
Chapter 1

Background and Introduction

1.1. General introduction

As the global need for energy rises, energy supplies are becoming scarcer. Renewable energy sources are needed for everyday needs and sustainable growth in addition to being in demand now and soon. Interest in producing renewable energy has increased globally due to the need for sustainable development, the energy crisis, and the effects of climate change. Fossil fuels, including gasoline, coal, and natural gas, are presently the vital sources of energy globally. Our society relied on plant biomass to supply its energy needs before discovering cheap fossil fuels. According to the International Energy Agency act 2040 (IEA, 2040), industrial energy demand might reach up to 250 quadrillion Btu, while transportation and building energy consumption would be 150 qBtu and 120 qBtu, respectively. (Figure 1.1). The 19th century's discovery of crude oil led to the creation of a low-cost liquid fuel source that helpful in the world's industrialization and raised living standards. Since petroleum has been the primary energy source for a long time and due to increased demand, its supplies have been on decline. The emergence of new economic, political, and environmental reasons compelled the search for alternate fuels. For the manufacturing of fuels and chemicals to be sustainable, energy-efficient methods have to be developed. Plant biomass is thus a renewable supply of chemicals and energy [1–4]. The only existing source of liquid fuels that is sustainable is biofuel, which is a fuel made from plant biomass. Comparing biofuels to fossil fuels, the emissions of greenhouse gases are much lower in case of biofuels [5, 6–9]. Biofuels such as bioethanol, bio methanol, and biodiesel are substitutes for liquid fuels that emit no greenhouse gases such as CO, CO₂, NO_x, SO₂, or methane. The massive use of petroleum oil in transportation industry was discouraged by releasing these hazardous gases from burning fossil fuels. As a result, biodiesel has gained attention over the past few decades as a sustainable and renewable energy source to replace petroleum fuel [10-11].

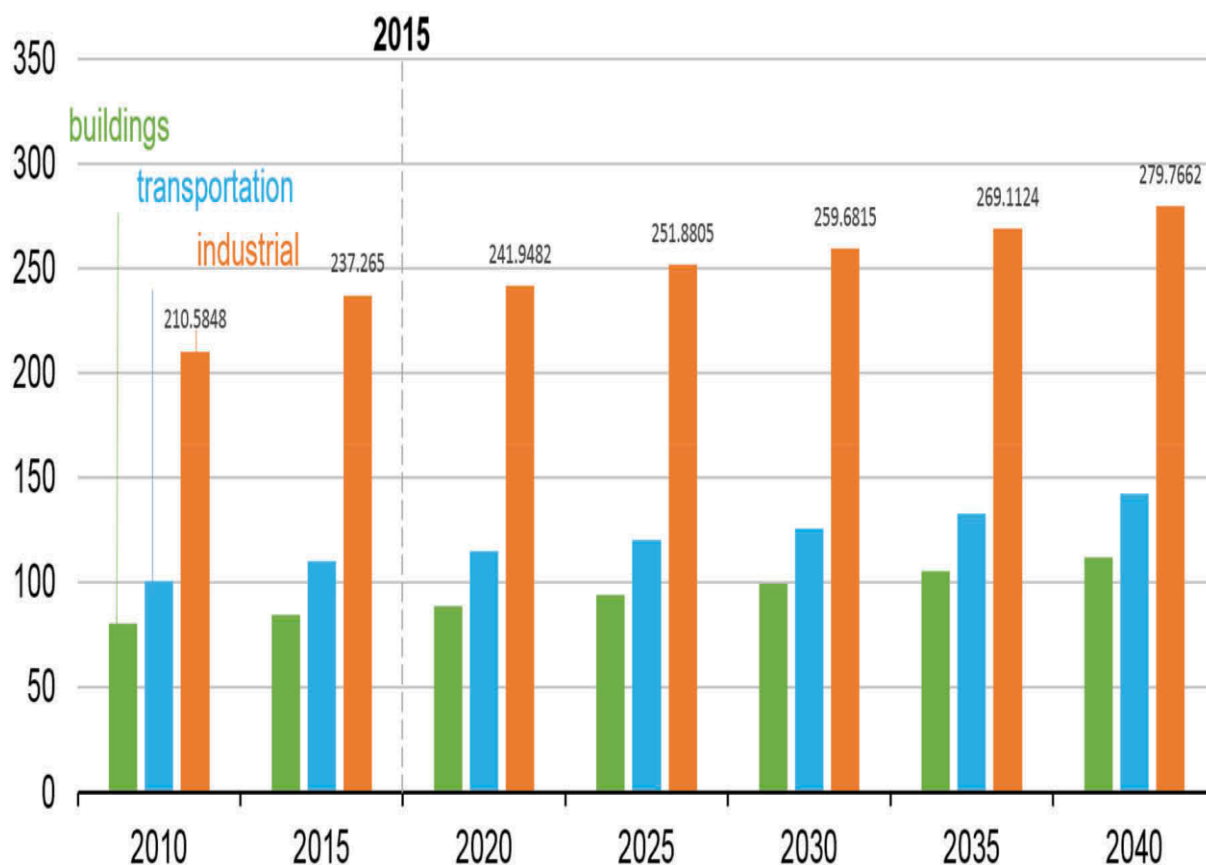


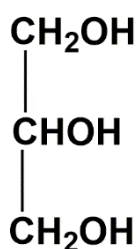
Figure 1.1 World energy consumption by end-use sector (quadrillion Btu) [2].

Most produced biofuels are made from the renewable fuels namely ethanol and biodiesel. During the methanolysis reaction, waste cooking oils, animal fats, microalgae, and fungus are converted into biodiesel. After being blended with petroleum diesel to create B2, B5, B20, and B100 blends, it can be used in diesel engines with minimum modification. In recent years, biodiesel has been produced on a vast scale, and it is anticipated that this will continue in the years to come. In the manufacture of biodiesel, glycerol is the principal by-product. One kilogram of glycerol is produced as a by-product for every ten kilograms of biodiesel [12-13]. Food, cosmetics, pharmaceuticals, polyethers/polyols, explosives, alkyd resins, triacetin, detergents, and the tobacco industry are a few industries where glycerol is used. However, due to the almost complete saturation of the markets, large quantities of glycerol produced by the rising biodiesel production cannot be absorbed completely. It's a fact that energy needed to produce biodiesel is frequently obtained by burning glycerol. So, almost over the past decade,

there has been a worldwide surge in research into new and lucrative applications of glycerol. Therefore, developing innovative methods to use glycerol efficiently can help reduce environmental restoration and financial losses to industry.

1.2. History and discovery of glycerol

Glycerol (i.e., 1,2,3-propanetriol) also known as glycerine is a dihydric alcohol with a very sweet flavour and is colourless, odourless, viscous, and non-toxic. The presence of three hydroxyl groups is mainly accountable for its high solubility in water. Chemically, it was discovered by Swedish Chemist Carl Wilhelm Scheele in 1783 when he worked on a reaction between lead oxide and olive oil. He got glycerine from the mixture and named it sweet oil. Similarly, French chemist Michael Eugene extracted glycerol from tri esters (fat). The Greek word "glykys" which means sweet, gave glycerol its name. The term "glycerine" refers to glycerol in commercial water solution whose main ingredient is glycerol. He did so by demonstrating, among other things, how natural polyol was glycerol. He did so by establishing, among other things, how this natural polyol was crucial to the formation of triglycerides, the primary building block of fats and oils [14]. He reported that hydrolysis converts all animal lipids into fatty acids and glycerol. Glycerol is present in various foods, including coconut and palm oils, tallow, and soy oil (17%, 11%, 10%, and 10%, respectively). Molecular structure of glycerol has been depicted in Figure. 1.2. Additionally, it is found in blood cells, bile, brain tissues, egg yolk, and neural tissues. During the fermentation of alcohol, glycerol is produced, though at a smaller level. However, a significant amount of glycerol is synthesized from propylene, even though the majority is still produced alongwith soap [15].



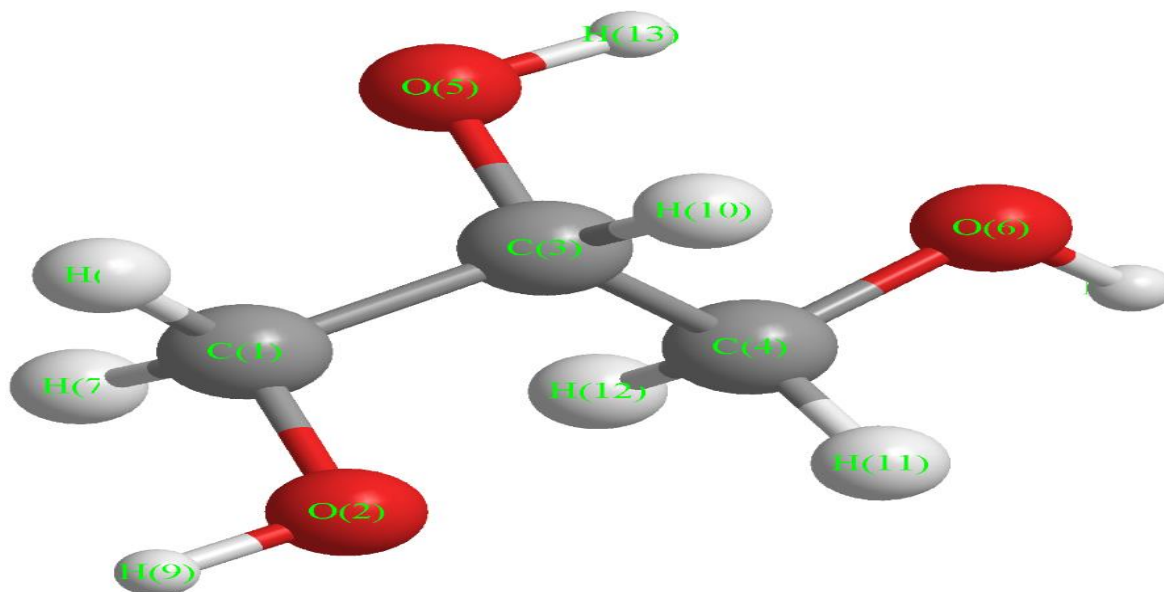


Figure 1.2 Molecular structure of glycerol.

1.3. Significance of glycerol

Glycerol, i.e., $C_3H_8O_3$ is a chemical species found as the main component of triglyceride in natural lipids (crude oil, animal fat, vegetable oil, etc.). It is commonly recognized as glycerin, 1,2,3- propanetriol, 1,2,3- trihydroxypropane, glycerol or glycol alcohol. One of the top ten building blocks in the feedstock for bio-refineries, glycerol is recognized for its wide range of uses. It is utilized in food industry, pharmaceuticals, children's care items, explosives, plasticizers, tobacco humectants, antifreeze, emulsifiers, and cosmetics [16 - 17]. Due to its high viscosity and propensity to remain fluid at moderately elevated temperatures, glycerol is frequently used as a lubricant. In the production of cosmetics, medications, and food, it is used just as it is. As a result of its ability to hold onto moisture, glycerol prevents drying and slows the rate at which tobacco burns. Glycerol can also be used as a thickening agent in liquor and beverages. It is also used in the tincture extraction method as a 10% solution. It is highly helpful in preventing tannins from precipitating in ethanol extracts of plants. For herbal extraction, it is used as an alternative to ethanol as a solvent. The broad applications of glycerol are depicted in Figure 1.3 below.



Figure 1.3 Various application of glycerol [17].

1.4. Physical properties of glycerol

Glycerol is one of the organic compound which is highly stable and compatible with other chemicals at normal storage conditions. It is non-toxic and has no adverse effect on the environment. It is a highly flexible and simple chemical with an affinity to form hydrogen bonds with other chemicals via intra and inter-hydrogen bonding. It is entirely soluble in water and alcohol. The occurrence of three hydroxyl groups enhances the solubility of glycerol in water and simple aliphatic alcohols [17]. It is considerably soluble in ethyl acetate, ether, and dioxanes, whereas it is insoluble in hydrocarbons. The common properties of glycerol are given below.

Table 1.1 Basic characteristics of glycerol [17].

Properties	Standards
Chemical Name	Glycerol
Chemical Formula	CH ₂ OH-CHOH-CH ₂ OH
Form	Viscous liquid
Colour	Colourless
Molecular Weight	92.05 g
Surface tension	63.4 dyne/cm
Melting Point	20 °C
Viscosity	1499 c.p
Relative Density	1.2613
Specific heat	0.5779 cal/gm
Boiling Point	290 °C
Thermal conductivity	0.29 w/K
Flash point	177 °C
Fire point	204 °C
Food energy	4.32 Kcal/g
Compressibility	2.1 × 10 Mpa

1.5. Global production of glycerol

The production of renewable fuels, supported by subsidies, tax incentives, and consumption requirements, has dramatically expanded in recent years, increasing global glycerol production [18]. In India, Canada, and South America, the creation of new renewable fuel legislation will guarantee increase in the supply of crude glycerol shortly [19]. A detailed international report on the glycerol market, as seen in Figure 1.4, has just been released, according to GIA (Global Industry Analysis). It is estimated that; 5.8 billion pounds are anticipated to be spent on glycerol consumption by the year 2025. Currently, annual biodiesel production of USA reached 250 million gallons per year which are highly responsible for 400 million pounds of glycerol as a by-product [20 - 21]. To deal with the oversupply of crude glycerol as the world supply rises, research and development for new glycerol uses will be necessary.

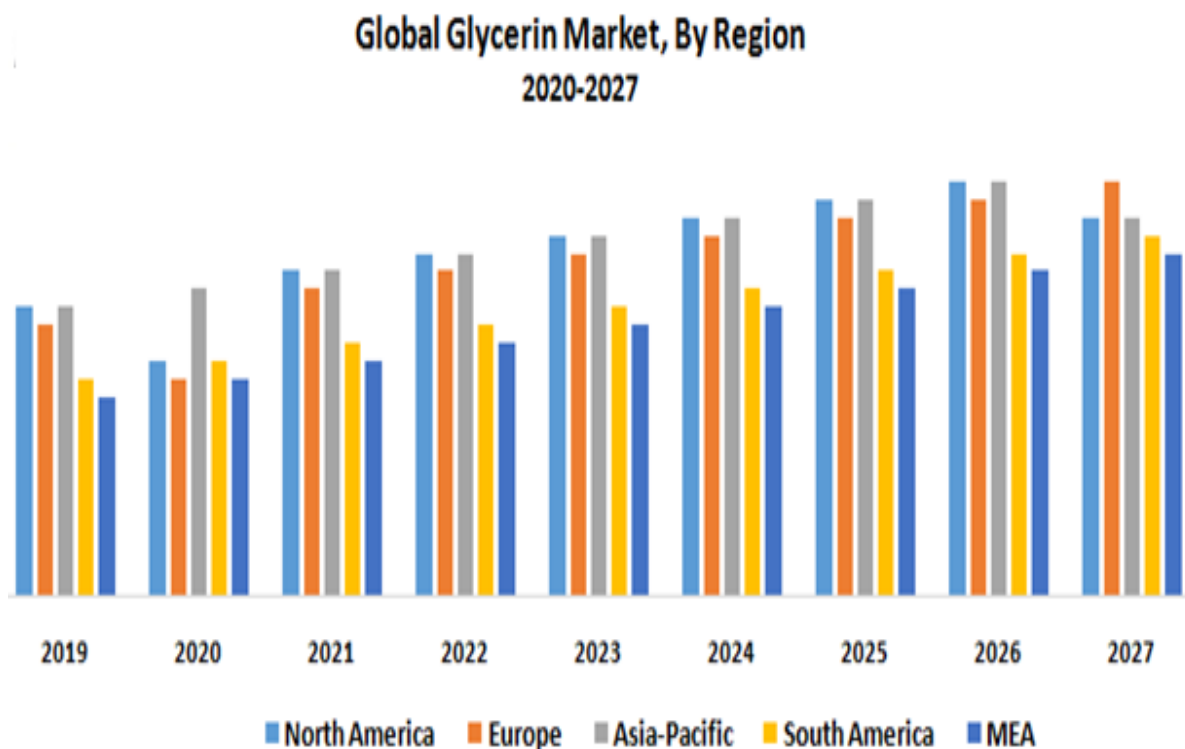


Figure 1.4 Worldwide production of glycerol from biodiesel industries [21].

1.6. Need for value addition of glycerol

Generally, for production of every 10 kg of biodiesel, 1 kg of glycerol is obtained as a by-product. It is commercially known as glycerine. Due to its non-toxicity and environment-friendly quality, glycerol can be used as a cheap raw material for production of different products such as food additives, surfactants, cosmetics, and lubricants. Glycerine has been classified as GRAS (Generally regarded as safe) by US Food and Drug Administration (FDA). Due to its unique physical and chemical properties, glycerol found broad applications in various fields. Its high boiling point makes it physically stable at ambient temperature. The three OH groups present in glycerol moiety makes it hygroscopic and reactive yet stable at most reaction conditions. The existence of the polar hydroxyl group in glycerol moiety makes it to miscible in polar solvents like alkanols, ethylene glycol, phenol, and pyridine while immiscible in non-polar solvents like fatty oils, higher alcohols (containing larger carbon chain), hydrocarbons, chlorinated solvents, C_6H_{12} , C_6H_6 , $CHCl_3$ etc. [22]. Table 1.1 shows the essential

physical and chemical characteristics of glycerol that are important for its broad applications. Traditionally, Gly was used in pharmaceuticals, cosmetics, food industries, anti-freezers, e-cigarette liquids, botanical extracts, explosives and as an intermediate in many other processes. Conventionally, glycerol can be synthesized by saponification of triglycerides using soap manufacturing, while synthetically, manufactured from propylene by several routes. The obsolete production procedures are not so economically viable on an industrial scale, emphasizing global BD production where glycerol is a by-product. In bio refineries, Gly can be used as a green source for biodegradable value-added products, which further supports the non-reliance and exhaustible fossil fuel stocks. Various scientific teams are working to create novel paths to enable the effective usage of glycerol as a natural building block. Using glycerol for advanced chemical synthesis is an exciting challenge now [23]. Since the generated products are used mainly in lower-tonnage methods that are more compatible with the production proficiency of glycerol producers, the conversion of Gly into higher value-added chemicals offers appealing alternatives. Glycerol has also undergone certain chemical functionalization's in the workplace. In future, glycerol will be a practical raw resource for making necessary chemicals and gasoline additives. Specifically highlighting current advancements in the transformation of glycerol into value-added chemicals, new chemistry of glycerol will be established. Future bio-refineries will significantly benefit from this research because its derivatives are used in many industries, including the building, chemical, automotive, pharmaceutical, detergent, and detergent industries. The biodiesel sector will become more profitable if the glycerol is valorised to different value-added products via other chemical processes depicted in Figure 1.5 [24-25].

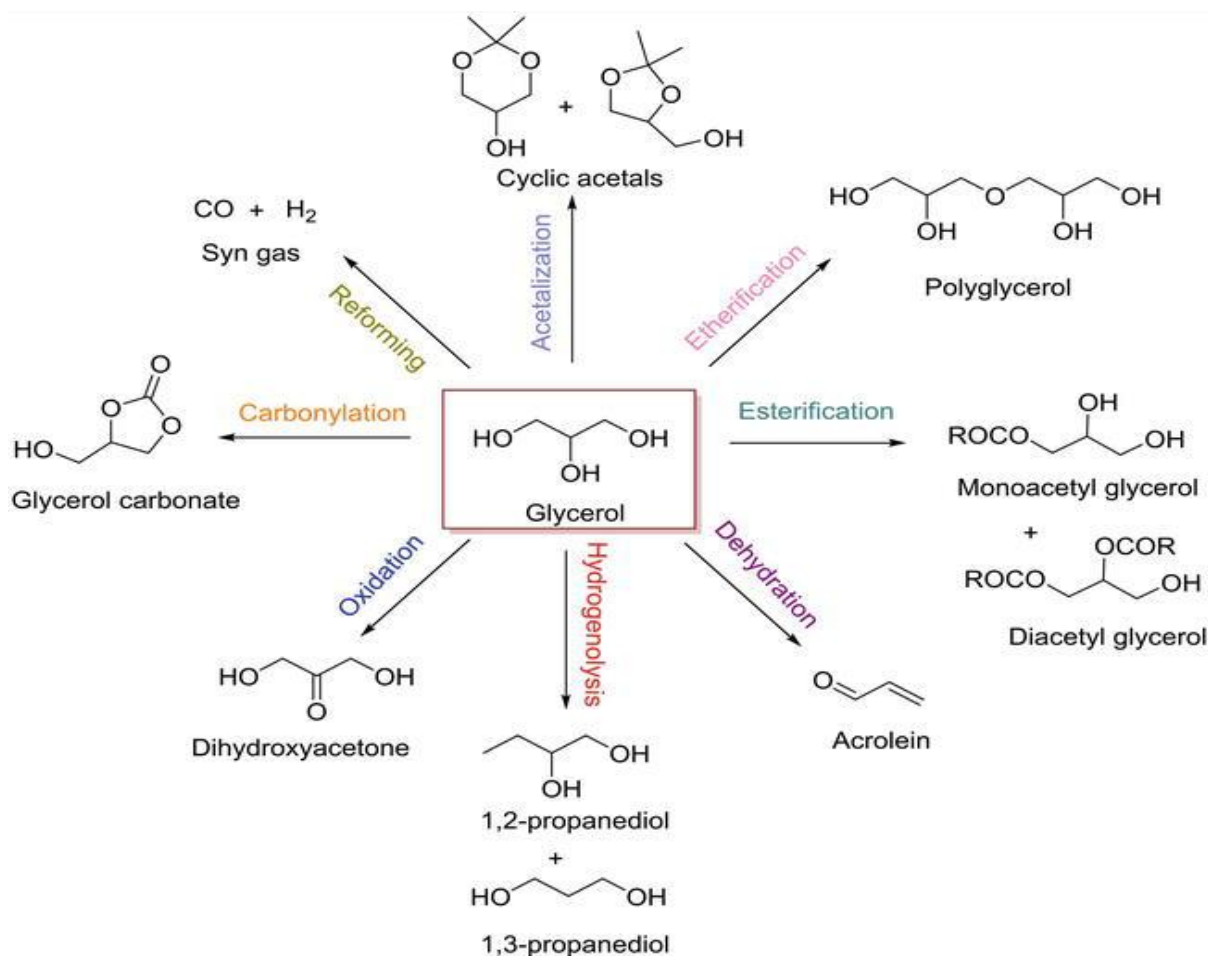


Figure 1.5. Valorisation of glycerol to different value-added products.

1.7. Valorisation of glycerol

1.7.1. Acetalization of glycerol

Glycerol can be used for the synthesis of acetals and ketals by reactions with aldehyde and ketones synthesizing five or six-membered cycles, which are further used for surfactant production. Besides, glycerol oxygenates like acetal and ketals are tremendous fuel additives that upsurge viscosity, octane, cetane number, and oxidation stability. Acetals are significantly helpful in reducing carbon monoxide emissions from diesel engines and improving the cold flow characteristics of transportation fuels. It acts as a useful solvent and plasticizer in the polymer industry, solubilizing and suspending agent in pharmaceuticals. Solketal acts as an active agent to lessen the gum formation increases oxidation stability, and improves the octane number when added to gasoline. The ketalization reaction of glycerol continues via an acidic

catalytic mechanism; therefore, catalysts with strong acidity might lead to high glycerol conversion [26-27].

1.7.2. Dehydration of glycerol

Recently, the dehydration of glycerol has instigated expectancy and interest as it may produce acrolein as a main product based on the catalyst used and the adopted reaction conditions. Acrolein is a valuable chemical used as a reagent or intermediate in industries to produce various compounds like methionine, acrylic acid, glutaraldehyde, etc. Acetol is generally used in textile trade as a reducing agent for dyes instead of sodium dithionite. Also it is frequently a food additive to confer odour and flavour to bread and milk goods. In the cosmetic production, it is used as a constituent in skin tanning products. Acetol can be used as a raw material to synthesise chemicals like acetone, propanol and 1,2- propane diol. Many catalysts like zeolites, naflon composites, phosphoric acid, silicotungstic acids, alumina etc., are extensively used to produce acrolein by dehydration glycerol [28 - 29].

1.7.3. Etherification of Glycerol

Recently glycerol ethers have been used as an excellent fuel additive by directly blending with diesel fuel. The etherification of glycerol takes place via different alcohols like ethanol, isopropanol, t-butanol and isobutene over Amerlyst type catalysts such as Amberlyst-15, amberlyst-36, montmorillonite K10, strong acidic ion-exchange, etc. The reaction between Gly and alcohols was proceed mainly at ambient pressure through the optimized boiling temperature at diverse reaction time. Glycerol ethers can be added in varied proportions to diesel engines, improving cold properties and reducing contaminant emissions and viscosity [30-31].

1.7.4. Esterification of glycerol

One of the advantageous methods to create value-added compounds from glycerol is to acetylate it with acetic acid, which results in glycerin acetates. Glycerol and acetic acid are

esterified to produce various products, including acetins. Acetins are the names for glycerol's mono-, di-, and tri-esters. These acetins have excellent importance as a fuel additive in transportation. Triacetin demand has increased recently at a rate of about 5% yearly growth. Solvents, food additives, explosives, and safety plasticizers are all common uses of monoacetins. Diacetins can be used for the same purpose as acetins and can also be used as a raw material to make biodegradable polyesters. Triacetin (triacyl glycerol, TAG) is the utmost significant Gly derivative and accounts for around 10% of the market. It is frequently used as a cigarette filter, as a fuel additive, as an antiknock additive for gasoline, as a cosmetic constituent, as a food additive, as a solvent, and in other applications. Triacetin is a useful solvent and fixative for various flavours and perfumes due to its strong solvency power and low volatility [32-33].

1.7.5. Glycerol to synthesis gas

Synthesis gas (syn gas), the mixture of H_2 , CO, and CO_2 might be utilized as a potential intermediate for the biomass conversion into fuel. Syn gas is a common feedstock for various processes like Fisher-Tropsch synthesis (FT), methanol, dimethyl ether (DME) production, and ammonia synthesis. Recently, the generation of H_2 and syngas has become another potential route for glycerol valorisation. Hydrogen can be produced by synthetic routes like steam reforming, dry reforming, partial oxidation, aqueous phase reforming, autothermal reforming, pyrolysis, and anaerobic fermentation. A diverse range of catalysts comprising noble metals such as Pd, Rh, Ir, Pt and Ru is used for providing excellent conversion of glycerol to syngas. Furthermore, catalysts centred on transition metals like Ni, Co, and Cu are used considerably for syngas production. Among all these metal-containing catalysts, Ni is the best conventional catalyst applied in the steam reformation of glycerol due to its superior catalytic activity [34-35].

1.7.6. Halogenation of glycerol

The halogenation of glycerol produces glycerol halohydrins, like glycerol chlorohydrin and glycerol bromohydrins. These compounds are applied in pharmaceutical preparation because of their antibacterial, mucolytic, and fungicide characteristics. Glycerol iodohydrin can be utilized to synthesize cardiolipins which is a key intermediate in treating type 2 diabetes. Iodohydrins and bromohydrins are naturally present in marine algae's essential oils. Similar to this, dichlorohydrins are inexpensive glycerol derivatives that are extensively employed in industrial uses. Industries use chlorohydrin to synthesize further epoxide, epoxy resins, elastomers, pesticides, plasticizers, rubbers, etc. Epichlorohydrins (ECH) mainly produce wind turbine blades in Asia Pacific regions. It is also helpful in the reinforcement of paper and teabags. The sustainable synthesis of halohydrins is catalysed by hydrochloric acid, acetic acid, halogens, hydrotalcites, $\text{NaI}/\text{Al}_2\text{O}_3$, $\text{NaBr}/\text{Al}_2\text{O}_3$, $\text{KI}/\text{Al}_2\text{O}_3$ etc. at optimized reaction condition providing up to 99% conversion of glycerol and 100 % selectivity towards halohydrins [17, 36].

1.7.7. Hydrogenolysis of glycerol

In this reduction process known as hydrogenolysis, chemical bonds in the organic substrate are broken and hydrogen is added to the resulting fragments. When glycerol is reduced selectively, 1,2-propanediol, 1,3-propanediol, acetol, and ethylene glycol are produced. Propanediol is commercially used in paints, antifreeze coolants, liquid detergents, de-icing reagents, cosmetics, food, and tobacco industries. 1,2-propanediol are extensively used as feedstock for preparing polyester resins for film in fiber making and in medicinal industry. Similarly, 1,3-propanediol is used as a monomer in polyether, polyurethanes, polytrimethylene terephthalate (a biodegradable polyester having great potential for use in carpet and textile manufacturing). Some industries apply synthetic processes like hydroformylation-hydrogenation, hydration, and fermentation to synthesize propane diol (PD). Glycerol can be converted to propane diol

via a catalytic hydrogenolysis process. The reaction process for the conversion of Gly to PD has been widely studied in the past few decades. There are three typical reaction mechanisms involved through which glycerol can be transformed to propane diol viz., (I) dehydration-hydrogenation (II) Dehydrogenation-dehydration-dehydrogenation (III) direct-hydrogenolysis. In the dehydration-hydrogenation mechanism, glycerol is dehydrated through an acid-catalysed reaction forming an intermediate and further hydrogenated to generate the final product. In the Dehydrogenation-dehydration-dehydrogenation mechanism, glycerol reactions occur in neutral water and alkaline conditions. Here, the reaction follows three steps, dehydrogenation, dehydration and hydrogenation, to give the final product PD. In direct hydrogenolysis reaction, glycerol directly undergoes hydrogenation to form propane diols using many heterogeneous catalysts. Traditionally, transition metal-based catalysts like CuO/CuCr₂O₄, Cu/SiO₂, BaCuO/CuCr₂O₄, Cu/Al₂O₃, PdCuO/CuCr₂O₄ are used for the transformation of glycerol to propanediol with high yield percentage of about 95%. Many transition metals like Cu, Ni, and Co are extensively utilized for propanediol production [37-38].

1.7.8. Oxidation of glycerol

Glycerol having multifunctionality properties, can be oxidized to several valuable chemicals such as glyceric acid, glyceraldehyde, hydroxyl pyruvic acid, dihydroxy acetone, meso oxalic acid, formic acid and tartaric acid. Glyceraldehyde, one of the oxidized products of glycerol, extended its applications in the skin-care, organic, and medicinal industries. Numerous heterogeneous catalysts used to selectively oxidise glycerol are designed on noble metals like platinum, gold, silver, and others. Dihydroxy acetone is one of the various chemicals made from oxidised glycerol and is a key component in sunless tanners and cosmetics. Although DHA exhibits a dimeric structure, in water, it dissociates easily to the monomer-containing carbonyl group, which acts as a tanning agent. Many heterogeneous catalysts like Pt, Pt/C, Ce/C, Bi-Pt/C, etc., provided appreciable conversion of glycerol with 70 – 90 % selectivity

towards DHA at optimized reaction conditions using a trickle bed reactor. One of the byproducts of glycerol's oxidation is glyceric acid, which serves as a crucial intermediary for the subsequent byproducts of tartronic acid (TA), mesoxalic acid (MA), and keto-malonic acid oxidation. With a maximum yield of 54.2% and 96.1% conversion of glycerol, respectively. Various effective catalysts, such as Pd/C and Pt/C, when used with NaOH as a base, create the disodium salt of glyceric acid. Similarly, many other value-added chemicals like pyruvic acid, formic acid, and mesoxalic acid are an oxidized products of glycerol and have vast applications in food, pharmaceuticals, and cosmetic industries [39-40].

1.7.9. Polymerization of glycerol

Polyglycerol is a useful biodegradable biomaterial based on its regulating mechanical characteristics. It is mostly employed in tissue engineering and biomedical applications. Polyglycerols and polyesters have wide applications in lubricants, surfactants, cosmetics, and food additives. The reaction of glycerol to form polyglycerol and polyglycerol esters is catalysed by homogeneous and heterogeneous catalysts like Na_2CO_3 , MCM-41, and mesoporous materials via polymerization and polycondensation reaction. The glycerol polymerization mainly occurs at a temperature of 120 -130 °C for 24 h under an inert atmosphere. On the other hand, in the condensation stage, terminal groupings of branched chains are what lead to the network's gelation. Commercial microwave reactors also use glycerol to polymerize glycerol into polyglycerols [41-42].

1.8. Transesterification of glycerol

The transesterification reaction is one of the most accessible process for producing GlyC from dialkyl carbonate and Gly. It is a reaction widely used in industrial operations and has attracted more interest in recent years for producing biodiesel. Transesterification can be used in industry to yield GlyC from glycerol, ethylene carbonate, or dialkyl carbonates. Glycerol 1,2-carbonate is an environmentally benign, least harmful, and biodegradable compound. Its chemical name

is 4-(hydroxymethyl)-1,3-dioxolane-2-one. It is a five-membered cyclic carbonate with particular chemical reactivity because it has two distinct functional groups, hydroxyl and cyclic carbonate. These chemically active functional groups can aid in the transformation of glycerol into a number of molecules that have added value. [43]

1.8.1. Introduction to glycerol carbonate

Glycerol carbonate synthesis is one of the significant glycerol transformations with perfect physicochemical characteristics. Some of the important properties of glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one), includes its high stability, strong biodegradability, low toxicity, high boiling point, and low flammability which makes it one of the most promising chemicals. Numerous industries use glycerol carbonate as a solvent, including the manufacturing of resins, plastics, medicines, polycarbonates, polyurethanes, and glycidol-based polymers. It is also used as an intermediate in organic synthesis and surfactant. The common properties of glycerol carbonate are presented in Table 1.2 [44]. The different application of glycerol carbonate is depicted in Figure 1.6. In the semiconductor industry, glycerol carbonate is used as an electrolyte in lithium-ion batteries. In contrast, in the chemical industry, it serves as an intermediate in the production of glycidol, bio-lubricants, bio based polar solvents, liquid membranes for gas separation, surfactants and detergents, and blowing agents. Glycerol carbonate is a curing agent in cement and concrete in the building and construction industries, whereas it works as a plant-activating agent in agricultural fields. The cosmetic and personal care industries often use glycerol carbonate, which has nutraceutical and cosmeceutical qualities, as an emollient and solvent in nail polish remover, lipsticks, and wetting agents for cosmetic clays. GlyC is used in the polymer and plastics industries to create polyesters, and polycarbonates [45].

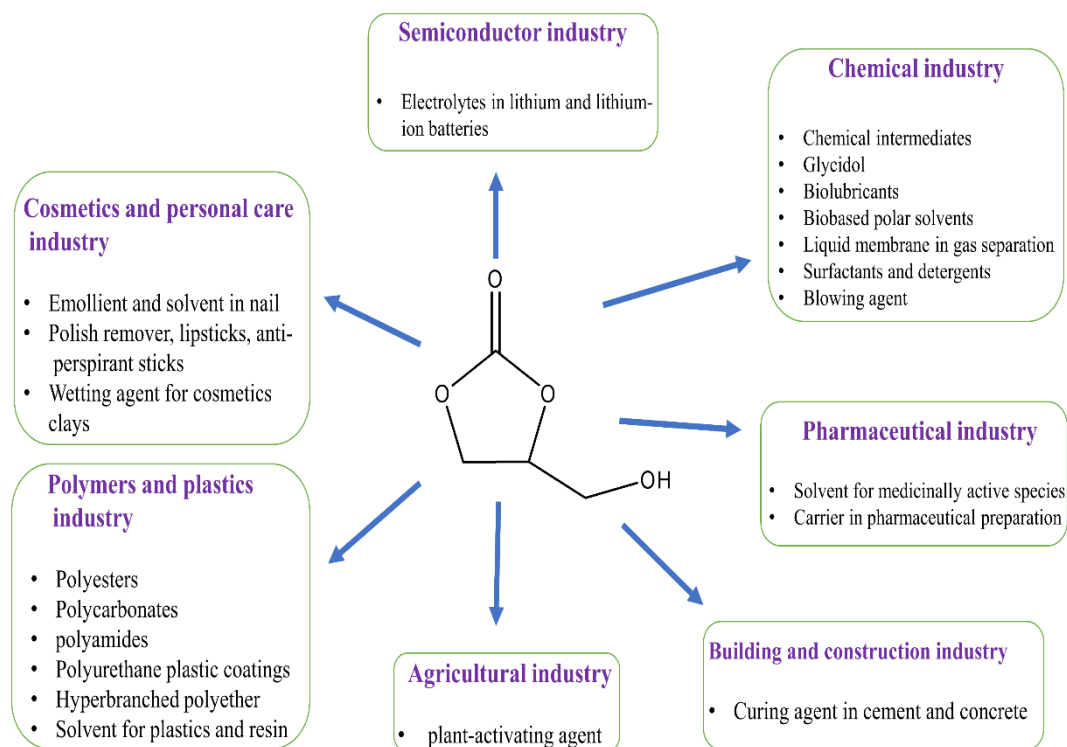


Figure 1.6 Application of glycerol carbonate

Table 1.2 Physical property of glycerol carbonate

Properties	Glycerol carbonate
Chemical Formula	CH ₂ OH-CHOH-CH ₂ OH
Form	liquid
Colour	Colourless
Molecular Weight (gmol ⁻¹)	118.09
Boiling Point °C	137
Melting Point °C	-69
Relative Density (25 in gml ⁻¹)	1.4
Vapour pressure, 177 C(bar)	0.008
Flash point	190
Dielectric constant (ESU)	111.5
Hansen solubility parameter delta P, 25C (MPa ^{1/2})	19.5
Hansen solubility parameter delta D, 25C (MPa ^{1/2})	17.9
Hansen solubility parameter delta H, 25C (MPa ^{1/2})	21.5
Hildebrand solubility parameter 25C (MPa ^{1/2})	34.1

1.9. Synthetic routes for glycerol carbonate from glycerol

According to reports, there are numerous ways to convert enormous amounts of waste glycerol into glycerol carbonate [46]. Figure 1.6 illustrates promising pathways for synthesizing glycerol carbonate that centre on reactions centered on cheap, bio-based, and easily accessible raw materials.

1.9.1. Reaction of carbon monoxide with glycerol

Glycerol carbonate can be formed by the reaction between CO and O₂ in the presence of an appropriate catalyst. This synthetic procedure, also known as oxidative carbonylation of glycerol, involves carbonation and oxidation. The reaction of glycerol with CO and O₂ in the presence of catalysts can produce glycerol carbonate. Cu(I)-catalysts and PdCl₂ (1,10-phenanthroline) with KI are catalytic systems that have been reported to provide good yields. Due to carbon monoxide's toxicity and the inherent challenges associated with handling it safely at both laboratory and commercial sizes, this process is limited and cannot be proceeded to a larger scale [47-48].

1.9.2 Reaction of carbon dioxide with glycerol

Glycerol and carbon dioxide can also be combined to create glycerol carbonate in the presence of catalysts. Glycerol carbonate can be produced by adding carbon dioxide (CO₂) directly in a supercritical state in the presence of several catalysts under 453K temperature and 5MPa pressure. The first catalyst for producing glycerol carbonate from a CO₂ source was a tin-based catalyst called n-Bu₂Sn (OMe). At 13.8 MPa and 120°C for 4 hours, a catalyst containing around 1 mol% nBu₂SnO produced 35% of the glycerol carbonate yield, while the above reaction conditions only produced 5% GlyC yield [46]. A variety of heterogeneous catalysts, including Amberlyst A26 OH-, Amberlyst A26 HCO₃-, 13X Zeolite (8–12 mesh), TBA Br-, TBA, NH₄SO₄-, etc., were employed to produce glycerol carbonate under supercritical carbon dioxide (SC-CO₂) conditions. A source of organic carbonate called ethylene carbonate was

used in SC-CO₂ conditions to get a greater GlyC yield, and this method produced a yield of 32.15% GlyC [49]. The pace of the reaction was speed up, and the yield of GlyC was markedly increased by adding alcoholic solvents like methanol and isopropanol. Thermodynamic analysis showed that the generation of GlyC under the SC-CO₂ scenario is thermodynamically constrained. However, the carbonation of Gly with CO₂ suffers from high-pressure requirements and thermodynamic limitations. This leads to a meagre GlyC yield, which greatly increases the production cost of glycerol carbonate; as a result, the synthetic process of GlyC using carbon dioxide is not encouraged in recent times [50].

1.9.3. Reaction of phosgene with glycerol

Utilizing phosgene (COCl₂) as one of the carbonylation sources, glycerol can also be converted into glycerol carbonate. The process of creating cyclic carbonate by the reaction of ethylene glycol with phosgene. With the addition of liquid phosgene, carbonate chloroformate ester was also made from glycerol. In this procedure, liquid COCl₂ and Gly were slowly combined while stirring for nearly 6 hours at room temperature, yielding 90%. Although using phosgene to generate organic carbonate appears to be a relatively straightforward and efficient method, the reaction process is not desired due to the gas's toxicity and handling challenges [51, 52-53].

1.9.4. Reaction of urea with glycerol

An attractive process is the formation of GlyC from Gly and NH₂CONH₂ in the presence of an appropriate catalyst. The use of NH₂CONH₂ for the production of GlyC in the presence of a appropriate catalyst is one of the interesting paths. It is also one of the conventional techniques for creating glycerol carbonate. Catalysts with Lewis acidic sites in this reaction process play a major role in producing a considerable yield of GlyC under ideal reaction conditions. For the manufacture of GlyC using urea as the solvent, catalysts including magnesium sulphate, zinc oxide, zinc sulphate, metal oxides such as CaO, La₂O₃, ZrO₂, zirconium phosphate, HTC-Zn produced from hydrotalcite, and zeolites ZSM-5 are utilized [54-55]. The conversion of urea

to isocyanic acid is the first stage in the glycerolysis of urea. Further, it reacts with glycerol in the second step. The key benefit of this procedure is that urea is easily accessible and inexpensive, and the by-product (ammonia) created in this process can be used further for urea production. Glycerolysis with urea has several difficulties. Like all reaction processes, it necessitates continual removal of the NH_3 gas created during the reaction process to improve the GlyC yield. However, the GlyC yield rate is hampered by the generation of highly undesired compounds such as biuret, isocyanic acid, and isocyanates [56-57].

1.9.5. Reaction of alkylene carbonate with glycerol

Glycerol carbonate can be synthesized from glycerol by trans carbonation reaction with alkylene carbonate. By trans-carbonating glycerol with alkylene carbonates, GlyC can also be produced from glycerol. Several catalytic systems, including quaternary ammonium salts immobilized on mesoporous MCM-41, basic oxides (MgO) or mixed oxides (Al/Mg, Al/MgO) derived from hydrotalcite, zeolite with basic sites, and Amberlyst A26 (HCO_3) ion exchange resin, have been reported to produce good yields. For example, Cho et al. (2016) reported that the reaction of Gly with EC in the presence of RNX-MCM41 provided 92% GlyC yield, while Clement et al. (2010) stated that 7wt% Mg/Al₂O₃ hydrotalcite catalyst provided 82% GlyC yield [46]. Ethylene carbonates are more frequently used as a reactant with glycerol for GlyC production in solvent-free conditions to provide the highest conversion of glycerol at optimized reaction conditions. The primary downside of this procedure is that it necessitates using lower pressure (35mmHg) to eliminate the ethylene glycol by-product and shift the chemical reaction to synthesizing glycerol carbonate [58-59].

1.9.6. Reaction of dialkyl carbonate with glycerol

Dialkyl carbonates, such as dimethyl carbonate (DMC) and diethyl carbonate (DEC), can be used to transesterify glycerol. As they are considered to be green solvents and have an eco-friendly character, these compounds are thoroughly researched for the synthesis of GlyC. This

method uses DMC as its solvent and produces CH_3OH as a by-product, which is easily separated by distillation and used in the subsequent synthesis of biodiesel. Because the catalysts and solvent can be easily separated throughout this process and no special conditions are required, it is a safer and more environmentally friendly alternative to producing GlyC. Many catalytic methods are being researched for the transesterification of glycerol using DMC and DEC. Many different kinds of catalysts, whether homogeneous or heterogeneous, are used to improve glycerol conversion. The often-used DMC as a carbonate source exhibits improved efficiency at mild reaction conditions, minimal toxicity, and high yields of GlyC from glycerol. Numerous homogeneous catalysts, such as CaO , MgO , K_2CO_3 , KOH , NaOH , etc., produce glycerol carbonate and have high turnover frequencies. However, the separation process of the catalyst was much more challenging, so a heterogeneous catalyst was used to produce GlyC to eliminate these problems. For the transesterification reaction of Gly with DMC, numerous heterogeneous catalytic systems, such as KNO_3/CaO , Mg-La , Mg/Zr/Sr , Li/ZnO , hydrotalcites, Mg/Al/Zr , hydroxyapatite modified with KF , $\text{LiNO}_3/\text{Mg}_4\text{AlO}_{5.5}$, CaO/ZrO_2 , etc., have been thoroughly explored [60, 61, 62, 63]. In addition to taking less time than the reactions using phosgene and alkylene carbonates, this synthesis approach employing DMC does not necessitate high energy usage or strict separation. DMC's lower boiling point ($90\text{ }^\circ\text{C}$) makes it simpler to separate methanol and unreacted DMC from the resultant mixture during distillation. Like DMC, diethyl carbonate (DEC) also utilized as a carbonate source, and glycerol carbonate is synthesized using DEC and ionic liquids, including quaternary ammonium salts, Mg-Al hydrotalcite, CaO , and MgCO_3 . Other catalysts for the process, including 1,3 dichloro distannoxanes and 1-n-butyl-3-methylimidazolium-2-carboxylate, were as well reported [64].

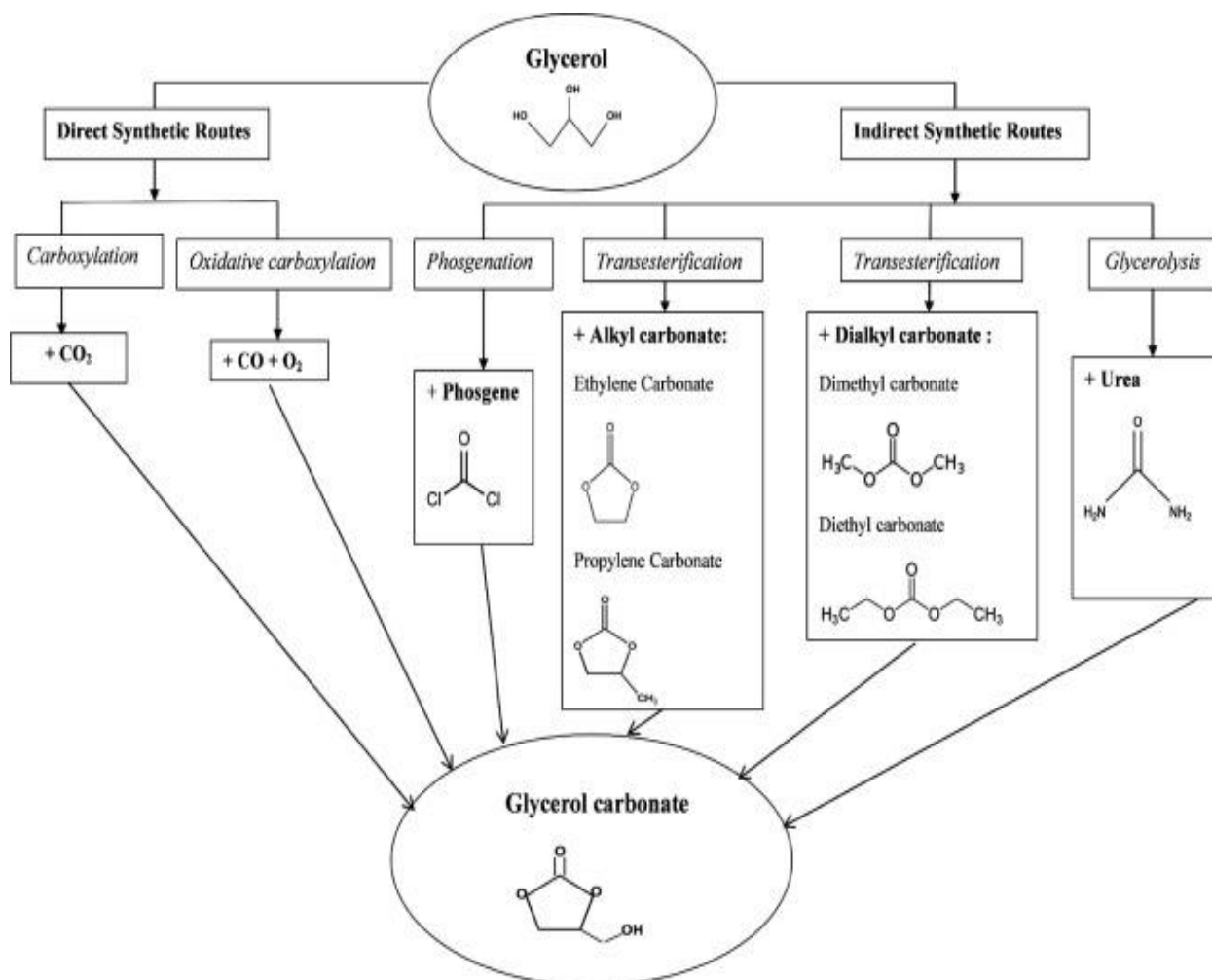


Figure 1.7 Synthetic pathways for glycerol carbonate.

1.10. Knowledge gaps

The transesterification reaction of Gly with DMC employing both acidic as well as basic catalysts is a remarkable process. Glycerol carbonate has attracted much attention over the past couple of decades due to its adaptable reactivity and as a technique to valorize waste Gly, aided by the growing sustainability awareness. There were many other techniques to make this molecule, some of which were quite promising and were just about to be used commercially. Regardless of the relative efficacy of catalysts in transesterification reaction of glycerol, several have low concentrations of useful basic sites and quickly degrade upon re-use. By removing a proton from glycerol, catalysts' fundamental nature speeds up reactions. To get a high yield of GlyC by the transesterification of glycerol and take into account all the aforementioned

characteristics, it is necessary to build a highly active and reasonably priced heterogeneous basic catalyst with strong basic sites. Many homogeneous catalysts, such as MgO, NaOH, K₂CO₃, CaO, CaCO₃, KOH, LiOH, etc., have demonstrated remarkable catalytic action for the transesterification reaction of Gly with DMC. Still, removing these catalysts from the final mixture is very challenging. On the other hand, the production of glycerol carbonate makes considerable use of a variety of heterogeneous catalysts, such as CaO/Al₂O₃ (polyamide), Li/Mg₄AlO_{5.5}, Ti-SBA-15, CaAl-LDHs, Mg/ZrO₂, KF/La-Zr, HTC-Ni, and Li/ZrO₂ [65,66,67,68,69]. Most catalysts displayed decreased GlyC selectivity. The drawbacks of these catalysts comprise low recyclability, instability, prolonged reaction duration, the requirement for several solvents, and significant energy consumption [70,71,72]. Numerous publications emphasize the necessity for creating new heterogeneous catalytic materials that have strong basic sites, are recyclable, and are simple to recover. For the logical design of catalysts, it is essential to comprehend the connection between the physicochemical characteristics of the catalyst and its activity in glycerol conversion. Although it has been shown that basic metal oxides have a high basic strength, these compounds' stability poses serious issues. Preparing bimetallic oxides with enough basic strength is helpful since it increases catalysts' basic strength and stability. Enhancing the catalyst's reusability under the same reaction conditions is another consideration. Due to the basic nature of alkali and alkaline metal oxides, much research is being done on investigating their catalytic activity. Few transition metal-based catalysts have been used in the study of glycerol carbonate synthesis, although numerous literature studies have revealed the study of alkaline metal-based oxides like Ca, Ba, and Sr on the transesterification of glycerol as well as biodiesel generation process. Our primary goal is to investigate transition metal-based heterogeneous catalysts for glycerol transesterification reactions thoroughly. In this thesis, an attempt is undertaken to test a transition metal-based heterogeneous catalyst for glycerol conversion. Whatever the synthetic method for producing

GlyC at industrial and laboratory scales, it must satisfy some fundamental requirements for the viability of products, including

- If catalytic, it is necessary to utilize a less expensive, easily separable, and recyclable catalyst.
- A simple way of separation and purification ought to be used.
- Refraining from using solvents.
- A catalyst with a shorter reaction time and higher inherent safety (both hazardous and extremely combustible substances must be avoided).

These parameters make it clear that a synthetic method employing glycerol and DMC and transition metal-based catalyst seems to be the perfect choice. On the one hand, both the substances are environmentally friendly and inexpensively accessible on the market.

1.11. Literature Review

The study of previous literature on glycerol carbonate synthesis utilizing bio-waste glycerol obtained from the biodiesel industry via heterogeneous catalysts has been reviewed. Several catalysts created and explored for the transesterification reaction of Gly and the production of glycerol carbonate have also been discussed. Particular emphasis has also been given to the characterization of the catalysts and the co-relationship between the catalysts and their catalytic activity in the glycerol transesterification reaction.

1.11.1 Glycerol production and consumption

Glycerol is formed as a by-product of the transesterification reaction of edible and non-edible oils. A waste product of the biodiesel production procedure is glycerol, which is produced at a rate of about 10%. With 90% of the world's biodiesel production, Europe is one of the biggest producers and consumers of fuel. Compared to Europe, the U.S. and Brazil are scaling up production more quickly, and both are anticipated to succeed soon. By 2025, biodiesel is predicted to replace more than 30% of all on-road diesel in Brazil, Europe, India, and the United

States [73]. Biodiesel has been demonstrated to be a valuable fuel for petro-diesel engines since it is cleaner, renewable, and greener. In addition, US replaced 2% of the on-road diesel with BD under a B2 programme by 2012, and the market received an additional 363 million kg of glycerol. By 2027, the size of the worldwide glycerol market is anticipated to upsurge at a CAGR of 4.0, reaching USD 3.5 billion [74]. Throughout the forecast period, the market is anticipated to be driven by an improved standard of living along with a rising consumer desire for new, high-quality personal care products. Asia Pacific is one of the key regions for glycerol imports and exports, with Indonesia and Malaysia serving as the leading exporting nations. Glycerol manufacturing in the area is further aided by the region's abundant raw material supply and high biodiesel production. The region's most significant imports come from several nations, including Russia, Germany, the Netherlands, and Denmark. The Department of Energy (DOE) USA has highlighted glycerol as crucial for constructing future bio refineries [75]. Economic projections have shown that by increasing the value of the glycerol by-product, the net production cost of B100-type biodiesel can be decreased from US\$0.35 per litre [76,77].

1.11.2. Catalytic conversion of glycerol to high value added products

Due to its abundance and excellent properties, such as non-toxicity, bio sustainability, and biodegradability, glycerol with three hydroxyl groups offers numerous opportunities for developing numerous value-added products. Technically, various chemical routes can be used to customize glycerol's multifunctional structure and characteristics. Glycerol is also transformed into several chemicals with additional value, which promotes the utilization of clean, renewable energy sources. Regarding the activation and utilization of glycerol, catalysis is a crucial component of green chemical technology. The conversion of Gly into different value-added products has been shown to utilize both homogeneous and heterogeneous catalysts. The consequence has been the employment of numerous unique catalytic techniques through various reactions [78,79,80].

1.11.3. Catalytic approach in transesterification of glycerol

Numerous catalytic systems have been documented in the literature for synthesizing GlyC from glycerol with DMC up to this point. The transesterification process is one of the diverse and simple methods for producing glycerol carbonate. The transesterification process's key benefits include its adaptability requirement in both the lab and industry. In addition, both homogeneous and heterogeneous catalysts are used to catalyse this chemical process. Rokicki et al. (2005) reported using Mg-Al hydrotalcite as a catalyst for the transesterification reaction of Gly with DMC to produce GlyC, yielding 82% of GlyC under optimal conditions at 100 °C for 1h [81]. Due to the charge compensation of positively charged ions, they used the layer of anionic clay hydrotalcite, in which the anionic species carbonate and hydroxide were situated between the layer. Song et al. (2017) reported using a Li/ZnO catalyst to produce glycerol carbonate and reported 96% glycerol conversion at an optimal reaction temperature of 85°C for 90 min [82]. Although the catalyst effectively converted glycerol, it was only stable for the fourth run of the reaction. The primary cause of the deactivation of catalysts, i.e., after four runs in the transesterification reaction, was the leaching of metal ions. Galadima et al. (2017) developed ionic liquids immobilized on mesoporous MCM-41 and evaluated the catalyst's efficiency in synthesizing GlyC [83]. The catalytic reactivity benefited from the higher temperature and extended duration. Without experiencing any loss of its primary activity, the catalyst was utilized three times in a row. Wang et al. (2018) suggested Mg/Al/Zr catalysts for the transesterification reaction of Gly with DMC and achieved excellent conversion of glycerol 99% within 1h at 90 °C reaction temperature [61]. Similar to this, Simanjutak et al. (2013) reported using an Mg/La catalyst to synthesize GlyC and achieved a 94% yield of GlyC under mild reaction conditions (75 and 90 min of reaction duration) [65]. The mechanistic routes for the generation of GlyC were also thoroughly explained. Marakatti et al., (2015) reported metal ion-exchanged zeolites as a highly active solid acid catalyst for the transesterification reaction

of Gly with DMC, which is how GlyC is produced. It was also highly stable and recyclable up to six times. They suggested a reactor mathematical model get the kinetic parameters under optimal reaction conditions. In this experiment, the reactor model's mass balances were built in, and the reaction sequence was fixed. The chemical equilibrium for GlyC synthesis was estimated, and theoretical calculations were compared with experimental data and matched. According to the equilibrium constant, the authors concluded that the transesterification of Gly and DMC was thermodynamically advantageous for generating GlyC. In this reaction process, temperature plays a vital role as well. Increasing the temperature can also enhance the chemical equilibrium constant. The deactivation of solid alkali and alkaline-based catalysts, such as CaO, Ca(OH)₂, KOH, and Ca(OCH₃)₂ was suggested in the literature for the transesterification of glycerol. Because all of the basic catalysts were converted into their respective carbonates during the first run of the reaction procedure, the conversion of glycerol was drastically reduced when the catalysts were recycled [83, 84]. The catalysts in the reaction medium suffered from dissolving losses. According to Bai et al. (2011) [70], KF-modified hydrotalcite is a very good heterogeneous catalyst for producing GlyC utilizing DMC and glycerol. At the optimal reaction temperature of 78 °C for 50 minutes, this catalyst produced 93% yield of GlyC with 99% conversion of glycerol. Its catalytic activity was comparable to that of homogeneous KF catalysts, and it was easily recovered and regenerated. Similarly, Bai et al. (2013) reported using another catalyst to produce glycerol carbonate, NaOH/ γ -Al₂O₃. Furthermore, the transesterification of glycerol using this catalyst was demonstrated to be one of the most effective heterogeneous catalysts. The authors discovered the conversion of glycerol to 97.9% and 99% selectivity of GlyC under the reaction conditions of 2:1 molar ratio of DMC to Gly at 78 °C for 1 h of reaction time. The NaOH/ γ -Al₂O₃ comparative investigation of catalytic activity with another catalyst, especially K₂CO₃, revealed that the former catalyst was significantly superior to the latter in terms of its conversion percentage of glycerol and basicity

as well [85]. In the transesterification reaction of Gly with DMC, Ochoa-Gomez et al. (2012) used trimethyl amine (TMA), one of the homogeneous catalysts [86]. They investigated the conversion of glycerol while optimizing reaction parameters viz., temperature, the ratio of DMC to glycerol in molar form, and reaction time, among others. They discovered that at 68 °C, 4:1 DMC to glycerol in molar form, and after 2.5 h, at 90 °C, the GlyC yield reached up to 98%. They also put up a reaction theory to support the product yield achieved with such a homogenous catalyst. The conversion of glycerol was quite effective, but it was too difficult to separate the catalyst for use in the same reaction step later. For example, Naik et al. (2009) reported using quaternary ammonium salt to synthesize GlyC and obtained an excellent yield of 93% [87]. Many researchers also used basic ionic liquids for the synthesis of GlyC. This procedure isolated a quantitative yield of pure product using a threefold excess of DMC and 15% ionic liquids. They discovered that the IL might be used at least four more times without noticeably lowering conversion and yield. Similar methods were used by Sandesh et al. (2013) to transesterify glycerol with DMC utilizing a catalyst supported by KF. Numerous oxides and non-oxide support, such as SiO₂, Al₂O₃, ZnO, and ZrO₂, increased the support's catalytic activity. To get rid of KF that was only weakly adsorbed to the catalyst surface, they changed the way supported KF catalysts were created. The creation of simple basic sites primarily depends on how much KF interacts with the support material. The most active supported KF catalyst, KF/Al₂O₃, demonstrated 100% selectivity for GlyC and a glycerol conversion rate of 95.8%. Compared to existing supported KF catalysts, the catalyst had no metal atom leaching and demonstrated superior catalytic activity with 5-time recyclability [88]. Using a co-precipitation method, Liu et al. (2013) presented a variety of hydrotalcite-like layered double hydroxides (LDH) with various Mg/Al atomic ratios. They discussed the impact of calcination temperature on the function of the Mg/Al catalyst and discovered varying glycerol conversion rates. They also looked into the relationship between a catalyst's surface basic density and its

catalytic activity. They discovered that the latter was directly correlated with the former for the LDH catalyst [89]. Finally, they concluded that LDH calcined at 600 °C demonstrated maximal conversion of glycerol, i.e., 96% at optimal reaction conditions. Similarly, Khayoon and Hameed (2013) described a very efficient catalyst called $Mg_{1+x}Ca_{1-x}O_2$ calcined at 850 °C for transesterification of glycerol. The optimum reaction conditions for achieving the maximum conversion of glycerol at roughly 98% with 100% GlyC selectivity were a 1:2 glycerol to DMC molar ratio, 70 °C for 90 min of reaction time, and atmospheric pressure. The effective synthesis of glycerol carbonate was largely attributed to the synergistic interaction between metallic centres i.e., Ca and Mg species in the crystal structure of the catalyst [90]. N-heterocyclic carbenes were described by Hervert et al. (2014) as an effective organo-catalysts for the production of GlyC from glycerol and DMC. For a reaction duration of 30 mins at room temperature, they obtained an excellent yield of GlyC [91]. Qing et al. (2018) investigated various amine-based catalysts for the synthesis of GlyC from glycerol using DMC. In this study, amidines such as 1,8-diazabicyclo [5,4,0] undec-7-ene (DBU) and 1,5-diazabicyclo [4,3,0] non-5-ene (DBN) were discovered to be excellent catalysts for this reaction. DBU as a catalyst achieved 98% glycerol conversion with 96% GlyC selectivity [92,93]. For the transesterification of glycerine with DMC, Wang et al. presented a catalyst made from used baby diapers (DBDWS-500) in 2019. At the optimal parameters like 4:1 of DMC to Gly molar ratio, for 60 min at 75 °C, they achieved 95.6% of Gly conversion with 93.6% GlyC yield. The catalyst provided 92% conversion of glycerol and was extremely stable up to the eighth cycle [94]. Similar to this, Mohanty et al., 2019 produced and used RK-30% - 800, a waste material-derived catalyst, in the transesterification of glycerol. In this research, they looked at the effects of doping several alkali and alkaline earth metals (K, Sr, and Mg) onto red mud at various weight percentages and calcination temperatures. They concluded that K-doped red mud catalysts used for the transesterification process of glycerol had superior activity and catalytic

stability than other Sr and Mg-doped catalysts. The existence of the highest surface active sites of K_2O , which considerably increased the fundamental features of the catalyst compared to other metals doped RM catalysts, was the primary cause of RK-30%-800's superior activity. At optimal conditions of 90 min reaction time at 75 °C under normal atmospheric pressure and 3:1 of DMC to glycerol molar ratio, they achieved 98% of glycerol conversion with 94% GlyC yield [95].

These are the few reports published on the use of transition metal-based heterogeneous catalysts in the transesterification reaction of Gly with DMC, even though it has excellent fundamental properties. Due to their great thermal stability, biological and chemical activity, high surface area, high thermal conductivity, nanocrystalline structure, and redox characteristics, transition metals are the substances that are extensively investigated for using catalysis. They are used as catalysts in various chemical reactions, including dry reforming, oxidative dehydrogenation, dehydrohalogenation, water gas shift reaction, and transesterification. In this study, we explored the catalytic activity of transition metal-based heterogeneous catalysts for synthesizing GlyC and reported several characteristics of the catalyst responsible for effective activity towards GlyC. Major goal our research was to create transition metal-based catalysts and use them to transesterify glycerol with DMC to produce GlyC. Also, the role of active metal sites on the transition metal support towards transesterification of glycerol and the role of support metal on the activity of catalyst towards glycerol carbonate synthesis is studied.

1.11.4. Reaction mechanism involved in transesterification of glycerol

Transesterification reaction occurs between the reactants Gly and DMC to produce GlyC in the presence of a heterogeneous catalyst, as shown in Figure 1.8. Based on earlier mechanistic studies of the transesterification of Gly to GlyC, a likely mechanism has been proposed. The transesterification reaction follows the Langmuir-Hinshelwood (L-H) mechanism. The

transition metal site functions as the acidic centre on the catalytic surface, whereas the active metal (alkali or alkaline earth metal) centre operates as the basic centre in the designed catalyst. Following the adsorption method, glycerol first connects with the basic sites, whereas DMC then interacts with the acidic sites that are present on the catalyst surface, and both of these interactions take place close to one another (A). Deprotonating the main -OH group of Gly is done by the catalyst's basic sites (B). The carbonyl group of DMC coordinates with the Lewis acidic sites of the produced catalyst and increases its electrophilicity. Subsequently, the deprotonated primary -OH group of Gly acts in a nucleophilic attack on the activated carbonyl group of DMC, removing one molecule of methanol to produce an intermediate (C). The created intermediate (C) is subjected to intramolecular nucleophilic substitution to produce the desired product GlyC. Another molecule of methanol is removed from the mixture during the reaction [90, 96-97].

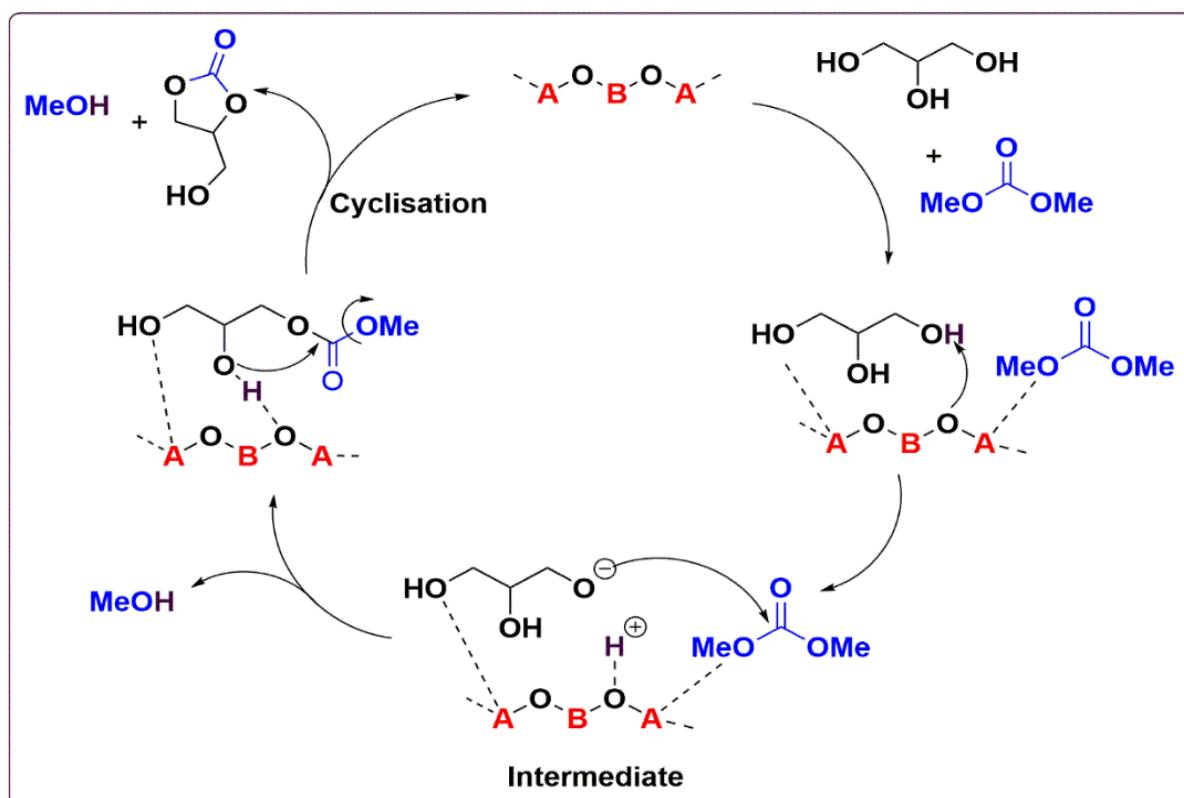


Figure 1.8 Reaction mechanism of glycerol carbonate synthesis.

1.12. Research objectives

Following are the point-wise objectives of the research undertaken:

1. Design of transition metal oxide supported heterogeneous catalysts for glycerol carbonate synthesis using dimethyl carbonate as carbonylating source.
2. Development of Li/TiO₂, Na/TiO₂, Ni/CaO, Mg/MnO₂ and Mg/CuO catalysts via simple wetness impregnation and coprecipitation method.
3. Disseminating knowledge of the Physicochemical properties of the catalyst by performing various characterization techniques.
4. Thoroughly characterizing the catalysts and establishing a link between those traits and the activities of the catalysts in glycerol conversion.
5. Assessment of catalytic activity towards glycerol carbonate synthesis.
6. Establishment of optimum reaction conditions for transesterification of glycerol.
7. Analysing the factors that contribute to the stability and reusability of catalysts.
8. Checking the environmental compatibility of the process by calculating green matrix parameters.