# CHAPTER 1

## Introduction

## 1.1 General introduction

The increase in population, environmental pollution concerns, and industrialization subsequently increase global energy consumption. Various natural resources, including sunlight, wind, oil, natural gases, etc., can be transformed into different types of secondary energy like solar, wind, nuclear, and electrical energy, meeting the energy demand globally [1]. As per the projection of the International Energy Agency for the year 2040 (IEA,2040), industrial energy demand is estimated to potentially reach up to 250 quadrillion Btu, whereas transportation and building energy consumption are estimated at 150 and 120 quadrillion Btu, respectively (illustrated in Fig 1.1). While crude oil extracted from biomass-based plants in the 19th century facilitated industrialization, fluctuations in some factors like price volatility, rapid oil depletion rates, and emerging economics and environmental concerns have become pivotal factors in driving the search for alternative energy sources to petroleum oil. To tackle the above-mentioned challenges, develop efficient and cost-effective processes for the sustainable production of fuels and chemicals [2,3]. Plant biomass serves as a renewable source of both energy and chemicals. The available sustainable source of liquid fuels is biofuel derived from plant biomass. It is evident that biofuel produces significantly lower greenhouse gases as compared to fossil fuels [4]. Various biofuels, including bioethanol, bio-methanol, and biodiesel, are considered alternative fuels which having zero emissions of environment-affecting gases like CO, $CO_2$, $NO_x$, $SO_2$, etc considered a greenhouse gas. These harmful gases contribute to global warming and are the primary culprits of environmental distress. Consequently, biodiesel has garnered increasing attention in recent decades as a sustainable and renewable energy alternative to petroleum fuel [5,6]. Biodiesel is produced by using edible and non-edible vegetable oils, animal fats, and microalgae via the transesterification process. It can be used as a fuel in a diesel engine with or without any modification in the engine. B2, B5, B20, and B100, which are different concentration terms, are blended with petroleum diesel.

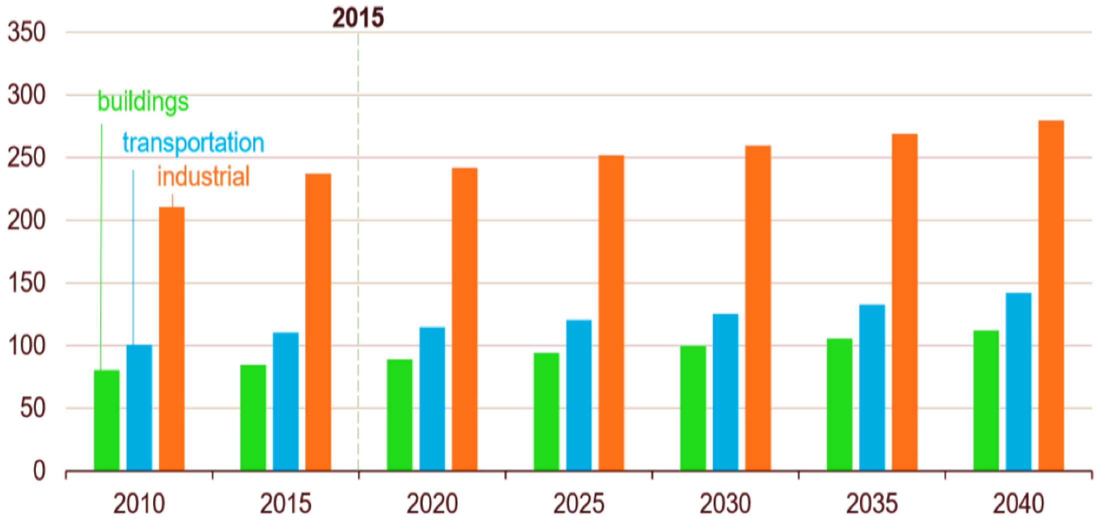

**Figure 1.1 World energy consumption by end-use sector (quadrillion Btu)**

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In recent years, there has been significant improvement in the production of biodiesel at a large scale, and this trend is expected to persist in the foreseeable future [7,8]. Excess amounts of crude glycerol are produced as a byproduct during biodiesel production as a glut in the market, which hampers the biodiesel industry. For every 100 % of biodiesel production, approximately 10 % of glycerol is produced as a byproduct [9]. Glycerol is used in several fields, like cosmetics, pharmaceuticals, food, polyethers, polyols, explosives, alkyd resins, triacetin, detergents, and the tobacco industry. Nevertheless, a substantial amount of glycerol generated from the biodiesel industry can not be fully absorbed due to the saturation in the market. The valorization of glycerol into various value-added products such as solketal, acrolein, polyhydroxyalkanoate, butanol, monoglyceride, citric acid, triacetin, and glycerol carbonate, which are extensively used as fuels, fuel additive, explosive materials, and detergents. Over the past decades, there has been a global upsurge in research aimed at discovering new and profitable ways for glycerol utilization. Consequently, the synthesis of innovative methods to utilize glycerol can play a crucial role in mitigating environmental impacts and minimizing biodiesel industrial losses [10–12].

## 1.2 History and discovery of glycerol

Glycerol, commercially referred to as glycerin, is a significant biodiesel byproduct produced by transesterification. Glycerol is considered non-toxic for both the environment and humans. Glycerol contains three hydroxy groups, which makes it more versatile: sweet taste, colorlessness, viscosity, and solubility in water. In 1783, the Swedish chemist Carl Wilhelm Scheele made a chemical discovery while studying the reaction between lead oxide and olive oil. From this mixture, he got the glycerine, which he named "sweet oil." Likewise, French chemist Michel Eugene derived glycerol from triesters, also known as fat. The term glycerol originated from the Greek word “glykys” in 2800 BC, meaning sweet[13,14]. The molecular structure of glycerol has been illustrated in Fig 1.2.

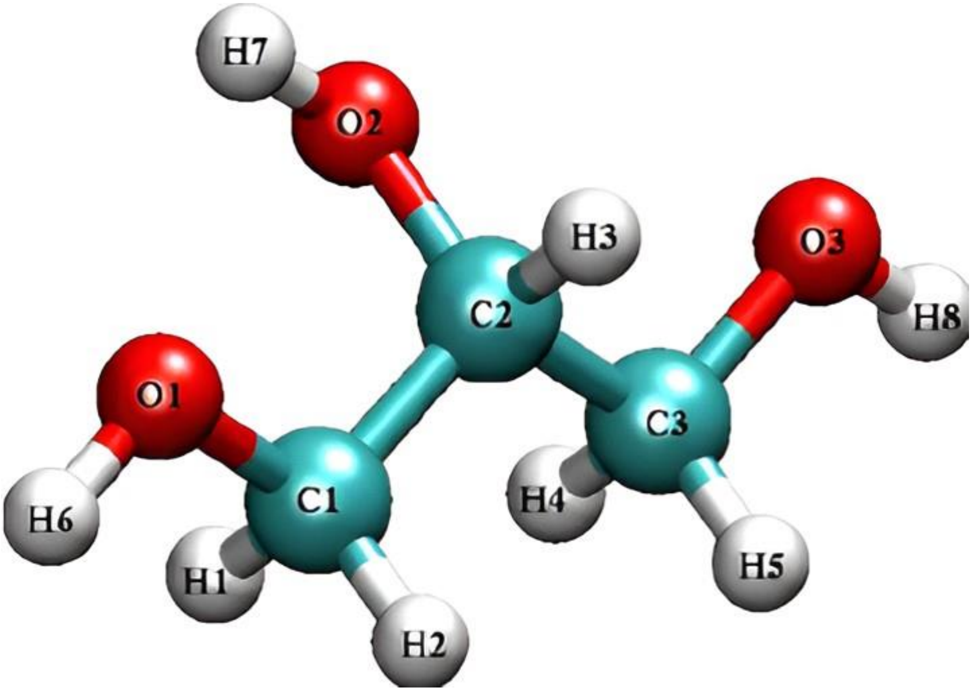


**Figure 1.2 Molecular structure of glycerol**

## 1.3 Physical properties of glycerol

Glycerol, an organic compound, exhibits remarkable stability and compatibility compared to other chemicals under normal storage conditions. Due to its simplicity, it is highly able to form hydrogen bonds within the same molecule and with the neighboring molecules. Its boiling point is very high due to its solid intermolecular force of attraction. Glycerol is highly soluble in polar solvents like water, methanol, and ethanol and also soluble in phenol, amines, glycol, aliphatic alcohols, fatty oils, and chloroform due to the presence of its hydroxyl groups. Additionally, it shows significant solubility in ether, dioxane, and ethyl acetate while insoluble in hydrocarbons. At 20 $^{o}$C the viscosity of glycerol is 15.0 poise. However, with an increase in temperature and the addition of water, its viscosity decreases. Conversely, the addition of electrolytes leads to increases in viscosity [15–17]. Some common properties of glycerol are given in Table 1.1.

**Table 1.1 Properties of Glycerol**

| **Properties** | **Standards** |
|---|---|
| Chemical Name | Glycerol |
| Chemical Formula | $CH_2OH\text{-}CHOH\text{-}CH_2OH$ |
| Density | 1.26 g cm$^3$ |
| Color | Colorless |
| Molecular Weight | 92.05 g |
| Surface tension | 63.4 dyne/cm |
| Melting Point | 20 $^{o}$C |
| Viscosity | 1499 c.p |
| Relative Density | 1.2613 |
| Specific heat | 0.5779 cal/gm |
| Boiling Point | 290 $^{o}$C |
| Thermal conductivity | 0.29 w/K |
| Flash point | 177 $^{o}$C |
| Fire point | 204 $^{o}$C |
| Food energy | 4.32 Kcal/g |

| | |
|---|---|
| Compressibility | 2.1 × 10 Mpa |

## 1.4 Importance of Glycerol

Glycerol, i.e., $C_3H_8O_3$, is a key constituent of triglycerides found in various natural lipids, including crude oil, animal fat, and vegetable oil. It is also referred to as glycerin, 1,2,3-trihydroxypropane. It is one of the main constituents in biorefinery feedstocks and also holds a prominent position due to its versatile behavior. It shows broad applications in various fields like the food industry, explosives, plasticizers, emulsifiers, pharmaceuticals, baby care products, antifreeze, humectants, and tobacco [18,19]. Glycerol is generally employed as a lubricating agent because of its elevated viscosity and ability to maintain fluidity. Due to its moisture-retaining properties, glycerol inhibits drying and reduces the tobacco combustion rate. Additionally, glycerol serves as a thickening agent in alcoholic beverages and liquors. It is also used in personal care product synthesis as it is used in toothpaste, hair care products, shaving cream, skincare, mouthwashes, and water-based lubricants. Its application extends to the tincture extraction process, where it is utilized as a 10 % solution. This solution is notably effective in inhibiting the tannins from precipitation in ethanol plant extracts. In herbal extraction procedures, glycerol is often employed as an alternative solvent to ethanol [20,21]. The broad application of glycerol in various fields is illustrated in Figure 1.3.

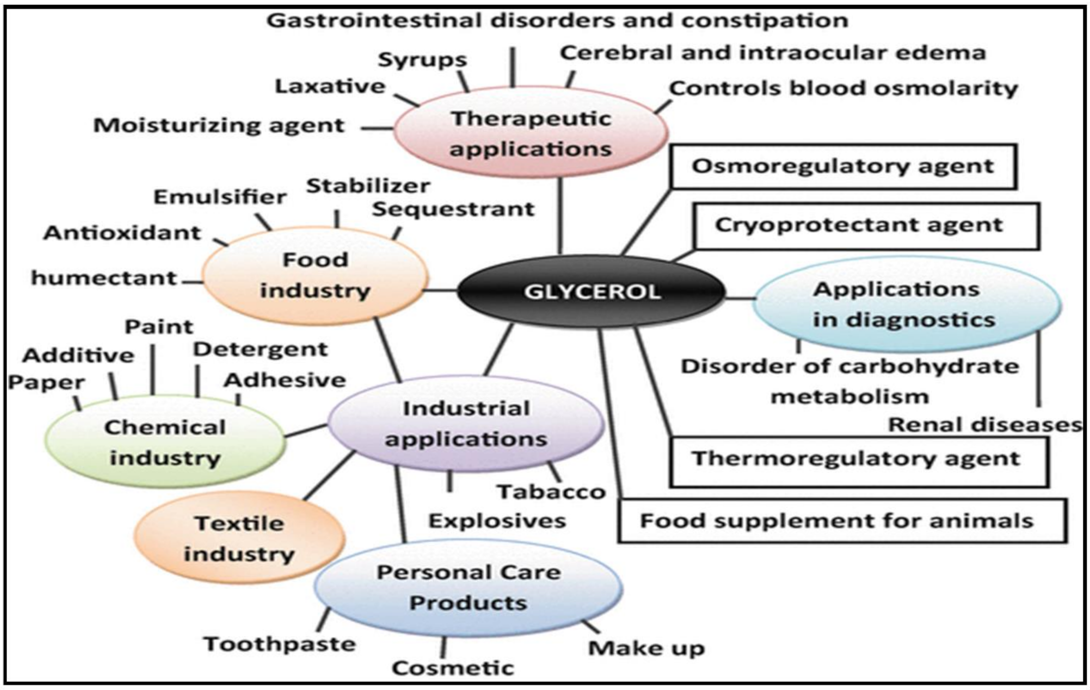
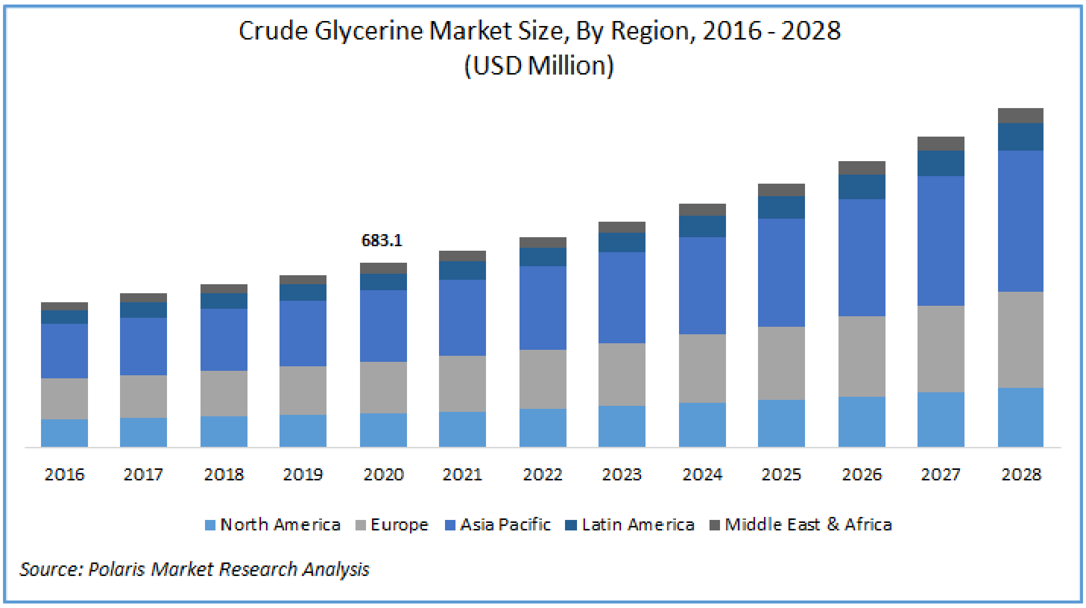


**Figure 1.3 Application of glycerol**

### 1.5 Global production of glycerol

The global demand for biodiesel production is attributed to its eco-friendly and renewable characteristics. Biodiesel is highly favored in the energy sector due to its unique attributes, such as a higher cetane number, elevated flash point, non-toxicity, absence of sulfur content, innate lubricating properties, and biodegradability. This surge in demand for global glycerol can be predominantly attributed to biodiesel's rising popularity. The renewable fuel regulations emerging in India, Canada, and South America are poised to ensure a notable increase in the supply of crude glycerol in the near future. At present, the USA's annual biodiesel production has achieved 250 million gallons per year, resulting in substantial production of glycerol as a by-product of 400 million pounds. By the year 2025, it is estimated that the global market size of glycerol will reach 5.8 billion pounds. Maintaining the surplus of crude glycerol due to the increasing global supply will require the research and development of new applications for glycerol. The production of crude glycerol by 2016-2028 is projected by the Global Industry Analysis (GIA), which is illustrated in Figure 1.4 [22].



Source: Polaris Market Research Analysis

**Figure 1.4 Worldwide production of glycerol from biodiesel industries**

## 1.6 Need for value addition of glycerol

One of the primary drawbacks in the biodiesel industry is the production of approximately 10 wt. % of glycerol as a byproduct. The surplus of glycerol is a major challenge in the biodiesel industry, and it requires valorizing glycerol in various value-added products to address both economic and environmental concerns. Outdated production methods lack economic viability for large-scale industrial use, particularly in the context of global biodiesel production, where glycerol emerges as a byproduct [23,24]. Within biorefineries, glycerol presents a sustainable resource for producing value-added biodegradable products, further reducing dependence on finite fossil fuel reserves. Numerous scientific groups are actively exploring innovative pathways to maximize the utilization of glycerol as a foundational element. Using glycerol for advanced chemical synthesis represents an engaging and urgent challenge. Exploring the alternative pathways for glycerol valorization is also advantageous. Glycerol can be valorized in various chemicals like dihydroxy acetone, succinic acid, 1,3-propanediol, lactic acid, esters, polyglycerols, and glycerol ether. A variety of valorized chemicals, from glycerol, were also used in industries and in individuals' daily requirements. This research will play an immense role in future bio-refineries, as its derivatives find application across multiple industries such as construction, chemicals, fuel additives, pharmaceuticals, and detergents [25–27]. By valorizing glycerol into various value-added chemicals through alternative pathways, as illustrated in Figure 1.5, the biodiesel sector stands to enhance its profitability.

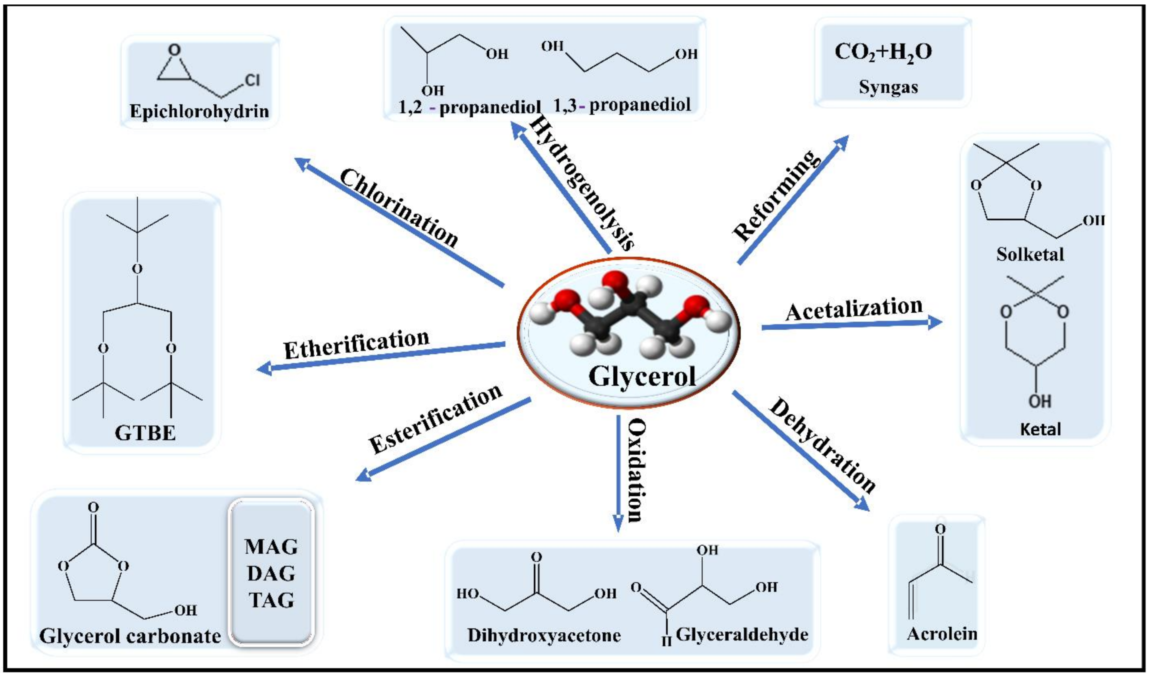


**Figure 1.5 Valorization of glycerol to different value-added products**

## 1.7 Value-added products of glycerol

### 1.7.1 Dehydration of glycerol

Acrolein can be widely produced by the dehydration reaction of glycerol using homogeneous (like sulfonic acid and benzene sulfonic acid) and heterogeneous catalysts (like zeolite, clays and solid acid catalysts). Acrolein serves as a reagent or intermediate in various industries for the synthesis of various compounds such as acrylic acid, glutaraldehyde, and more. Acrylic acid, deriving from acrolein oxidation over Mo and V-based catalysts, stands as a fundamental product utilized in producing superabsorbent polymers, paints, adhesives, pads, and diapers due to its commendable absorbent characteristics. The conversion and selectivity depend on the type of catalyst and reaction conditions used. Supported heteropolyacids produce acrolein with 98 % glycerol conversion with 86 % selectivity, but the major problem associated is catalyst deactivation. Acrolein is commonly used in the textile industry as an alternative reducing agent for dyes. Additionally, it is often used as an additive to food products to impart aroma and flavor to items like bread and milk goods. In cosmetics manufacturing, it serves as an ingredient in formulations for skin tanning products. Moreover, Acetol serves as a precursor for synthesizing chemicals such as acetone, propanol, and 1,2-propanediol [28,29].

### 1.7.2 Oxidation of glycerol

Oxidation of glycerol is a very complex reaction process, posing challenges in achieving selective product formation. Due to its multifunctional properties, glycerol can be oxidized to various valuable chemicals, including glyceric acid, glyceraldehyde, hydroxypyruvic acid, dihydroxyacetone, meso-oxalic acid, formic acid, and tartaric acid. Dihydroxyacetone (DHA) is synthesized by oxidizing the secondary hydroxyl group of glycerol, serving as a significant intermediate in cosmetics and diverse organic synthesis processes. It also serves as a vital ingredient in sunless tanners and cosmetics. Despite its dimeric structure, DHA readily dissociates into its monomeric form, containing a carbonyl group in water and functioning effectively as a tanning agent. Numerous heterogeneous catalysts, including Pt, Pt/C, Ce/C, Bi-Pt/C, and others, give a significant glycerol conversion with selectivity ranging from 70 % to 90 % towards DHA under optimized reaction conditions in a trickle bed reactor. When the primary hydroxy group involves oxidation, glyceraldehyde intermediate is produced. This intermediate undergoes oxidization and production of glyceric acid, which can be further converted into tartaric acid (TA). Both glyceric acid and tartaric acid hold significant economic importance. Additionally, the oxidation of all three hydroxyl groups results in the formation of keto-malonic acid. These acids show commercial significance and find diverse applications in various fields. They are utilized as polymers or biodegradable emulsifiers and are also used in the treatment of skin disorders. Moreover, they function as monomers for packaging materials for volatile agents. Tartaric acid, in particular, functions as a potentiating substance, enhancing the blood absorption of tetracycline antibiotics and addressing the treatment of osteoporosis and obesity conditions [5,30,31].

### 1.7.3 Etherification of glycerol

The glycerol etherification takes place by using glycerol with both tert-butanol and isobutene. On the reaction of glycerol with isobutene, mono-, di-, and tr-tertiary butyl ether is produced. Mono-glycerol tertiary butyl ether (m-GTBE), containing two hydroxyl groups, exhibits solubility in polar solvents, whereas di- and tri-ethers, referred to as higher glycerol ethers (h-GTBE), are insoluble in polar solvents but soluble in non-polar solvents such as hydrocarbons. This characteristic of h-GTBE allows it to be utilized as a fuel additive with diesel fuel, effectively reducing particulate emissions. The reaction of glycerol with isobutene proceeds in the presence of catalysts like p-toluene sulfonic acid, an acidic ion exchange, Amberlyts-15, and zeolites. Glycerol has the tendency to polymerize at elevated temperatures; it is not directly used with conventional fuel because it causes engine clogging and is partially oxidized into toxic acrolein. However, when glycerol tertiary butyl ethers (GTBEs) are blended with fuels, they mitigate emissions of CO, $CO_2$, particulate matter, and hydrocarbons during combustion. Additionally, GTBEs lower the cloud point and enhance the octane properties of non-conventional fuels, resembling those of conventional diesel when GTBEs are added [32,33].

### 1.7.4 Glycerol to syngas

Synthesis gas, also referred to as syn gas comprises a mixture of $H_2$, CO, and $CO_2$ and serves as an intermediate for converting biomass into fuel. It acts as a common feedstock for various processes, including Fisher-Tropsch synthesis (FT), methanol and dimethyl ether (DME) production, and ammonia synthesis. Recently, the generation of $H_2$ and syn gas has emerged as a potential route for valorizing glycerol. Hydrogen production can be achieved through synthetic routes such as steam reforming, dry reforming, partial oxidation, aqueous phase reforming, autothermal reforming, pyrolysis, and anaerobic fermentation. A wide array of catalysts, including noble metals like Pd, Rh, Ir, Pt, and Ru, demonstrate excellent conversion of glycerol to syn gas. Additionally, catalysts based on transition metals such as Ni, Co, and Cu are extensively employed for syn gas production. Among these metal-containing catalysts, Ni stands out as the preferred conventional catalyst for steam reforming of glycerol due to its superior catalytic activity. $H_2$ has become one of the most demandable, attractive renewable resources, having the potential to address numerous challenges associated with the current energy crisis, as well as environmental and mental pollution [34,35].

### 1.7.5 Polymerization of glycerol

Polymerization and polycondensation reactions catalyze the conversion of glycerol into polyglycerol and polyglycerol esters, facilitated by both homogeneous and heterogeneous catalysts such as $Na_2CO_3$, MCM-41, and mesoporous materials. This process predominantly occurs at temperatures ranging between 120 °C and 130 °C for a duration of 24 h under an inert atmosphere. Polyglycerol, valued for its controllable mechanical properties and biodegradability, serves as a valuable biomaterial extensively utilized in tissue engineering and various biomedical applications. Additionally, polyglycerols and polyesters find diverse uses across industries, including lubricants, surfactants, cosmetics, and food additives. Glycerol is utilized in commercial microwave reactors for the polymerization process to produce polyglycerols [36,37].

### 1.7.6 Esterification of glycerol

The esterification process stands out as another process for utilizing glycerol by reacting it with either carboxylic acid or acetic acid. Glycerol acetalization produces mono-, di-, and tri-acetylated glycerol, each having diverse and significant industrial applications. Various catalysts like zeolite, heteropolyacids, niobic acid, amberlyst, mesoporous silica, ion exchange resin, etc., are used in the acetylation of glycerol with acetic acid. Mono and diacetylated esters can be used in synthesizing cryogenics and polyesters, solvents, food additives, and explosives and act as a starting material for the production of biodegradable polyesters. Triacetylated esters represent the most pivotal derivatives of glycerol, constituting roughly 10 % of the glycerol market share. Its versatile applications include serving as a cigarette filter, a fuel additive, an antiknock additive for gasoline, a cosmetic ingredient, a food additive, a solvent, and various other purposes. Its use in the transportation sector as an additive makes it more important to improve the biodiesel properties and also enhance the yield of biodiesel. Another esterification product is glycerol carbonate, produced by the glycerol with dimethyl carbonate. Glycerol carbonate emerges as a novel chemical with vast potential, acting as an innovative component in gas separation techniques and as a solvent for various uses such as dyes, adhesives, cosmetics, surfactants, polycarbonate synthesis, pharmaceuticals, and bio-lubricants [38,39].

### 1.7.7 Hydrogenolysis of glycerol

This process involves the hydrogenation of glycerol in the presence of both homogeneous and heterogeneous catalysts to produce 1,2 propanediol, also known as propylene glycol and 1.3-propanediol. 1,3-Propanediol serves as a significant diol for the production of polyesters, resins, liquid detergents, paints, polycarbonates, and polyurethanes. Additionally, it also serves as a crucial starting material within the polymer industry as a monomer in the synthesis of polyether, polyurethanes, and polytrimethylene terephthalate[40]. Propylene glycol (PG) has various applications, like as a humectant in the food industry, ensuring moisture retention in pharmaceuticals, enhancing cosmetics products, and in the tobacco industry. Furthermore, it is employed as a food coloring and flavoring agent and exhibits properties as an effective antifreeze and de-icing agent, among other uses. Glycerol can be converted into propane diols by following three consecutive reaction routes viz.,

1) dehydration-hydrogenation route
2) dehydrogenation-dehydration-hydrogenation route
3) direct hydrogenolysis route

In the dehydration-hydrogenation route, glycerol is dehydrated in an acidic catalyst with the formation of an acetol intermediate, which further hydrogenates to propylene glycol [41]. Dehydrogenation-dehydration-hydrogenation route involves three steps; firstly, glycerol is dehydrogenated to produce glyceraldehyde, followed by dehydration and then hydrogenation to produce propylene glycol. In direct hydrogenolysis routes, glycerol undergoes direct hydrogenation to yield propane diol. Transition metal-based catalysts like Cu-chromite, Cu-ZnO, Cu-$SiO_2$, or Cu-$Al_2O_3$ catalysts are employed for glycerol hydrogenation within the temperature range of 150 °C to 329 °C and at pressures between 100 and 250 bars. Additionally, nickel, palladium, platinum, copper, and copper-chromite catalysts are also utilized at 200 °C and less than 10 bars of hydrogen pressure to produce propanediols [41–43].

### 1.7.8 Halogenation of glycerol

Glycerol halohydrins like glycerol chlorohydrin and bromohydrins are produced by halogenation of glycerol. Due to their antibacterial, mucolytic, and fungicidal properties, they find applications in the pharmaceutical industry. Glycerol iodohydrin is utilized in the synthesis of cardiolipins, a crucial intermediate in the treatment of type 2 diabetes. Iodohydrins and bromohydrins occur naturally in the essential oils of marine algae. Similarly, dichlorohydrins, economical derivatives of glycerol, are widely utilized in various industrial applications. Chlorohydrins are utilized for the synthesis of epoxides, epoxy resins, elastomers, pesticides, plasticizers, rubbers, and other products. Epichlorohydrin (ECH) is also produced by the hydrochlorination and dehydrochlorination pathways. Due to their highly resistant cross-linked networks against moisture and heat, these materials are also employed in enhancing paper quality and in the production of tea bags and coffee filters. Halohydrins can be sustainably synthesized by using catalysts such as hydrochloric acid, acetic acid, halogens, hydrotalcite, $NaI/Al_2O_3$, $NaBr/Al_2O_3$, $KI/Al_2O_3$, and similar agents under optimized reaction conditions, achieving up to 99 % glycerol conversion with 100 % selectivity towards halohydrins [44,45].

## 1.8 Introduction of solketal

Acetalization stands out as a prominent method for solketal synthesis from the condensation of acetone with glycerol, presenting a widely adopted industrial process. Its relevance has grown notably in recent times, particularly for biodiesel production. This versatile reaction pathway can generate solketal from glycerol. Solketal, chemically known as 2,2-dimethyl-1,3-dioxane-4-methanol.  Solketal is environmentally friendly, has minimal harm, and is biodegradable in nature. As a five-membered cyclic ring, it possesses unique chemical reactivity attributed to its distinct functional groups: hydroxyl and cyclic acetal [46,47].

### 1.9 Significance of solketal

Solketal, an oxygenated compound, has garnered significant attention in recent years due to its notable ability to blend effectively with gasoline, thereby enhancing fuel properties and promoting increased biodiesel utilization. Solketal is a colorless, odorless liquid that exhibits vast potential across various domains. The common physical properties of solketal are illustrated in Table 1.2. The diverse application of solketal is depicted in Figure 1.5. It serves as a green solvent, serves as a foundational material for synthesizing diverse organic liquids, functions as a plasticizer in the polymer industry, and acts as a solubilizing and suspending agent in pharmaceuticals[48,49]. Furthermore, solketal finds application as a fuel additive to improve fuel characteristics and mitigate greenhouse gas emissions. Its versatility extends to serving as a surfactant, disinfectant, and flavoring agent in food, as well as in cosmetics. Moreover, solketal plays a role in enhancing biofuel properties when blended with gasoline and biodiesel, enhancing cold flow properties, boosting oxidation stability, improving flashpoint, and reducing gum formation and environmental impact [50–52]. Typically, acetalization is a reaction catalyzed by acids, commonly mineral acids like HF, HCl, $H_2SO_4$, $H_3PO_4$, $FeCl_3$, and $SnF_2$, acting as homogeneous catalysts. Nonetheless, there's been a surge in interest in recent research toward developing environmentally friendly and cost-effective heterogeneous solid acid catalysts. Various literature sources have reported the utilization of solid acid catalysts in glycerol acetalization, encompassing hetero-poly acids, zeolites, amberlyst, ion exchange resins, acid clays, and mesostructured silicas, among others. Solid acid catalysts exhibit comparable acidity, surface area, and production costs to their homogeneous counterparts[53–55]. Undoubtedly, they hold great promise due to their non-toxic nature, ease of separation from the reaction matrix through simple filtration, minimal corrosion, and generation of reduced waste. Similar to acetone, benzaldehyde can also be used as source of carbonyl moiety in the presence of $MoM_3/SiO_2$ catalyst for solketal synthesis. Some solvents like toluene, methyl cyanide, and methanol are also used to increase the glycerol conversion to solketal [56].

**Table 1.2 Physical properties of Solketal**

| **Properties** | **Solketal** |
|---|---|
| Molecular weight (g $mol^{-1}$) | 132.16 g/mol |
| Density | 1.064 $g/cm^3$ |
| Color | Colorless |
| Melting Point | - 26.4 $^oC$ |
| Viscosity | ~ 11 cP |
| Refractive index | 1.434 |
| Boiling Point | 188 $^oC$ |
| Flash point | 80 ℃ |
| Freezing point | - 26 $^oC$ |

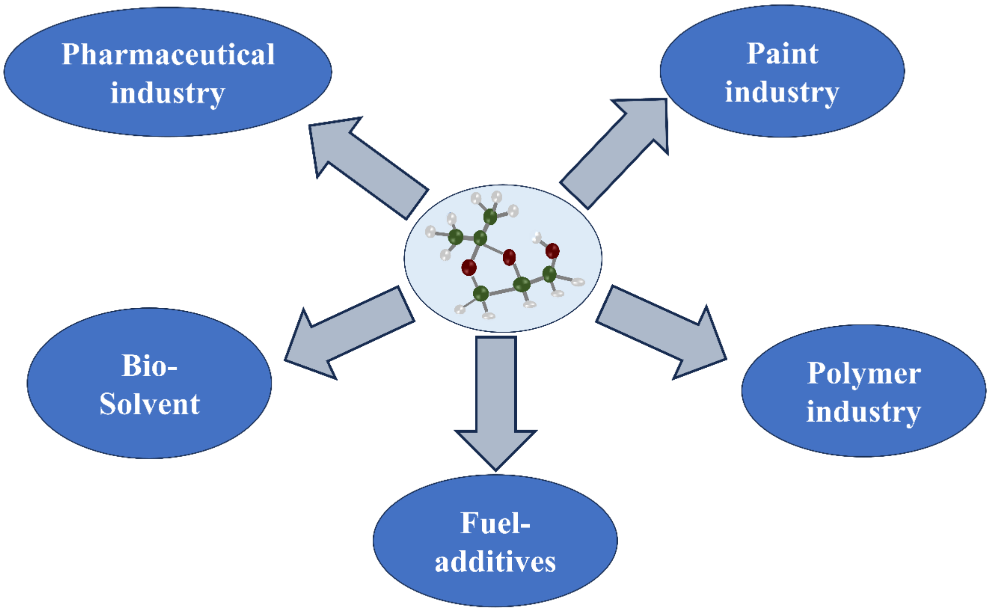


**Figure 1.6 Application of solketal**

## 1.10 Research gaps

The acetalization reaction between glycerol (Gly) and acetone, employing the presence of acidic catalysts, stands out as a noteworthy process. Solketal has garnered significant attention in recent decades due to its versatile reactivity and its role in valorizing waste glycerol, particularly in light of increasing sustainability awareness. However, despite the relative effectiveness of catalysts in glycerol acetalization, many exhibit low concentrations of active acidic sites and degrade rapidly upon reuse [57,58]. Catalysts accelerate reactions by abstracting a proton from glycerol, enhancing their fundamental nature. To achieve high yields of solketal while considering these factors, it becomes imperative to develop a highly active and cost-effective heterogeneous acidic catalyst with robust acidic sites. Both homogeneous and heterogeneous acidic catalyst was employed in glycerol acetalization reaction. Various homogeneous acid catalysts, such as HCl, $H_2SO_4$, $H_3PO_4$, $SnCl_2$, HF, $SnF_2$, etc, have exhibited notable catalytic activity in the acetalization of glycerol with acetone. However, separating these catalysts from the resulting mixture presents significant challenges. Conversely, the production of solketal extensively employs various heterogeneous catalysts, such as zeolite, hetero-poly acids, ion exchange resins, montmorillonite, metal-organic frameworks, metal oxides, amberlyst resins, and others. The majority of catalysts exhibited reduced selectivity towards glycerol solketal synthesis. These catalysts are burdened with drawbacks, including poor recyclability, instability, extended reaction times, dependency on multiple solvents, and high energy consumption [59–62]. Several publications underscore the importance of developing novel heterogeneous acid catalytic materials with robust acidic sites, recyclability, and ease of recovery. To rationally design catalysts, it is crucial to understand the correlation between the physicochemical properties of the catalyst and its efficacy in glycerol acetalization. Developing bimetallic oxides with sufficiently strong acidic properties proves beneficial as it enhances both the acidic strength and stability of the catalysts. Additionally, improving the catalyst's reusability under identical reaction conditions is another crucial consideration.

Given the inherently acidic nature of transition metal-based oxides, extensive research is being conducted to investigate their catalytic activity. To increase the acidic strength of transition metal-based catalysts, some modification was performed by the sulphonation process. Various sulfonated-based literature is available, which increases the glycerol conversion and solketal selectivity by increasing the catalyst stability in further cycles. Our main objective is to extensively explore transition metal-based heterogeneous acid catalysts for glycerol acetalization reactions. This thesis endeavors to evaluate a transition metal-based heterogeneous catalyst for glycerol conversion. Regardless of the synthetic method used for producing solketal on industrial and laboratory scales, it must meet certain fundamental criteria for the viability of the products, including

- When employing catalysis, it is essential to utilize a catalyst that is cost-effective, readily separable, and recyclable.
- A straightforward method for separation and purification should be employed.
- Avoiding the use of solvent
- A catalyst with reduced reaction time and enhanced safety features is preferable, minimizing the use of hazardous and highly combustible substances.

On the basis of these criteria, it is indicated that a synthetic approach utilizing glycerol and acetone with a modified sulphonated transition metal-based catalyst appears to be the ideal option. Furthermore, both substances are environmentally friendly and readily available at low cost in the market.

### 1.11 Objectives of Research

The following points of my research objectives are defined in this work:

1. Design of transition metal-based heterogeneous acid catalyst for solketal synthesis using glycerol with acetone.
2. Synthesis of $SO_4^{-2}/ZrO_2-Al_2O_3$, $SO_4^{-2}/CoAl_2O_4-TiO_2$, and $SO_4^{-2}/ZnAl_2O_4-ZrO_2$ catalyst via co-precipitation followed by wet-impregnation process.
3. Various characterization techniques determined the physiochemical properties of the modified catalyst.
4. Conducting characterization of the synthesized catalyst and stabilizing the co-relation between the catalyst's properties and their performance in solketal synthesis.
5. Evaluating the catalytic performance of the catalyst in glycerol acetalization reaction.

6. Assessment of optimal reaction conditions for solketal synthesis.
7. Examine the reaction-affecting parameters that affect the catalyst stability and reusability.
8. Analyzing the environmental friendliness of the process by calculating the green matrix parameters.