166].

Based on the above figure, the three-step method for the complete glycerol esterification reaction results in mono-, di-, and triacetin formation [166]. With the assistance of an acid catalyst, the mechanism for glycerol's reaction with acetic acid primarily entails a first protonation encouraged by the acid catalyst upon that oxygen electronic pair of the acetic acid, preceded by a succession of nucleophilic attacks on the hydrophilic group of glycerol to generate monoacetin and water. A third acetic acid molecule can be combined with diacetin to create triacetin, a compound having three acyl groups, and a fourth electrophilic acetic acid molecule can be combined with monoacetin to create monoacetin and water. From previous works, the presence of catalysts is essential for enhancing these reactions' selectivity to produce the three acetins and speeding up the reaction [165,167]. In another work, using a laboratory-made carbon-based catalyst by sulfonating carbonized sucrose, Sanchez et al. [168] examined the esterification of glycerol. The results indicated a high selectivity to triacetin, approximately 50%, at 105 °C for 4 h. On the other hand, Khayoon and Hameed [169] studied the effect of utilization of different catalyst, sulfonated carbon catalysts with high glycerol conversion (90%) and found comparable selectivity of about 40, 30, and 35% for mono-, di-, and triacetin, respectively, under 3 h reaction at processing temperature of 120 °C. According to the aforementioned findings, sulfonated carbon catalysts may serve as a promising acid catalyst replacement for enhancing glycerol esterification operations.

4.3.2. Transesterification

The process of allowing crude glycerol to chemically react with alcohol is known as transesterification or alcoholysis [15]. Methanol and ethanol are the alcohols that are used in this process the most frequently since they are affordable and widely accessible. This process has been widely used to turn triglycerides into esters and to lessen the viscosity of crude glycerol. Catalytic and noncatalytic transesterification are two methods that may be used to carry out transesterification. Industrially, transesterification employs an acyl acceptor of dimethyl carbonate (DMC) assisted with a heterogeneous catalyst that mainly yields glycerol carbonate, as well as methanol as a byproduct [22,54]. Potassium or calcium carbonate (K₂CO₃ or CaCO₃) and hydroxides (KOH or Ca(OH)₂) are two candidates of homogeneous catalysts that can be utilized in the process. Isahak et al. [170] and Ochoa-Gomez et al. [171] utilized catalysts which improved the conversion ratios and higher glycerol carbonate yields (about 95%) with shortened reaction times.

4.3.3. Catalytic Etherification

Glycerol can be transformed into branching, oxygen-containing components during the etherification process by reacting with either alcohols or alkenes [19]. Tert-butyl ethers, one of the reaction products, has the potential to be exploited as lucrative fuel additives. A lot of studies have been done on this etherification of crude glycerol [74,76,172]. In order to

improve the yields and selectivity of the end-products, various type of catalysts have been investigated with its significant affects. Heterogeneous catalysts such zeolites [173,174], mesoporous silica [175,176], and metal oxides as well as homogenous catalysts have been widely investigated. The commercially strong acid ion-exchange resin Amberlyst 15 has proven to be the most effective heterogeneous catalyst to date, whereas p-toluenesulfonic acid has proven to be the most effective homogeneous catalyst. Klepáčová et al. [174] conducted a thorough investigation into the catalytic selectivity and activity of large-pore zeolites and Amberlyst 15-type ion-exchange resins on the tert-butylation of glycerol with isobutylene and tert-butyl alcohol. According to Karinen and Krause [177], approximately five ether products can be produced during the liquid-phase etherification of isobutene and glycerol which assisted with an acidic ion-exchange resin catalyst, in addition to side products in the form of C_{8–16} hydrocarbons.

There are various advantages of utilizing heterogenous catalysts in this approach; it is low in cost, reusable, able to be recovered following the reaction process, and easily separated from the reaction [178,179]. Thus, heterogenous catalysts are anticipated to replace traditional homogeneous catalysts in the near future for both financial and environmental reasons.

4.4. Electrochemical Approaches—Electrolysis

Glycerol derived byproducts manufacturing using an innovative and straightforward process called electrochemical conversion of glycerol has not received enough attention in prior studies [180]. In contrast to electrochemical reductions, which can take place in an aqueous medium at ambient pressure and temperature with electrons acting as the reduction equivalent (while protons are supported by protic solvents and/or by electrode), catalytic hydrogenation reactions typically require high temperatures (250–400 °C) and hydrogen pressures [181]. Electrochemical conversion of crude glycerol has been studied because of its straightforward structure and robust functionality. When compared to chemical methods, the electrolysis process uses less energy and operates at ambient pressure and temperature. Moreover, renewable resources such as solar energy have the potential to replace fossil fuel derived electricity [181]. Adjusting selectivity and boosting efficiency in a thermochemical process requires changing temperatures and pressures, which significantly raises operating costs. When compared to chemical technologies, electrochemical processes do not need to be equipped with pressure or heat equipment within the system, thus, lead to lesser operating costs and smaller space required for industrial scale setup.

Additionally, from published literature, there are several main processing parameters including the electrical characteristics of electrodes, applied potentials, pH of the electrolyte, and electrocatalyst choice which significantly altered the selectivity and product yields [77,78,80,182–185]. Adsorption, atomic bond breaking, electronic charge transfer, interaction between oxygenated species and alcohol fragments, and desorption of reaction products are a few of the general processes that are involved in the electrochemical conversion of alcohols [186]. Accordingly, the contact of the electrocatalyst surface with the reactant molecules, the interaction of the catalyst surface with the molecules of the adsorbed fragments, and the production of surface oxides all affect the overall efficiency.

Because of the distinctive advantages of electrocatalysis, the electrooxidation of glycerol has attracted increased attention in recent years and is widely reported [187–189]. However, based on the literature review of previous published works, there is still a lack of research on electroreduction of crude glycerol. Electroreduction of crude glycerol, theoretically, has a promising future to be discovered especially in the effort of upgrading the crude glycerol via deoxygenation and hydrogenation pathways. This approach can be a promising candidate to substitute the conventional thermochemical hydrotreating technology to convert crude glycerol into lower oxygen content compounds including diols, alcohols and alkane. As a byproduct, electrochemical upgrading technology produces H₂ and pure O₂ that can be used as a final product or an in situ supplement for downstream processes [11,125].

Electroreduction technology has a potential to be an alternative pathway for future upgrading technology. Currently, there are several types of electrochemical reactor/cell which apply slightly different state-of-the-art in upgrading crude glycerol as feedstocks as illustrated in Figure 10, which includes undivided cell, single membrane cell or two-chamber cells or H-cell or polymer exchange membrane (PEM) cell, also known as anion/cation exchange membrane (AEM/PEM) cell, double membrane cell, and continuous flow cell. Within this underdeveloped pathway, crude glycerol, as the feedstock, acts as the anolyte in electrooxidation setup, while, for electroreduction pathway, the glycerol will become the catholyte placed in the cathode chamber. In the electroreduction of crude glycerol, the crude glycerol is electrolyzed or reduced at the cathode which is used to ionize the oxygen from the oxygenated organic substance. Simultaneously, the water (in divided cell) or moisture content within the crude glycerol (in undivided cell) is electrolyzed or oxidized at the anode into H^+ ions and oxygen (O_2). Thus, the residual hydrocarbon radical in electrolyte reacts with the hydrogen proton (H^+) and leads to hydrodeoxygenation or hydrogenation reaction. Therefore, crude glycerol may be theoretically deoxygenated by electrochemical conversion assisted with electrocatalysts to an alcoholic product, with release of oxygen gas as O_2 at anode. Release of O_2 is not attainable through thermal catalytic methods under high-pressure H_2 . However, there is hindrance in terms of coking deposition at the cathode which thus reduced the reaction rate and conversion efficiency within the system [11,82]. Thus, researchers have explored new electrochemical cell designs with dividing the cell into two or three chambers using ion exchange membrane to address this issue of coking formation.

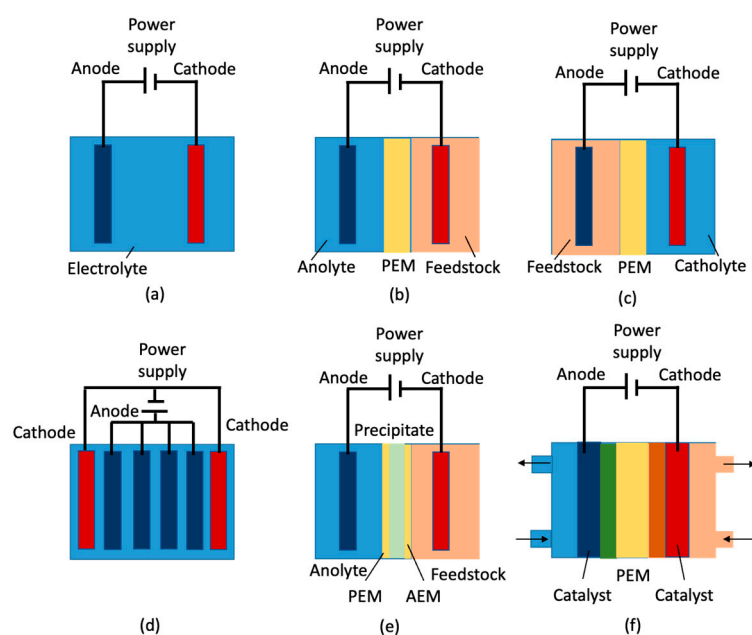


Figure 10. Electrochemical cell/reactor design, which includes (a) undivided cell, single membrane cell for (b) electroreduction, and (c) electrooxidation, (d) multi-layered electrodes cell, (e) double membrane cell, and (f) continuous-flow reactor, for crude glycerol upgrading.

5. Future Outlooks for Crude Glycerol Upgrading

The current technology to upgrade bio-oil or crude oil into biofuels as a substitute for conventional fuels is via full deoxygenation refining of hydrotreating process [137]. The hydrotreating approach is an established upgrading technology as it successfully removes oxygen along with other heteroatoms (impurities) from the bio-oil and increase its cetane number for higher quality biofuels that uses hydrogen supply under high reaction temperatures and pressure, plus, assisted by catalysts. However, since a significant volume of hydrogen gas must be used to allow hydrodeoxygenation reaction, a large operating

cost may be required for this process. Furthermore, the requirement for hydrogen volume increases when the hydro denitrogenating process is involved [137], especially for crude glycerol and raw bio-oil.

Thus, in previous sections, the aforementioned studies were aimed to counteract this hindrance in order to produce techno economically stable technology for crude glycerol upgrading. To maximize the effectiveness and profitability of particular entities and keep them competitive in the market, a number of technologies and conversion routes (such as thermochemical, biological, physicochemical, electrochemical) have been introduced and integrated during the past 20 years.

For enhancing crude glycerol quality and addressing existing upgrading issues, such as high operating costs of thermochemical conversion, low conversion of physicochemical approaches, and time-consuming microbial pathways, the electrochemical technique is currently being explored as the number of works are increasing. The main problem with this method is membrane fouling and glycerol instability, as well as the reaction's ineffectiveness due to the poor conductivity of crude glycerol [181]. However, retaining hydrogen from the water (H₂O) content during deoxygenation is the distinct advantage of electrochemical treatment, which lowers the amount of additional hydrogen required for further upgrading. Since this approach exhibits mild operating conditions, it has been shown to have an impact on the quality of crude glycerol, but it cannot yet be said to be productive of usable liquid hydrocarbons. Electrochemical applications, on the other hand, stabilize the crude glycerol by lowering the acid and oxygen contents. Although crude glycerol to biofuel conversion procedures via electrochemical pathways have not been shown to be efficient because of present complexities, there is a big chance that these methods can be improved from where they are now.

Further research and development efforts in order to advance crude glycerol upgrading technologies are as follows—exploration of integrated energy systems by combining two or more approaches which can ensure low operating costs with high value-added chemicals production, for example, the combination of thermochemical and electrochemical conversion, deeper investigations of existing treatments with mild-operating process such as electrochemical technology by utilizing artificial intelligence (AI) and machine learning for prediction modeling and simulation as well as technoeconomic analysis (TEA) comparing various available approaches for commercialization are needed. Similar approaches of application of AI [190,191] and TEA [192,193] have been applied in bio-oil sector which is currently widely expanding. These further works to advance the crude glycerol upgrading are significant to compare suitable technology to be utilized according to different intended end-products, to optimize the overall process condition, and to study its availability to be used on a larger industrial scale with comparing its manufacturing cost with the profit that can be earned in the future.

6. Conclusions

Crude glycerol is a promising renewable energy source which has attracted attention from researchers, industrial players, and environmentalists for its unique properties as chemical precursors for various applications including transportation fuels, pharmaceutical sectors, and food/beverage use, and others. In this review, various existing crude glycerol upgrading strategies have been summarized and discussed according to their processing conditions and their performance to convert glycerol into high value-added chemicals via specific chemical reaction pathways, including hydrogenation, deoxygenation, carbonylation, and dehydration. Furthermore, emerging technologies have been presented as well to highlight the shortcomings of current crude glycerol upgrading processes.

Several significant remarks can be achieved from this review. Currently, thermochemical treatment, including gasification, fast pyrolysis, liquefactions, aqueous steam and steam reforming, and supercritical fluids reforming, shows its dominance in upgrading processes. However, these treatments are less cost-competitive due to their demanding process requirements, which include heat and pressure. On the other hand, as a stand-alone

procedure, biological treatments are insufficient for upgrading crude glycerol as there is need of complex pre- and post-treatment steps despite their advantages with low startup costs and works under ambient condition without external heating devices. Physicochemical approaches work under mild process conditions; however, they are less efficient due to their slower reaction rate, but they can be combined with other technology for better conversion efficiency. Thus, looking in the future, electrochemical processes via electrooxidation and reduction of crude glycerol appear as promising routes for glycerol upgrading to be examined in the future, despite its underdevelopment, due to their mild process conditions, low assembly and maintenance costs, higher possibility of producing biofuels and bio-alcohol as end-products, and surplus advantage of hydrogen generation during the deoxygenation process which further leads to lower manufacturing costs. However, deeper investigations are still needed to prove its performance in this field as there is a big lack of knowledge about many facets of this novel technique that must be explored, especially in industrial applications, to provide new environmental solutions.

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