CHAPTER 1

Introduction

1.1 General Introduction.

The global energy consumption increases significantly with rapid increase in population and also with economic development. Many natural resources like oil, natural gas, wind sun etc could be converted to various energy forms like nuclear energy, solar energy, electric energy as secondary energy which fulfils the energy demand worldwide [1-4]. According to International Energy Agency act 2040 (IEA,2040) energy consumptions will reach up to approximately 250 quadrillion Btu in industrial aspect where as 150qBtu and 120qBtu in transportation and building aspects respectively (depicted in fig 1.1). Recently power sectors are driven by fossil fuels, especially petroleum oil, coal etc for industrial development as well as transportation. Although the crude oil derived from plant biomass in 19th century helped industrialization but high price instability, high rate of oil depletion, emerging economic, environmental issues are key factors for searching energy sources alternative to petroleum oil and to develop an efficient cost-effective process for sustainable production of fuels and chemicals [5–7] . Biofuels like bioethanol, bio methanol and biodiesel are alternative for liquid fuels having zero emission of pollutants like CO, CO_2, NO_x, SO_2 etc which are considered as greenhouse gases. Emission of these harmful gases from fossil fuel combustion discouraged enormous use of petroleum oil in transportation sector. As a result biodiesel has got attention as a sustainable and renewable energy in place of petroleum fuel for past few decades [8–10].

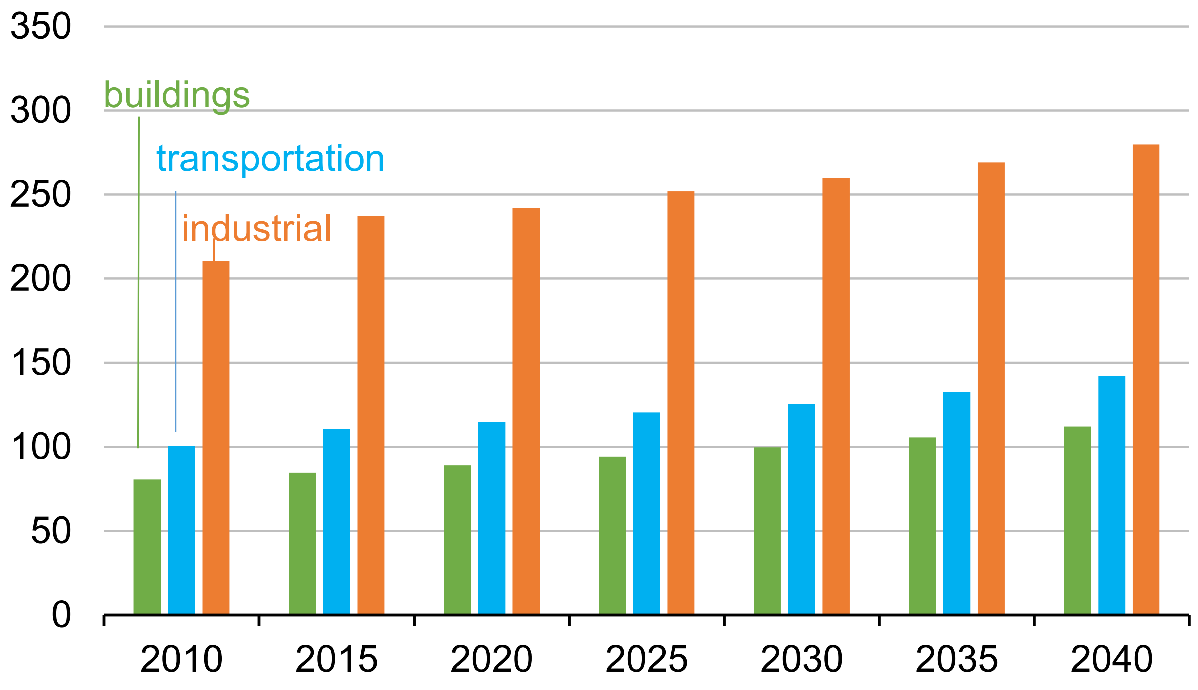

Fig 1.1 World energy consumption by end-use sector (quadrillion Btu).
(Source DOI: 10.1080/0951192X.2018.1493234)

Biodiesel is nothing, fatty acid methyl ester produced from both edible and non - edible vegetable oils, waste vegetable oil, animal fats, microalgae and fungus by methanolysis reaction. It can be used in diesel engines with little modification i.e., after blending with petroleum diesel as B2, B5, B20 and B100 forms. The production of biodiesel is increasing at large scale since last few years and it is expected to be maximum in coming years as well [11–15]. During biodiesel production process, excess amount of glycerol is produced as a by-product and remains as a glut in the market which affects the market competitiveness of biodiesel industries. Approximately 10 wt.% of glycerol is produced during that process i.e. for every 100 kg of biodiesel 10 kg of glycerol is generated as by product [16–19]. Glycerol having multi functionality behaviour has been applied in several fields like pharmaceutical industries, food and cosmetic industries, polymer industries and also in many chemical manufacturing industries. Glycerol can be valorised into various value-added products like butanol, poly hydroxyalkanoate, solketal, acrolein, monoglyceride, triacetin, citric acid, lactic acid and glycerol carbonate which are extensively used in fuels, fuel additive, detergents, explosive materials etc. The wide range of application of glycerol in several fields attracted the interest of researchers for its valorisation [20–22] .

1.2 History and Discovery of glycerol

Glycerol is a simply polyol with three hydroxyl groups having IUPAC name 1,2,3- Propane triol. The presence of three hydroxyl groups is mainly responsible for its high solubility in water and it is a colourless, odourless and viscous liquid. Chemically, it was discovered by Swedish chemist C.W. Scheele in 1977 when he worked on reaction between lead oxide and olive oil. He got glycerine from the mixture and named it as sweet oil [23]. Similarly French chemist, Michel Eugene extracted glycerol from tri esters (fat). It comes from the Greek word “glykys” in 2800BC which means sweet and the chemical structure of glycerol is depicted in fig 1.2

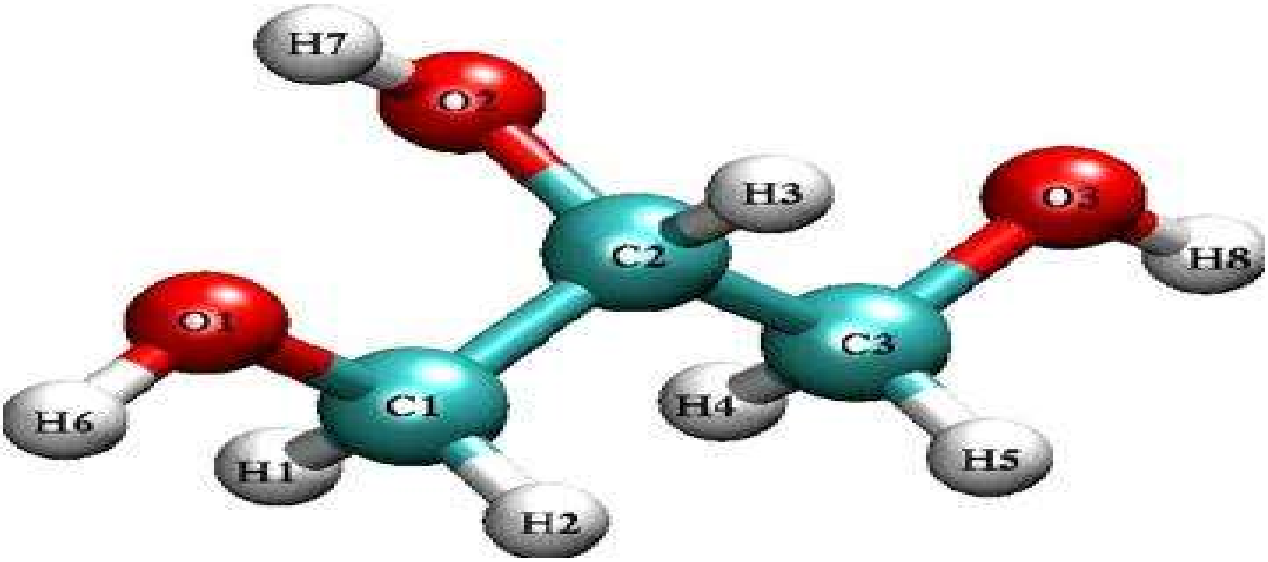

Fig 1.2: Structure of Glycerol

1.3 Physical properties of glycerol

Glycerol being one of the organic compounds is highly stable and very compatible chemicals with other chemicals at normal storage condition. It is nontoxic and has no negative effect on environment. It is highly flexible and simple chemicals having affinity to form hydrogen bond with other chemicals via both intra and inter hydrogen bonding. It is completely soluble in water and alcohol. The presence of three hydroxyl groups enhances the solubility of glycerol with water and in simple aliphatic alcohols. It is slightly soluble in ethyl acetate, ether, dioxane where as insoluble in hydrocarbons [24–27]. The general properties of glycerol are given in table 1.1.

Table 1.1 General properties of Glycerol

Molecular weight	92.09 g
Boiling point	290°C
Melting point	18.17°C
Density	1.26g/cm^3
Refractive index	1.474
Surface tension	63.4dyne/cm
Viscosity	1499 c.p
Specific heat	0.5779cal/gm
Thermal conductivity	0.29w/K
Flash point	177°C
Fire point	204°C
Food energy	4.32Kcal/g
Compressibility	2.1× 10Mpa

1.4 Importance of Glycerol

Traditionally glycerol is used as antifreeze agent for automotive applications and also have broad applications in several fields such as in food industries, pharmaceuticals, plasticizers, tobacco humectants, emulsifiers, cosmetics, explosives and baby care products etc. It is also considered as one of the main building blocks in biorefinery feed stocks. Glycerol is also used as lubricant because of its high viscosity and remains as a fluid at moderate temperature. It can also be used as thickening agent in liquors and beverages [28–30]. In medicinal field, it serves as tablet holding reagents in preparation of cough syrups, elixirins, and solid dosage forms like tablets. It has also broad applications in personal care as it is found in toothpaste, skin care, hair care products, mouth washes, shaving cream, soap and water-based lubricants etc. It is used in food and other cosmetic product manufacture without any modification and helps to retain moisture and prevents drying and burning rate of tobacco [31–33] . It is also utilized in tincture method of extraction specifically as 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 solvent [34-35]. The broad application of glycerol is represented in fig 1.3 below.

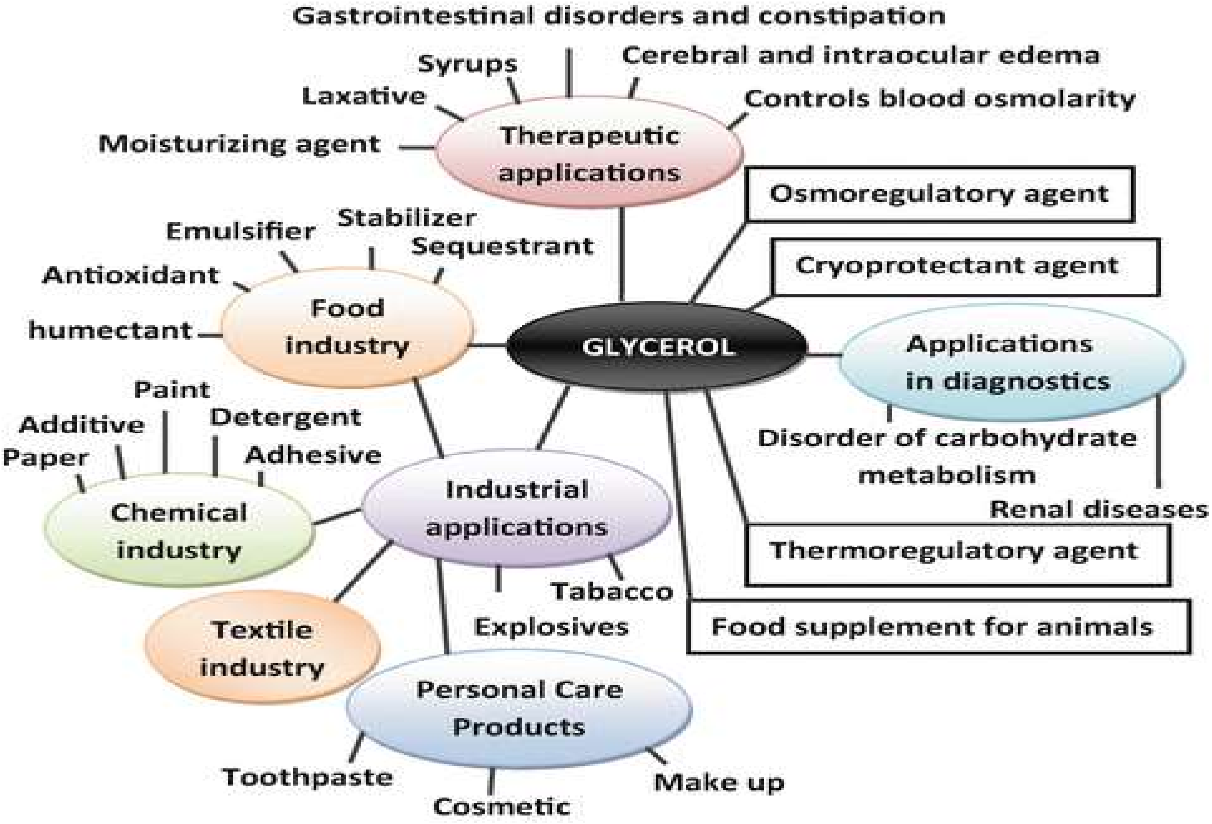

Fig 1.3 Application of glycerol!

1.5 Global production of glycerol

Currently the rate of production of glycerol is increasing drastically due to renewable fuel production driven by subsidies, tax breaks and usage mandates. The renewable fuel policies in developed countries like South America, Canada, Germany and India ensures increase in crude glycerol supply in near future. Currently annual biodiesel production of USA reached 250 million gallons per year which is highly responsible for 400 million pounds of glycerol as by-product. The global market for glycerol is projected to reach 5.8 billion pounds in consumption by the year 2025. The global Industry Analysis (GIA) estimated the production of crude glycerol in 2025 which is reflected in fig 1.4 [36].

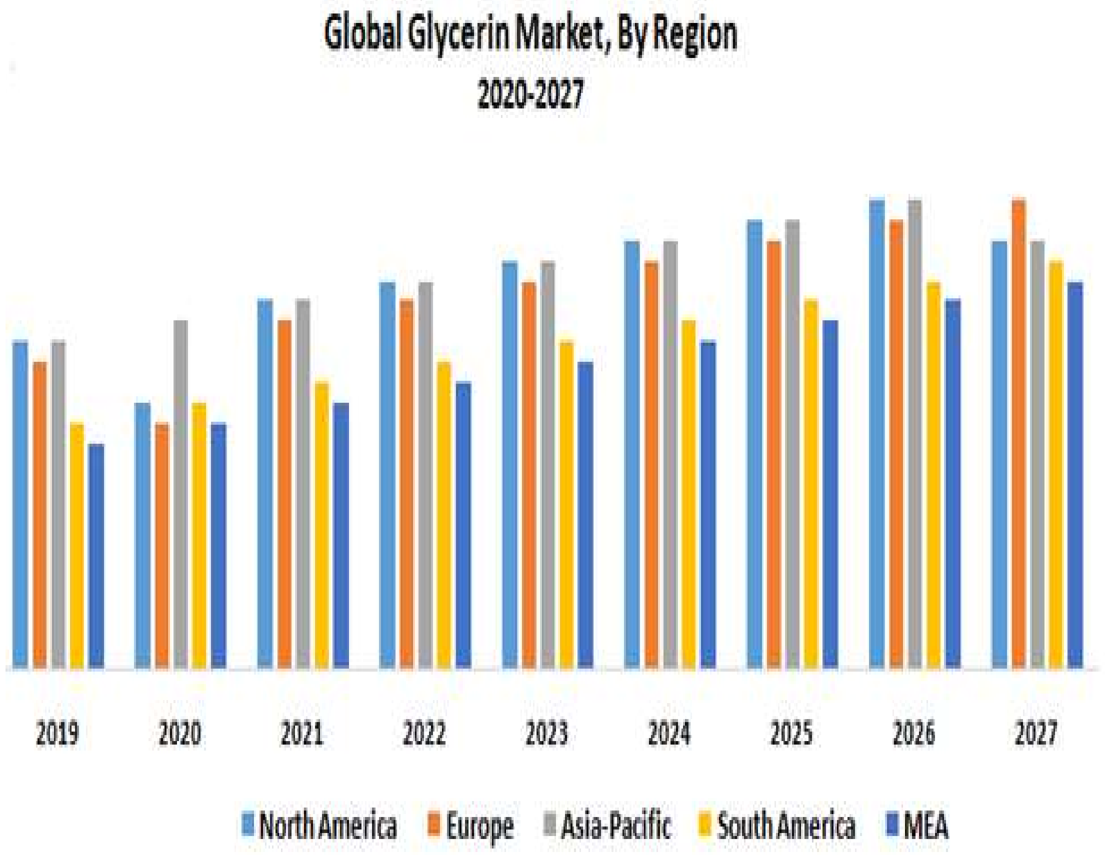

Figure 1.4 Worldwide production of glycerol from biodiesel industries (Source: DOI: 10.1080/17518253.2018.1444795)

1.6 Need for value addition of glycerol.

Glycerol is the major drawbacks in biodiesel industries, which is approximately about of 10 wt.% of biodiesels produced. That large surplus of glycerol is the major challenge in biodiesel industries which requires value addition for economic and environmental point of view. The use of glycerol for advance organic synthesis now-a-days emerging as a fascinating challenge and many researchers are trying to design new synthetic pathways for proper utilization of glycerol as a natural building block [37-38]. It is also beneficial to find alternative applications of crude glycerol. Glycerol can be transformed into varieties of products like succinic acid, lactic acid, 1,3- propanediol, citric acid, Dihydroxy acetone, glyceryl ether, esters, polyesters, polyglycerols etc. The conversion of glycerol into various value-added products indeed offers attractive solutions as the resulted products are mostly dedicated to lower -tonnage process that are more compatible with the production capacity of glycerol manufacture. Many chemical compounds derived from glycerol were also widely used in industries and also in daily need of human beings. Such type of value addition in glycerol biorefinery research will play a crucial role in future development in biodiesel industries [39]. A variety of reactions to produce valuable chemicals from glycerol are discussed below.

1.7 Value added products of glycerol

1.7.1 Esterification of glycerol

Generally, many homogeneous catalysts like sulphuric acid or sulfonic acid are used for the commercial synthesis of esters of glycerol by direct esterification of alcohol with fatty acids. The monoesters of glycerol act as surface active agents in food and pharmaceutical industries as having emulsifying properties and high biocompatibility [14,15].

Similarly, the acetylation of glycerol with acetic acid can be carried out in presence of various solid acid catalysts such as zeolites, niobic acid, heteropoly acids, amberlyst etc. Most of the solid acid catalysts provided less selectivity along with poor conversion towards the desired product. The glycerol acetate acts as fuel additive in transportation sector and improve the properties of biodiesel. This property of glycerol acetate not only makes the good use of reaction product but also enhances the overall fuel yield in biodiesel process. The demand of glycerol esters are increasing now- a-days and it is about 110000 tons annually [40-41].

1.7.2 Dehydration of glycerol

Recently, the dehydration of glycerol has caused expectation, and interest as it may produce acrolein or acetol as major products on the basis of catalyst used and the reaction conditions. Acrolein is a valuable chemical used as reagent or intermediate in industries for the production of varieties of compounds like methionine, acrylic acid, glutaraldehyde etc. Acetol generally used in the textile industry as a reducing agent for dyes instead of sodium dithionite avoiding sulphur salts in the waste water, also it is often a customary food additive to confer odour and flavour to bread and milk products and in the cosmetic industry, it is an ingredient in skin tanning products, furthermore acetol can be used as a raw material to synthesize chemicals like acetone, propanol and 1,2-propanediol. Many catalysts like zeolites, Naflon composites, phosphoric acid, silicotungstic acids, alumina etc are extensively used for production of acrolein by dehydration process of glycerol. The gas phase dehydration of glycerol to acrolein basically catalysed by solids exhibiting acid properties, which further classified into three distinct groups such as (i) Supported Keggin type heteropoly acids, (ii) Zeolites, (iii) metal oxides like WO_3-ZrO_2 or Nb_2O_5. Keggin type HPA opted glycerol conversion of 100% and acrolein selectivity of 98% , but the efficiency of catalyst decreased rapidly after some hours under stream [20].

1.7.3 Oxidation of glycerol

Glycerol having multifunctionality properties can be oxidised to several valuable chemicals such as glyceric acid, glyceraldehyde hydroxy pyruvic acid, dihydroxy acetone, meso oxalic acid, formic acid and tatronic acid. The oxidation of glycerol follows very complex reaction pathway and it is so difficult to obtain selective products. Glyceraldehyde, one of the oxidised products of glycerol extended its applications in cosmetic industry, organic chemistry and pharmaceutical industries. Many heterogeneous catalysts used for selective oxidation of glycerol are based on noble metals like platinum, gold, silver etc. Among many oxidised products of glycerol dihydroxy acetone is one of the compounds which enormously used in cosmetics, an active ingredient in sunless tanners. Although DHA exhibits dimeric structure but in water, it dissociates easily to monomer containing carbonyl group which acts as a tanning agent. Many types of heterogeneous catalysts like Pt, Pt/C, Ce/C, Bi-Pt /C etc provided appreciable conversion of glycerol with 70- 90% selectivity yield of DHA at optimized reaction conditions using a trickle bed reactor [42]. Glyceric acid is one of the oxidised products of glycerol which acts as an important intermediate for further oxidation product of tartronic acid (TA), mesoxalic acid (MA) and keto-malonic acid. Similarly, many efficient catalysts like Pd/C, Pt/C, with NaOH as a base produces' disodium salt of glyceric acid with maximum yield of 54.2% and 96.1 % conversion of glycerol [43]. Tartronic acid (hydroxy malonic acid) is one of the high value fine chemicals used as treatment of osteoporosis and obesity, anti-corrosive protective agent in boilers. Tartronic acid commercially used as oxygen absorber in food industries, for example Multisorb Technologies Inc patented iron salts of TA as packaging additives for air-sensitive products such as meat, fish and other edible or non-edible materials to prevent their oxidative decomposition. Several types of heterogeneous catalysts like Ce-Bi-Pd-Pt-C, Pt/ C, Pd/C etc are efficiently used for oxidation of TA [33]. Similarly, many other value-added chemicals like pyruvic acid, formic acid, mesoxalic acid are the oxidised product of glycerol and have vast applications in food, pharmaceutical and cosmetic industries.

1.7.4 Etherification of glycerol

Recently glycerol ethers are used as very good fuel additives by directly blending with diesel fuel. The etherification of glycerol takes place using different alcohols like ethanol, isopropanol, t-butanol and isobutene over Amberlyst type catalysts such as Amberlyst-15, Amberlyst-36, Montmorillonite K10, B-zeolite, B-toluene sulfonic acid, H-Y, H-B, strong acid ion-exchange etc. The reaction between glycerol and alcohols were carried out mainly under atmospheric pressure, by optimized boiling temperature at different reaction time [44] . Besides that, ultrasonic microwave conditions are adopted for the etherification of glycerol to get the best results. The synthesis of glycerol tert-butyl ethers from isobutene and glycerol catalysed by acidic homogeneous or heterogeneous catalyst mainly need autoclave as the reaction process follows thermodynamic equilibrium. As the etherification of glycerol is limited by thermodynamic equilibrium that can be modified by addition of solvents which selectively solubilize the products and progress the reaction process. Glycerol ethers can be added in different proportions to diesel engine results in improvement of cold properties and reduction of contaminant emissions and viscosity [45].

1.7.5 Acetalization of glycerol

Glycerol can be used for production of acetals and ketals by reactions with aldehyde and ketones yielding five or six membered cycles which further used for surfactant production. Besides that, glycerol oxygenates like both acetal and ketals are excellent fuel additives which increase viscosity, octane or cetane number, and stability to oxidation. Acetals are significantly helpful to reduce carbon monoxide emission from diesel engine and improve the cold flow properties of liquid transportation fuels. It acts as a versatile solvent and plasticizer in the polymer industry, solubilizing and suspending agent in pharmaceuticals. Solketal acts as active agent to reduce the gum formation, improves the oxidation stability, and enhances the octane number when added to gasoline. Acid catalysts like Amberlyst, K-10, p-toluene sulfonic acid, zeolites, Ar-SBA 15, tin chloride ($SnCl_2$) are mainly used for synthesis of ketals or acetals from glycerol. The ketalization of glycerol has very low equilibrium constant, so in order to reach high conversion of glycerol the equilibrium shifted towards formation of solketal by removal of water as side product which highly affects the conversion of glycerol. In the synthetic process of solketal batch reactor with continuous flow process are adopted for large scale production of solketal. The best yield of solketal were achieved by catalysts like Amberlyst-15, Amberlyst-35 and Ar-SBA, as all these catalysts possess higher acidic characters which influenced the yield up to 94±2%.The ketalization reaction of glycerol proceeds via acidic catalytic mechanism , hence catalysts with strong acidity might leads to high glycerol conversion [46-47].

1.7.6 Glycerol to synthesis gas

Synthesis gas (syngas) the mixture of H_2, CO and CO_2 could be used as a potential intermediate in the conversion of biomass into fuel. Syn gas is the common feedstock for various processes like Fischer-Tropsch synthesis (FT), production of methanol, dimethyl ether (DME) and ammonia synthesis. Recently, the production of H_2 and syngas has become another potential route for glycerol valorisation. Hydrogen can be produced by several synthetic routes like steam reforming, dry reforming, partial oxidation, aqueous phase reforming, autothermal reforming, pyrolysis and anaerobic fermentation. A diverse range of catalysts containing noble metals such as palladium, rhodium, iridium, platinum, ruthenium is used for providing excellent conversion of glycerol to syngas. On the other hand, catalysts based on transition metals like Ni, Co, and Cu are used significantly for syngas production. Among all these metal containing catalysts Ni is the most conventional catalyst which is applied in steam reformation of glycerol due to its superior catalytic activity. Now- a days H_2 has become one of the attractive renewable energy sources capable of solving most of the problems related to energy crisis and environmental pollution. Due to abundant availability and sustainability nature of glycerol, it has become one of the best substitute for fossil fuel sources [43-45].

1.7.7 Polymerisation of glycerol

Polyglycerol is a versatile biodegradable biomaterial on the basis of its adjustable mechanical properties. It is mainly used in biomedical and tissue engineering applications. It helps in tissue regeneration, substitution and enables mimicking the mechanical and structural features of several tissues like cornea, adipose, blood, cartilage, nerve, cardiac muscle and bones. Polyglycerols and polyesters have wide applications in lubricants, surfactants, cosmetics and food additives. The reaction of glycerol to form polyglycerol and poly glycerol ester are catalysed by both homogeneous and heterogeneous catalysts like Na_2CO_3, MCM-41, mesoporous materials via polymerisation and polycondensation reaction [48] . The polymerisation of glycerol mainly takes place at constant temperature of 120-130°C for 24 h under an inert atmosphere whereas in condensation step, terminal groups of branched chains cause the gelation of percolated network. The polymerisation of glycerol also takes place in commercial microwave reactor to obtain polyglycerols [49] .

1.7.8 Halogenation of glycerol

The halogenation of glycerol produces glycerol halohydrins, like glycerol chlorohydrin and glycerol bromohydrin. These compounds are applied in pharmaceutical preparation because of their antiseptic, mucolytic and fungicide properties. Glycerol iodohydrin are used for synthesis of cardiolipins since it acts as key intermediate in treating of type 2 diabetes. In nature iodohydrins and bromohydrins were found in essential oils of marine algae. Similarly, dichlorohydrins are low-cost glycerol derivatives vastly used in industrial application. Chlorohydrins are used further synthesis of epoxide, epoxy resins, elastomers, pesticides, plasticizers, rubbers etc in industries. Epichlorohydrin (ECH) mainly used for the production of wind turbine blades in Asia pacific regions. It is also helpful in the reinforcement of paper and teabags. The sustainable synthesis of halohydrins are catalysed by hydrochloric acid, acetic acid along with halogens, Hydrotalcites, NaI/Al_2O_3, NaBr/Al_2O_3, KI/Al_2O_3 etc at optimised reaction condition providing up to 99% conversion of glycerol and 100% selectivity towards halohydrins[17,41,50].

1.7.9 Hydrogenolysis of glycerol

Hydrogenolysis is a class of reduction which involves dissociation of chemical bonds in organic substrate and simultaneous addition of hydrogen to the fragments. The selective reduction of glycerol gives 1,2-propanediol,1,3-propanediol, acetol, ethylene glycol. Propanediols commercially used in paints, liquid detergent, cosmetics, food and tobacco industries and also used as antifreeze coolant, de-icing reagent. 1,2-propanediols are extensively used as feedstock for preparation of polyester resins for film in fibre manufacture and in pharmaceutical industry. Similarly, 1,3- propanediol used as a monomer in polyether, polyurethanes, polytrimethylene terephthalate (a biodegradable polyester having great potential for use in carpet and textile manufacturing). Various synthetic process like hydroformylation-hydrogenation, hydration and fermentation are applied by some companies for the synthesis of propanediols (PD). Glycerol can be converted to propanediols via catalytic hydrogenolysis process. The reaction process for conversion of glycerol to PD has been extensively studied in past few decades. There are three typical reaction mechanisms involved through which glycerol can be transformed to propanediols like (I) dehydration hydrogenation, (II) dehydrogenation-dehydration-hydrogenation, (III) direct- hydrogenolysis. In dehydration-hydrogenation mechanism glycerol is dehydrated through an acid catalysed reaction forming intermediate and further hydrogenated to generate final product [46]. In dehydrogenation-dehydration-hydrogenation mechanism, the reaction of glycerol takes place in neutral water and alkaline conditions. Here the reaction follows three steps such as dehydrogenation, dehydration and hydrogenation to give the final product PD. In direct hydrogenolysis reaction glycerol directly undergoes hydrogenation to form propane diols by use of many heterogeneous catalysts. Traditionally transition metal-based catalysts like $CuO/CuCr_2O_4$, Cu/SiO_2, Ba $CuO/CuCr_2O_4$, Cu/Al_2O_3, Pd $CuO/CuCr_2O_4$ are used for transformation of glycerol to propanediols with high yield percentage of about 95%. Generally, the metal component of catalyst plays important roles in activating hydrogens and the metal oxide whether acidic or basic supports provides acid-base function in the reaction process. Many transition metals like Cu, Ni and Co are extensively utilized for the production of propanediols[51-52].

1.8 Importance of glycerol carbonate

Glycerol carbonate is one of the important value-added products of glycerol due to its ideal physico-chemical properties like low toxicity, high stability, high boiling point, good biodegradability and low in flammability. The IUPAC name of glycerol carbonate is 4-hydroxymethyl-1,3-dioxolan-2-one. Glycerol carbonate has extended its application towards various fields such as solvent in cosmetics, medicine, intermediate in organic synthesis : polycarbonates, polyether, polyglycerols, surfactants, and production of resins, plastics etc[51-54]. The physical properties of glycerol carbonate are given in table 1.2. In semiconductor industries glycerol carbonate acts as electrolyte in lithium-ion batteries where as in chemical industries it acts as intermediate in glycidol, bio-lubricants, biobased polar solvents, for preparation of liquid membrane in gas separation, surfactants and detergents, blowing agent. Glycerol carbonate acts as curing agent in cement and concrete in buildings and construction industries, whereas in agricultural fields it acts as plant activating agent. Glycerol carbonate having nutraceutical and cosmeceutical properties broadly utilised in cosmetic and personal care industries as emollient and solvent in nail polish, remover, lipsticks and wetting agent for cosmetic clays. In polymer and plastic industries, glycerol carbonate is used for the synthesis of polyesters, polycarbonates, polyamides, polyurethane plastic coating, hyperbranched polyether and solvent for plastic and resins. Glycerol carbonate further converted to chemical intermediates which are again useful in the production of epichlorohydrin, surfactants and polymers. Depending upon the enormous application of glycerol carbonate, the importance of this compound is increasing worldwide in several industries [55-56].

Table 1.2: Physical properties of glycerol carbonate

Properties	**Glycerol carbonate**
Molecular weight (g mol^{-1})	118.09
Density ,25°C (g ml^{-1})	1.4
Melting point (° C)	-69
Boiling point (° C)	137
Vapour pressure ,177C(bar)	0.008
Flash point(°C)	190
Dielectric constant (ESU)	111.5
Hansen solubility parameter delta D ,25C($MPa^{1/2}$)	17.9
Hansen solubility parameter delta P, 25C($MPa^{1/2}$)	19.5
Hansen solubility parameter delta H ,25C($MPa^{1/2}$)	21.5
Hildebrand solubility parameter 25C($MPa^{1/2}$)	34.1
Viscosity, 25°C (cP)	85.4

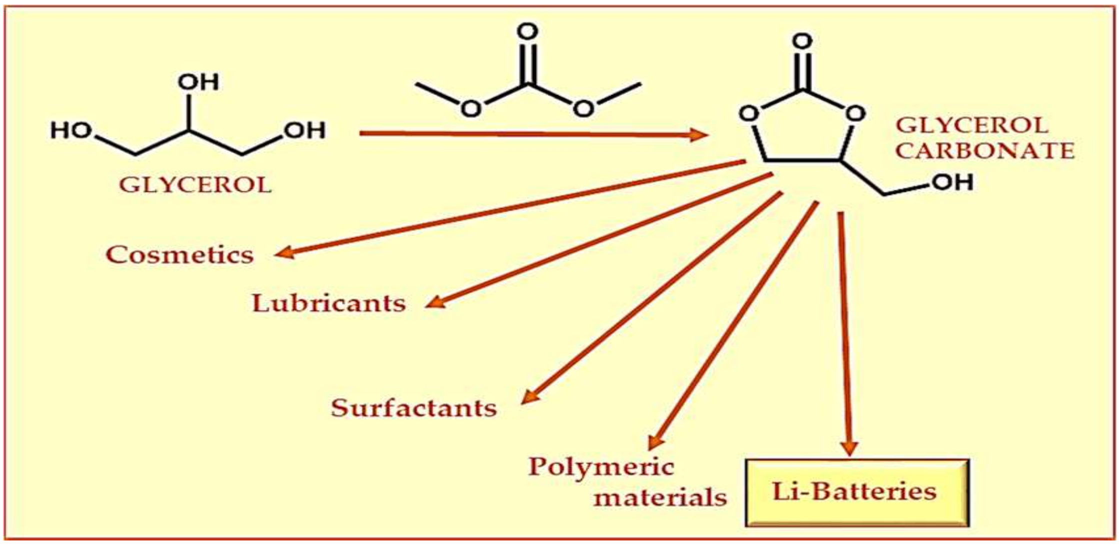

Fig 1.5 Applications of glycerol carbonate

1.9 Synthetic routes for glycerol carbonate

Glycerol carbonate can be synthesized from glycerol via several synthetic routes which are mainly of two types i.e., direct synthetic route and indirect synthetic route. Direct synthetic route further divided in to two types such as carboxylation process and oxidative carboxylation where as indirect synthetic route are further subdivided into three types like phosgenation, glycerolysis and transesterification [23] . The schematic representation of synthetic pathway of glycerol carbonate is shown in fig 1.6. All the processes have advantages as well as disadvantages in synthesis of glycerol carbonate. The broad study of synthetic process is explained here.

1.9.1 Carboxylation of glycerol

Glycerol carbonate can be synthesized by direct addition of carbon dioxide (CO_2) in its super critical condition or in presence of many catalysts. Carbonation of glycerol with carbon dioxide is one of the interesting and fascinating methods for production of glycerol carbonate where CO_2 is treated at 453K temperature and 5MPa pressure. Tin based catalysts namely n-$Bu_2Sn(OMe)_2$ was the first catalyst for production of glycerol carbonate using CO_2 source. About 1mol% nBu_2SnO catalyst in presence of carbon dioxide provided 35% of glycerol carbonate yield at 13.8MPa and 120°C for 4h reaction time whereas only 5% GLC yield was obtained using former reaction condition [23]. In super critical carbon dioxide (SC) condition several types of heterogeneous catalysts were used for glycerol carbonate production such as catalysts like AmberlystA26.OH^-, AmberlystA26. HCO_3^- , Zeolite 13X (8-12 mesh), TBA. Br-, TBA. $NHSO_4^-$ etc. Glycerol carbonate was not formed with SC-CO_{But} conditions for 3h, although in presence of basic resin Amberlyst A26 in OH^- or HCO_3^- as SC-CO_2 not acts as a carbonate source for carbonation of glycerol. In order to obtain the better GLC yield an organic carbonate source ethylene carbonate in SC-CO_2 condition was used and obtained 32.15% GLC yield [57]. Alcoholic solvents like methanol and isopropanol were added to accelerate the rate of reaction and significantly improve the GLC yield. Thermodynamic calculation reflected that GLC production using SC-CO_2 condition is thermodynamically limited. But the carbonation of glycerol with carbon dioxide suffers from high pressure requirement, thermodynamic limitations, and very low GLC yield which highly increases the production cost of glycerol carbonate, as a result the synthetic process of GLC using carbon dioxide is not encouraged in recent time [58].

1.9.2 Carbon monoxide + glycerol

Glycerol carbonate can be synthesized through reaction with carbon monoxide and oxygen in presence of a suitable catalyst. In this synthetic process, both carbonation and oxidation take place which is another way known as oxidative carbonylation of glycerol. Basically, two types of catalytic systems were reported to provide very good yield of glycerol carbonate such as Cu (I) catalysts and $PdCl_2$(1,10 phenanthroline) with KI. Although it is traditional synthetic process but it has many limitations like the toxicity of CO and difficulty to handle and to maintain safety both at laboratory and industrial scale [59-60].

1.9.3 Phosgene + glycerol

Glycerol carbonate can also be synthesized from glycerol using one of the carbonylation source phosgene ($COCl_2$). The synthesis of cyclic carbonate by reaction of ethylene glycol with phosgene. Carbonate chloroformate ester was also synthesized from glycerol with addition of liquid phosgene. In this reaction process liquid phosgene and glycerol were slowly mixed under vigorous stirring for 6h at room temperature resulting 90% yield [16-18]. The application of phosgene seems to be a very simple and effective way to produce organic carbonate but the toxicity nature of this gas and difficulty in handling makes the reaction process undesirable[61-63].

1.9.4 Urea + glycerol

The application of urea for synthesis of GLC in presence of a suitable catalyst is one of the attractive pathways which is also one of the traditional methods for glycerol carbonate production. In this reaction process catalysts exhibiting Lewis acidic sites are highly responsible for providing significant yield of GLC at optimized reaction conditions. The catalysts like magnesium sulphate, zinc oxide, zinc sulphate, metal oxides like (CaO, La_2O_3, ZrO_2 etc), γ-zirconium phosphate, HTC-Zn derived from hydrotalcite, zeolites ZSM-5 are used for synthesis of GLC by application of urea as solvent [64-65]. The glycerolysis of urea is based on two hypotheses like, the preliminary step involves conversion of urea to isocyanic acid and another step is direct attack of urea to glycerol. The major advantage of this process is that urea is readily available and cheap and the by-product (ammonia) produced in this process can be used further for synthesis of urea. As all the reaction process have both advantages as well as disadvantages, glycerolysis with urea has many issues like it requires continuous removal of ammonia gas produced during the reaction process in order to increase the GLC yield. However, the formation of very undesirable products like biuret, isocyanic acid , isocyanates hampers the rate of GLC yield [66-67].

1.9.5 Alkylene carbonate +glycerol

Glycerol carbonate can be synthesized from glycerol by trans carbonation reaction with alkylene carbonate. In this synthetic process catalysts like zeolites, Ion exchange resin Amberlyst A26, mixed oxides like (Al/Mg, Al/MgO etc), quaternary ammonium salts, ionic liquids immobilized on mesoporous MCM-41 are extensively used for GLC production. More frequently ethylene carbonates act as a reactant with glycerol for GLC production in solvent free conditions to provide highest conversion of glycerol at optimized reaction condition, for instance the reaction of glycerol with EC in presence of RNX-MCM41 provided 92% GLC yield which was reported by Cho et al., 2016 whereas 7wt% Mg /AlO hydrotalcite catalyst provided 82% GLC yield reported by Climent et al., 2010 [23]. The major drawbacks of this process is that it requires application of reduced pressure (35mmHg) to remove the ethylene glycol by product to displace chemical equilibrium towards glycerol carbonate formation [68–69].

1.9.6 Di alkyl carbonate + glycerol

The transesterification reaction of glycerol can be occurred with di alkyl carbonates like dimethyl carbonate (DMC) and diethyl carbonate (DEC) etc. These chemicals are extensively studied for GLC synthesis as possessing environmentally friendly nature and treated as green solvents. In this method DMC acts as itself solvents and methanol are produced as side product which can be easily separated by distillation and further used in biodiesel production process. It is a safer and greener alternative process for GLC synthesis as in this process the catalysts/solvent both can be easily separated and it does not need any special conditions. Numerous catalytic systems are investigated for transesterification of glycerol using DMC and DEC. Various types of catalysts whether it is homogeneous or heterogeneous are extensively applied for better conversion of glycerol. The widely adopted DMC as a carbonate source presents higher efficiency at mild reaction condition, low toxicity, and appreciably high yield of GLC from abundant glycerol. Many homogeneous catalysts like CaO, MgO, K_2CO_3, KOH, NaOH etc are used for glycerol carbonate synthesis and provided very good yield percentage with high turnover frequency value but the separation process of catalyst was much more difficult as a result in order to overcome these issues heterogeneous catalyst was applied for GLC synthesis. Many heterogeneous catalytic systems like KNO_3/CaO, Mg-La, Mg/Zr/Sr, Li/ZnO, hydrotalcites, Mg/Al/Zr, hydroxyapatite modified with KF, $LiNO_3/Mg_4AlO_{5.5}$,CaO/ZrO_2 etc are extensively studied for transesterification of glycerol with DMC [70–73]. This synthetic method using DMC does not require high energy consumption and rigorous separation, besides this it is less time consuming as compared to reaction involved in phosgene and alkylene carbonates. DMC having lower boiling point (90°C) facilitate easier distillation separation process of both methanol and unreacted DMC from the product mixture. Similar to DMC, diethyl carbonate (DEC) can be also used as a source of carbonate and catalysts like Mg-Al hydrotalcite, CaO, $MgCO_3$, enzymes like lipase, Novozymes, ionic liquids like quaternary ammonium salts are used for glycerol carbonate synthesis with DEC. More exotic catalysts like 1-n-butyl-3-methylimidazolium-2-carboxylate and 1,3 dichloro distannoxanes were also reported for the reaction [54] .

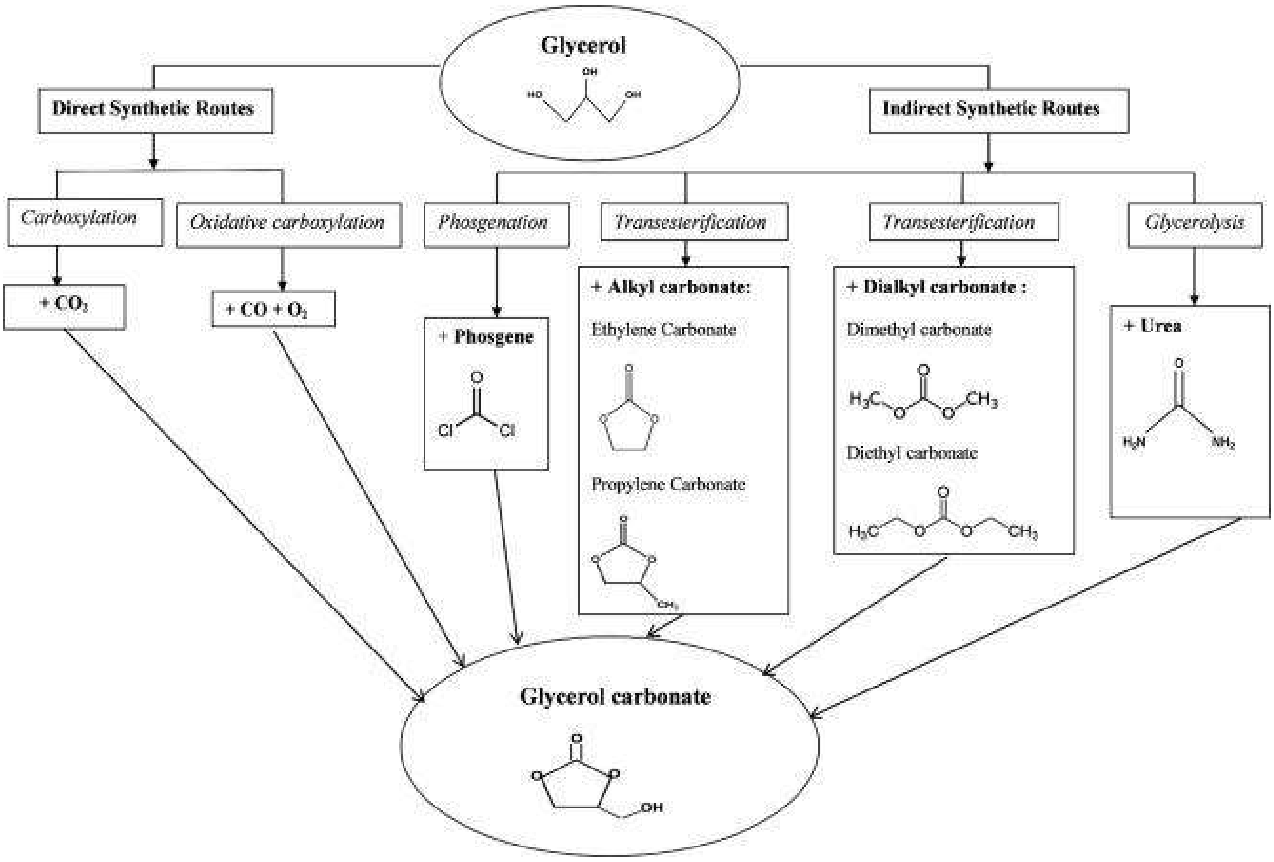

Fig 1.6 Various synthetic pathway for glycerol carbonate.

(W.K. Teng et al. / Energy Conversion and Management 88 (2014) 484–497).

1.10 Research gaps

The transesterification reaction of glycerol with DMC using both acidic and basic catalysts is an interesting reaction. Supported by the increasing sustainable awareness, glycerol carbonate has gained much interest over the last 20 years because of its versatile reactivity and as a way to valorise waste glycerol. Numerous synthesis pathways for this molecule were identified, some of them very promising and on the verge of being applied at an industrial scale. Despite the relative efficiency of catalysts in glycerol transesterification many of them have low densities of effective basic sites and rapid loss of catalytic activity with reuse. The basic nature of catalysts accelerates the reaction by abstraction of proton from glycerol. Taking into account all the above-mentioned features there is need for development of highly active and inexpensive heterogenous basic catalyst with strong basic sites desired for the transesterification of glycerol to obtain high yield of GLC. Many homogeneous catalysts like MgO, NaOH, K_2CO_3, CaO, $CaCO_3$, KOH, Li OH etc have showed excellent catalytic activity for transesterification reaction of glycerol with DMC, but the separation process of these catalysts from the product mixture is highly difficult. On the other hand, many heterogeneous catalysts like CaO/Al_2O_3 (polyamide), $Li/Mg_4AlO_{5.5}$, Ti-SBA-15, CaAl-LDHs, Mg/ZrO_2, KF/La-Zr, HTC-Ni, Li/ZrO_2 etc are extensively utilized for glycerol carbonate synthesis [74-78]. Most of the catalysts showed lower selectivity towards GLC. Moreover poor reusability, and stability , long reaction time, the need for more than one solvent, high energy consumption are the disadvantages of these catalysts [79–82]. There are many reports highlighting the need for the development of new heterogeneous catalytic materials with strong basic sites and are reusable and easily recoverable. One of the important factors is to understand the relationship between the physicochemical properties of catalysts and its activity in conversion of glycerol for the rational design of catalysts. Although basic metal oxides are found to have high basic strength but the stability of these are major problems. In order to increase the basic strength and stability of catalysts it is advantageous to prepare bimetallic oxides with sufficient basic strength. Another factor is to enhance the reusability of catalyst at same reaction condition. As both alkali and alkaline metal oxides are basic in character so many research is going on the study of catalytic activity study of these metal oxides. Numerous literature study reveals the study of alkaline metal-based oxides like Ca, Ba, Sr on transesterification of glycerol as well as biodiesel production process, but a very few of Mg based catalysts are used in the study of glycerol carbonate synthesis till date. The main motto of our work is to a broad study of Mg based heterogeneous catalysts for transesterification reaction of glycerol. An attempt is made to test Mg modified heterogenous catalyst for conversion of glycerol in this thesis. Whatever the synthetic strategy for manufacturing of GLC in both industrial and lab scale it must meet some basic criteria for the feasibility of products as

- If catalytic, a cheaper, easily separable and recyclable catalyst must be used.
- Simple separation and purification method should be adopted.
- Avoiding of use of solvent.
- A lower reaction time, intrinsically safe catalyst (both highly inflammable and toxic chemicals must be avoided.

According to these criteria it is apparent that a synthetic strategy from glycerol and DMC using Mg based catalyst seems to be obvious choice because on one hand both are green chemicals and commercially available at low price and the atom efficiency could be as high 88%.

1.11 Objectives of thesis

The present work aims at

- Development of Mg based heterogeneous catalysts for transesterification of glycerol with DMC.
- Designing of Mg doped ZnO, bimetallic NiMgOx and spinels like $MgCr_2O_4$ and MgV_2O_4 catalysts via simple wet impregnation and coprecipitation route respectively.
- Detailed characterization of designed catalysts to understand the surface and structural properties of catalyst and also the relation between the catalytic activities and their properties in glycerol conversion.
- Evaluation of catalytic activity for synthesis of glycerol carbonate.
- Establishment of optimum reaction conditions for transesterification of glycerol.