

Manufacturing of Glycerol Carbonate in Aspen Plus

Reshma Sarode-Dolas

AISSMS College of Engineering, Pune, Maharashtra, India

I. INTRODUCTION

Sustainable chemistry is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances. The synthesis of glycerol carbonate from glycerol and urea has currently attracted much attention from the angle of sustainable chemistry. The synthetic glycerol carbonate from glycerol and urea has several advantages [1-4]:

- It utilizes and reduces the undesired CO₂ emitted from various sources.
- The by product glycerol produced during the manufacture of biodiesels is well utilized here.
- The synthesis produces a value added organic product of glycerol carbonate which has many practical applications.
- It replaces the current method for production of glycerol carbonate using highly toxic compound such as phosgene.

The synthesis of glycerol carbonate from glycerol and Urea is one of indirect chemical transformations of CO₂ into organic compounds as the urea can be produced from CO₂ and ammonia. Scientists have investigated the direct and indirect utilization of CO₂ as a feedstock which also includes chemical reactions with urea. Various types of base catalysts have been tested for the synthesis of glycerol carbonate from glycerol and urea. This includes inorganic salts such as ZnSO₄ and MgSO₄ [4-7]. These are effective homogeneous catalysts. Heterogeneous catalysts may be more useful for post reaction procedures like easy recovery and reuse of catalysts when compared to homogeneous ones. One of the important glycerol conversions is synthesis of glycerol carbonate. Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is one of the most promising chemical due to its ideal physico chemical properties such as high stability, low toxicity, good biodegradability, high boiling point and low in flammability. Glycerol carbonate has many applications as a solvent in cosmetics, medicine, an intermediate in organic synthesis, in the synthesis of polycarbonates, polyurethanes, glycerol-based polymers, surfactant, production of resins, plastics and pharmaceuticals [8-11].

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is one of the most promising chemical due to its ideal physico chemical properties such as high stability, low toxicity, good biodegradability, high boiling point and

low in flammability. Glycerol esterification processes are carried out using heterogeneous catalysts having strong acidic sites [12-15]. Despite the relative efficiency of catalysts in glycerol esterification, many of them have low densities of effective acid sites and rapid loss of catalytic activity with reuse. Furthermore, the unavoidable generation of water as a by-product of esterification can have a serious impact on the catalytic performance of some solid acid catalysts. Taking into account all the above mentioned features, there is a strong heterogeneous catalyst with strong acidic sites. Consequently, design of a highly active, inexpensive, robust, and water-tolerant heterogeneous solid acid catalyst is highly desired for the esterification of glycerol [9-11].

Synthesis of glycerol carbonate from glycerol and urea in the presence of catalysts with Lewis acidic sites is an attractive method. The presence of Lewis acidic sites is able to activate the urea, which is an important feature of the catalyst to achieve high yields of the glycerol carbonate. Some of the reported catalysts contain Gold and Pd which are expensive and overall activity is not very high even at long reaction times. The catalysts with acidic and basic sites are effective for the selective synthesis of glycerol carbonate with high activity. However, these base catalysts exhibited low activity during recycling [15-17]. There are still many issues arising from these reports which highlight the need for development new catalytic materials. Taking into account all the above mentioned features, there exist a strong need for developing of new heterogeneous catalysts which should be highly active, recoverable, stable and selective. Apart from the development of catalysts there is a need to understand the relation between the catalyst characteristics and activity for the rational design of catalysts to the conversion of glycerol into chemicals [18-20].

The interest for developing synthetic procedures for GC manufacturing is growing in parallel with its applications. The direct synthesis from glycerol and CO₂ is not currently industrially possible due to low CO₂ reactivity resulting in yields below 32%. Consequently, indirect synthetic approaches are needed at present. The following processes have been analyzed:

- Carbamoylation/carbonation of glycerol with urea;
- Transesterification of ethylene carbonate or dimethyl carbonate with glycerol;
- Reaction of glycerol halo-derivatives (3-chloro-1,2-propanol and epichlorohydrin) with alkaline.

1.1 Synthetic Routes for Glycerol Carbonate from Glycerol:

There are several routes reported to upgrade in which the large quantities of waste glycerol into glycerol carbonate [21-22]. Out of all routes some are focused on reactions based on inexpensive, bio-based and readily available raw materials for the synthesis of glycerol carbonate as illustrated below.

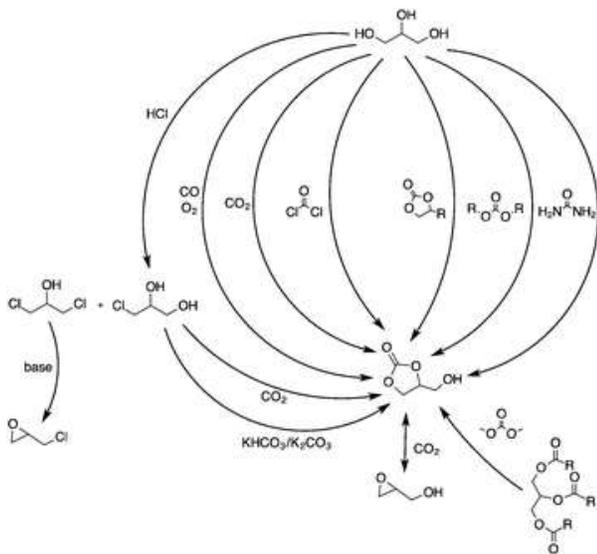


Fig. 1.1 Main routes to glycerol carbonate synthesis

A) Carbon dioxide + glycerol:

Glycerol carbonate can be obtained by reacting glycerol with carbon dioxide in the presence of catalysts. Sn-catalysts were the first reported catalysts for the carbonation of glycerol with CO₂ [18-23]. The Addition of alcoholic solvents such as methanol helps in accelerating rate. Though it improves the yield greatly the thermodynamic calculations showed that the reaction of glycerol with carbon dioxide was thermodynamically limited.

B) Phosgene + glycerol:

This follows the synthesis of a cyclic carbonate, ethylene carbonate, by reacting phosgene with ethylene glycol. Since then, several syntheses of molecules bearing an ODO group were reported through the reaction of 1,2-diols with phosgene. The synthesis of carbonate is chloroformate ester through the reaction between glycerol and liquid phosgene. Liquid phosgene and glycerol were slowly added under vigorous stirring for 6 h at 30 °C. The reported yield of carbonate chloroformate ester was about 90% [17-25]. However, because of the issues related to the handling of this highly toxic gas, phosgene use was very limited.

C) Alkylene carbonate + glycerol

Glycerol carbonate can be prepared from glycerol by transcuration with alkylene carbonates. Several catalytic systems such as zeolite having basic sites or ion exchange resins Amberlyst, basic oxides (MgO) or mixed oxides

(Al/Mg, Al/MgO) derived from hydrotalcites, quaternary ammonium salts ionic liquids immobilized on mesoporous were reported to provide good yields. Reduced pressure (35 mmHg) is often applied to remove the ethylene glycol a by product to displace chemical equilibrium toward glycerol carbonate formation.

D) Dialkyl carbonate + glycerol

Glycerol carbonate can also be prepared from glycerol by transcuration with dialkyl carbonates such as dimethyl carbonate (DMC) or diethyl carbonate (DEC). This synthetic route for producing glycerol carbonate is one of the most studied and, therefore, large selections of catalysts have been proven to work. Different catalytic systems such as alkyl ammonium (tetra-nbutylammonium bromide), K₂CO₃, Sn-catalysts (di(nbutyl) tin dimethoxide, di(n-butyl)tin oxide), basic catalysts (CaO, MgO, CaCO₃, K₂CO₃, KOH, NaOH), uncalcined Mg-Al hydrotalcite, hydroxyapatite (HAP) modified with KF, Mg/Al/Zr mixed oxide catalysts, calcined hydrotalcite hydromagnesite, Mg/Sr/Zr mixed oxide catalysts have been reported [18-24].

Similar to dimethyl carbonate, diethyl carbonate can be used as a source of alkyl carbonates. Mg/Al hydrotalcite-like compounds and enzymes are used as catalysts. More exotic catalysts such as 1-n-butyl-3-methylimidazolium-2-carboxylate and 1,3-dichlorodistannoxanes were also reported for this reaction [11-16].

E) Urea + glycerol

Synthesis of glycerol carbonate from glycerol and urea in the presence of a suitable catalyst is an attractive method. The practical route for carbonylation of glycerol is the use of urea as carbonate source. The major advantage of this method over other processes is that urea is readily available and cheap by product produced in this reaction (ammonia) can be utilized for the synthesis of urea. The catalysts such as, ZnO, zinc sulphate, ZnCl₂, γ-zirconium phosphate, mixed metal oxides, mixed oxides, HTc-Zn derived from hydrotalcite, Co₃O₄/ZnO, gold supported zeolite ZSM-5, manganese sulphate etc. produces high glycerol carbonate yields [21-25]. Calculations of the chemical equilibrium constants showed that higher temperature and lower pressure are favourable for the reaction of glycerol and urea. From an ecological point of view, this synthetic route has the advantage of using only bio-based reactants. In addition, the various synthesis methods reported do not require organic solvents. However, the formation of ammonia as a by-product, the uses of homogenous or uneasily recoverable catalysts and the relatively high reaction temperatures have negative ecological impacts on these synthesis methods [12-15].

1.2 Glycerol Carbonate as an Intermediate in Chemical Synthesis:

Glycerol carbonate undergoes all the reactions of cyclic carbonates plus those of alcohols. GC can react both as a nucleophile through its hydroxyl group, and as an electrophile through its ring carbon atoms [5-8]. The synthesis of glycerol carbonate esters by acylation of GC in the presence of TEA as HCl scavenger using dichloromethane as solvent. Typically this kind of reaction results in yields higher than 90%. The obtained esters have good thermal and oxidation stability, and some of them (octanoate, dodecanoate, and oleate) exhibit surfactant properties [8-11]. A very interesting chemical which can be obtained from Glycerol Carbonate is Glycol. As shown in following figure 1.2:

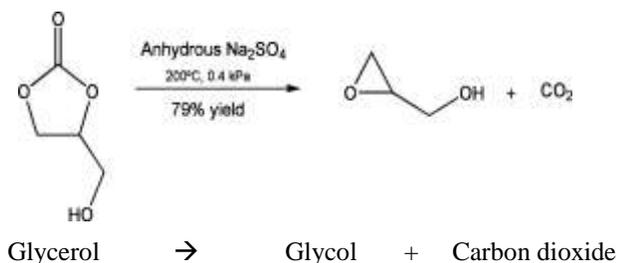


Fig. 1.2 Reaction of glycol

It is used as a raw material for obtaining polyglycerols, polyglycerol esters, glycidyl ethers, energetic matrices for solid propellants, pharmaceuticals as well as in perfumes and cosmetics, detergents, drugs, paints, UV curing agents for semiconductors, stabilizer for natural oils and vinyl polymers, demulsified, dye-levelling agent, etc. Currently, it is a high value chemical and, consequently, a wider range of applications are to be expected if a more economic synthetic route for its production is developed. Such a route could be the decarboxylation of GC which is usually carried out by continuously distilling glycidol at vacuum at temperatures of 180–200 °C in the presence of catalysts such as anhydrous sodium sulphate and zeolites in 70–85% yields [14-18].

II. LITERATURE SURVEY

Glycerol carbonate has wide usage. It has direct applications or as intermediate (indirect applications) for various industrial and synthetic applications as shown below in the figure 2.1. It has high boiling point, high flash point and low volatility, glycerol carbonate and its esters are potential low VOC (volatile organic compound) solvents. Therefore, glycerol carbonate found uses as a general purpose solvent, an electrolyte liquid carrier or an additive in lithium and lithium ion batteries, a curing agent in cement and concrete, an additive in cosmetics, in liquid gas separation system, a detergent, a plant vitalizer and a blowing agent. They can also be converted into chemical intermediates, which are then useful in the production of epichlorohydrin, surfactants and polymers [10-16].

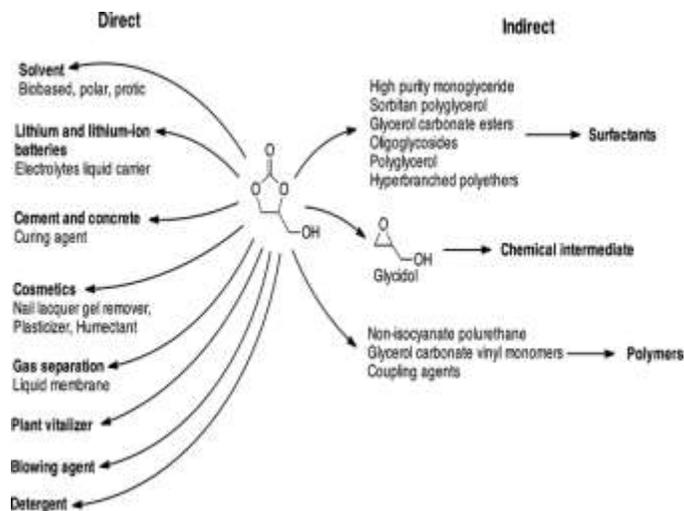


Figure 2.1 Direct and indirect applications of glycerol carbonate.

A conventional biodiesel production plant was retrofitted using thermodynamic analysis, which employs process heat integration, column grand composite curves, and energy loss profiles to assess the existing operation and suggest modifications. About 1 kg of glycerol is formed for every 10 kg of biodiesel produced. The production cost of biodiesel increases by \$0.021/litre for every \$0.22/kg reduction in glycerol selling price [16]. As a result, economical utilization schemes of bio glycerol can lead to a more economical biodiesel production plant. A recent study suggests that addition of glycerol carbonate production by direct carboxylation route may be more economical than the conventional biodiesel production plant. However, recently, direct carboxylation of glycerol and CO₂ is thermodynamically limited and the yield is very low (less than 35%). Low yield requires high energy for the separation of products and the recovery of reactants leading to high cost of manufacturing [16]. Thus the synthesis of glycerol carbonate by glycerolises route is developed and economics of the biodiesel-glycerol carbonate production by direct carboxylation and glycerolises plants are compared. Combination of bio based origin and wide reactivity has made glycerol carbonate a versatile and renewable building block for organic chemistry [5-7].

While promising from an environmental standpoint, applications of glycerol carbonate are slowly emerging. Glycerol carbonate can be converted into epichlorohydrin, a product that has a large industrial application, under very mild conditions [9–11]. Because of a high boiling point (110–115 °C at 0.1 mmHg), high flash point (190 °C) and low volatility (vapour pressure is 8 mbar at 177 °C), glycerol carbonate and its esters are potential low Volatile Organic Compound (VOC) solvents for many applications. Looking for a bio based alternate to organic solvents [1-4]. Also, glycerol carbonate has a considerable possibility to become a major chemical intermediate, for instance in polymer production.

2.1 Synthetic Strategy of Glycerol Carbonate:

Whatever the selected synthetic strategy for industrial manufacturing of GC, it is obvious that it must meet some basic criteria to be industrially feasible, namely the following [11-16]:

- C1: If catalytic, a cheap and easily separable and recyclable catalyst must be used.
- C2: Simple separation and purification methods
- C3: Avoiding or minimizing the use of solvents
- C4: High conversion and selectivity to facilitate accomplishment of criterion 2 and, together with criteria and 5, to increase productivity and minimize capital investment
- C5: A low reaction time
- C6: Intrinsically safe (Therefore, both highly inflammable and toxic chemicals must be avoided.)

There are basically two strategy are illustrate below:

- 1) Direct Synthetic Strategy
- 2) Indirect Synthetic Strategy

2.1.1 Direct synthetic strategy:

A synthetic direct strategy starting from glycerol and CO₂ seems to be the obvious choice because on one hand both are green chemicals commercially available at a low price, and on the other hand, the atom efficiency could be as high as 87%. However, attempts for synthesizing GC directly from glycerol and subcritical CO₂ carried out by using n-Bu₂SnO and nBu₂Sn(OMe)₂, or CeO₂/Al₂O₃ and CeO₂/Nb₂O₅ as catalysts, have been unsuccessful due to poor CO₂ reactivity leading to a peak yield of 10% using tetra(ethylene glycol)dimethyl ether as solvent [15-18]. Above all a more promising yield of 32% in milder conditions has been reported using nBu₂SnO as the catalyst [19-21] and methanol reaction scheme as the solvent as shown in following Figure 2.2 and reaction parameter shown Table 2.1:

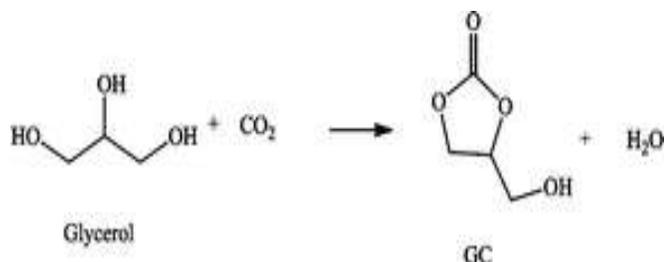


Figure 2.2 Direct synthetic strategy

Table 2.1 Direct synthetic strategy

Pressure	5Mpa	3.5Mpa
Temperature	180°C	80°C
Residence Time	15 hr	4 hr

Solvent	Tetra(ethylene glycol) dimethyl ether	Methanol
Catalyst	ⁿ Bu ₂ SnO, Al ₂ O ₃	ⁿ Bu ₂ SnO
Yield	≤ 10%	32%

GC production in industries must be carried out through an indirect synthetic approach starting from more reactive and easily synthesis able derivatives of glycerol and CO₂, leading to the two basic combinations of raw materials like (a) glycerol is reacted with CO₂ derivatives such as ethylene carbonate (EC), dimethyl carbonate (DMC), or urea; and (b) glycerol derivatives like 3-chloro-1,2-propanediol (HAL, glycerol α-monochlorohydrin) or epichlorohydrin (EPI) are reacted with carbon dioxide or with alkaline carbonates or bicarbonates [17-18].

2.1.2 Indirect synthetic strategy:

In Carbamoylation/Carbonation of Glycerol with Urea, glycerol is reacted with urea in equi-molar amounts at 130–150 °C in the presence of a catalyst and usually under vacuum to shift the thermodynamic equilibrium by removing continuously the ammonia formed, although the ammonia displacement by continuously flowing nitrogen at ambient pressure is also described [7-11]. Typical reaction conditions together with usual conversions and yields relative to glycerol are shown in following Figure 2.3.

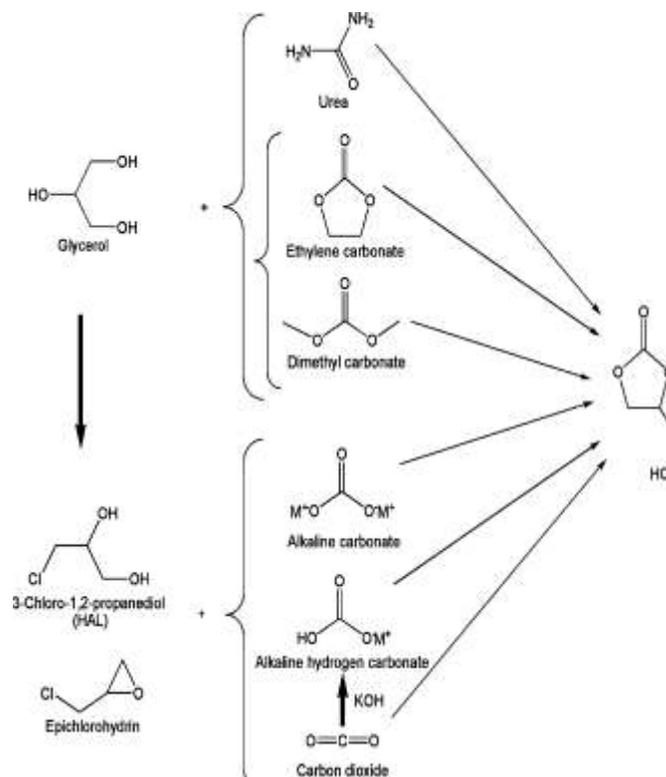


Fig.2.3 Indirect synthetic strategy

The formation of GC proceeds in two consecutive steps. Reaction conditions must be carefully selected to avoid a decrease in selectivity by reaction between glycerol carbonate and urea, leading to the carbamate of glycerol carbonate (CGC). Reaction proceeds thermally but with yields lower than 30%. Therefore, catalysts are needed. Initially, the reaction was carried out using ZnO and ZnSO₄ as catalysts with a conversion of 83% and a selectivity of 100% [16]. However, these catalysts have a major drawback in that they are soluble in the reaction mixture or are pulverized upon stirring, which makes their recovery difficult as well as the separation of GC.

2.2 Enzymatic Processing of Glycerol into value added Glycerol Carbonate

Glycerol carbonate was formed when reacting glycerol with dimethyl carbonate, diethyl carbonate or dibutyl carbonate in the presence of *Candida antarctica* lipase, using tert-butanol as a solvent [9-12]. Nearly 100% glycerol conversion was reached after 12 hr, with glycerol carbonate being the primary product [7]. The effects of reaction parameters including solvent choice and biocatalyst loading were also examined. The highest activity was found at restricted water conditions and when using tert-butanol as a solvent.

2.3 General market information of glycerol carbonate;

The cost detail of product GC is as shown in following Table 2.2:

Table.2.2 Market value of GC

Packing Unit	Price	Available Stock			Quantity
		Portland, OR	Philadelphia, PA	Japan	
25g	57.20 USD	3	8	>10	0↓
500gm	407.00 USD	2	5	>10	0↓

2.4 Properties

Synonym : 4-Hydroxymethyl-1,3-dioxolan-2-one
Synonym : 4-Hydroxymethyl-2-oxo-1,3-dioxolane
CAS Number : 931-40-8
Product Number : G0279

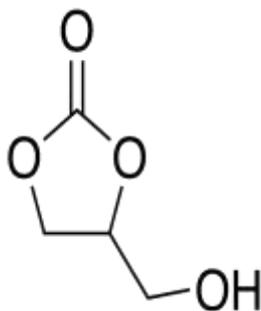


Figure 2.4 Structure of glycerol carbonate

Table 2.3

Property	Glycerol carbonate
CAS No.:	931-40-8
Appearance	Faint yellow viscous liquid
Molecular weight (g mol ⁻¹)	118.09
Density, 25 °C (g ml ⁻¹)	1.4
Boiling point (°C)	353.9 (760 mmHg)
Melting point (°C)	-69
Vapor pressure, 177 °C (bar)	0.008
Flash point (°C)	190
Dielectric constant, 20 °C	111.5
Hansen solubility parameter delta D, 25 °C (MPa ^{1/2})	17.9
Viscosity (Kinematic), 25°C (77°F)	61
Water Solubility	Miscible

2.5 Application and Uses

- Glycerol carbonate is used in cosmetics, pharmaceuticals, detergents, intermediate in chemical synthesis and in the production of useful polymeric materials such as polycarbonates, polyglycerol esters, hyperbranched polyols, and nonisocyanate polyurethanes.
- It can be used as a raw material for the synthesis of glycidol, polymers, surfactants, lubricating oils as emulsifiers, lustering agents, washing aids and detergents.
- Glycerol carbonate is an intermediate chemical such as, reactive protic solvent, a substitute for ethylene carbonate, propylene carbonate, cyclocarbonate derivatives, solvents for battery electrolyte, filming lubricants, filing plastifiers, agrosynthons, and monomers for polymerization.
- It is also a novel component of gas separation membranes, coatings, paints and surfactants. It can act as a non-volatile reactive solvent for several types of materials

III. MANUFACTURING PROCESS

3.1 Manufacturing of Glycerol Carbonate(C₄H₆O₄) from Glycerol and Urea:

Raw Materials

- Glycerol
- Urea
- Catalyst : ZnCl₂
- Conversion of Glycerol: 85%

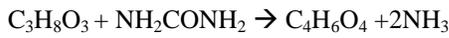
Reactor Condition:

- Temperature: 130^oC

b. Pressure: 3kpa

Glycerol + Urea → Glycerol Carbonate + Ammonia

Chemical Reaction:



Process Block diagram:

The process flow diagram is shown in Figure 3.1 (with recycle) and 3.2 (without recycle)

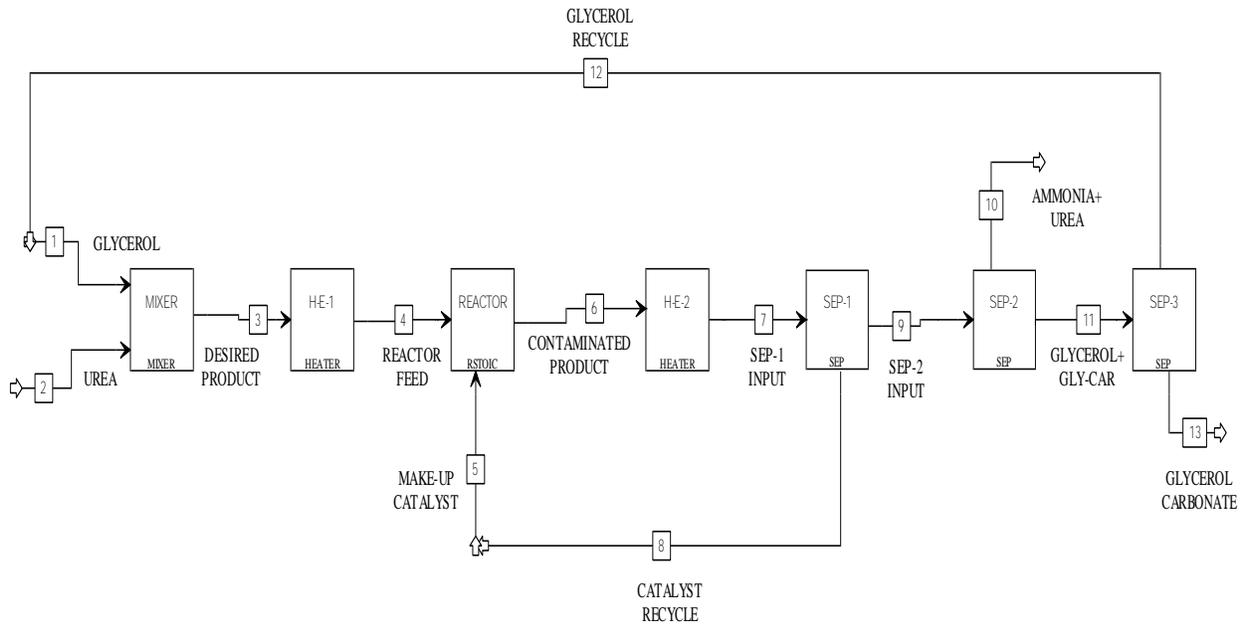


Figure 3.1 Manufacturing of glycerol carbonate from glycerol and urea with recycle

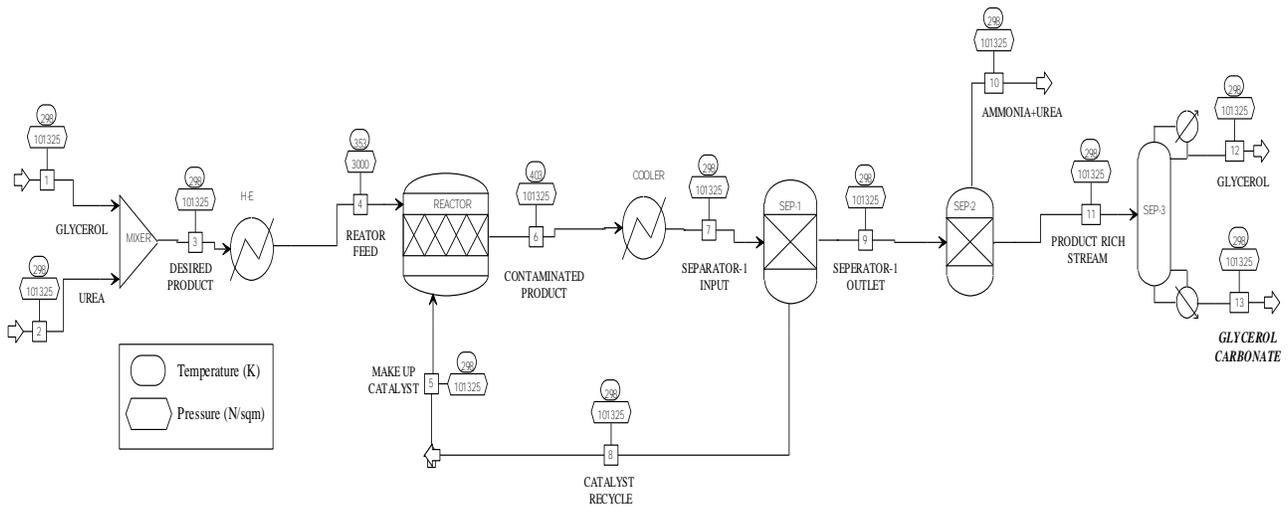


Figure 3.2 Manufacturing of glycerol carbonate from glycerol and urea without recycle

Process Description:

Stream No.	Description
1.	Mixer Inlet Stream content Glycerol
2.	Mixer Inlet Stream content Urea
3.	Mixer Outlet Stream content Glycerol + Urea which is inlet for heat exchanger
4.	Heat exchanger outlet stream and Reactor feed stream content Glycerol + Urea having high temp. than stream 3
5.	Make-up catalyst ZnCl ₂ is fed to the reactor.
6.	Product content stream having product Glycerol+ Ammonia and unreacted Glycerol + Urea + catalyst. .
7.	Sep-1 Inlet stream which content product + glycerol+ urea and catalyst also having low temperature.
8.	Sep-1 outlet stream content only catalyst ZnCl ₂ which is recycle back to reactor
9.	Sep-2 Inlet stream is the catalyst free stream which is sent to Sep-3 for further purification.
10.	Ammonia and Urea are separated from product stream
11.	Product rich stream send for purification of Glycerol Carbonate
12.	Unreacted Glycerol recycle back to process.
13.	Glycerol carbonate final product obtained.

In this process Glycerol is reacted with urea in presence of homogeneous Zn catalyst to give one mole of glycerol carbonate and 3 mole of ammonia. The best suited process conditions for this process are 130 °C and 3kPa temperature and pressure respectively. Compared to other Zn catalyst the ZnCl₂ give best result, % conversion and % selectivity is 85 and 97 respectively. After completion of reaction the formation of glycerol carbonate the catalyst is recycle back to the process and remaining product content stream send for purification process. After separation of ammonia and urea the contaminant stream of glycerol and glycerol carbonate is sent to the distillation column. Glycerol Carbonate is separated from glycerol due to difference is boiling point remaining glycerol is recycling to the process.

Simulation results

Characterisation of Zn catalyst: Comparative analysis of different catalyst used is shown in Figure 3.3. In the production of glycerol carbonate from glycerol and urea using Zn catalyst under solvent free conditions at 130⁰C temperature and 3kPa pressure proceed homogeneously not heterogeneously. For homogeneous catalyst such as ZnCl₂, ZnSO₄ or ZnBr₂ the Zn complex likely to form an active species for transformation of glycerol and urea to glycerol carbonate [17-19].

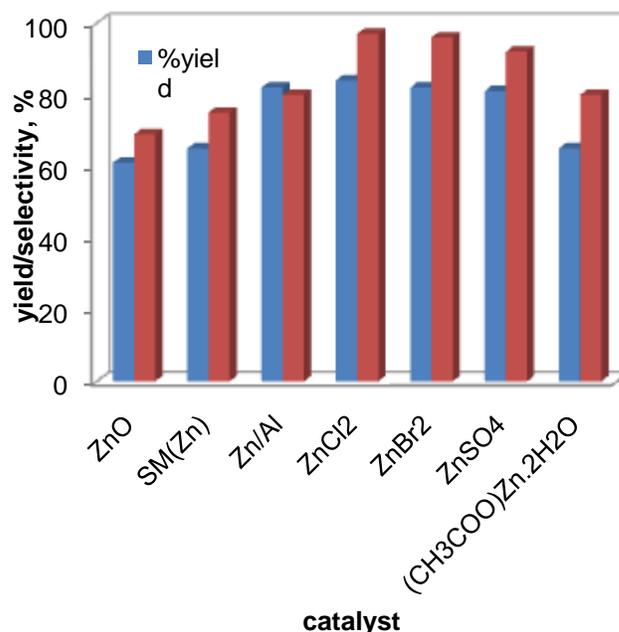


Figure 3.3 Comparison of Zn catalyst for manufacturing of glycerol carbonate using glycerol and urea

There are three different catalysts of ZnBr₂, ZnCl₂ and ZnSO₄ are used in this method. After comparing these three catalyst the result shows that the Selectivity to Glycerol carbonate was <100% mainly due to oligomerization of the product. It was found that ZnCl₂, ZnBr₂ and ZnSO₄ gave conversion values >80% and selectivity levels >90% [6-11]. Figure 3.3 indicates the difference in the performance among those heterogeneous and homogeneous catalyst. The yield reaction changes catalyst concentration. The yield was marginal higher than certain amount of the catalyst used. The yield of Glycerol carbonate formed against the amount of the dissolved Zn species. In this method the ZnO reacts with the isocyanic acid produced from urea transforming to zinc complex to which two ammonia molecules are weakly coordinated [15-18]. One of the coordinated ammonia molecule would be exchanged with one glycerol molecule resulting in the formation of complex two to which glycerol molecule reacts with then Zn center through its oxygen atom.

Table 3.1 Simulation result for synthesis of glycerol carbonate from glycerol and urea

Glycerol Carbonate from Glycerol and Urea													
Stream ID	1	2	3	4	5	6	7	8	9	10	11	12	13
Mole Flow (kmol/sec)													
GLYCEROL	50	0	50	50	0	7.5	7.5	0	7.5	0	7.5	7.5	0
UREA	0	50	50	50	0	7.5	7.5	0	7.5	7.5	0	0	0
GLY-CAR	0	0	0	0	0	42.5	42.5	0	42.5	0	42.5	0	42.5
AMMONIA	0	0	0	0	0	85	85	0	85	85	0	0	0
ZnCl ₂	0	0	0	0	1.86	1.86	1.86	1.86	0	0	0	0	0
Molar Flow (kmol/sec)	50	50	100	100	1.86	144.36	144.36	1.86	142.5	92.5	50	7.5	42.5
Mass Flow (kg/sec)	4604.7	3002.78	7607.518	7607.518	253.50944	7861.0274	7861.0274	253.50944	7607.518	1898.0149	5709.5	690.710	5018.79
Volume Flow (m ³ /sec)	3.55860	4.307847	8.11048054	41231.802	0.24501216	3367.04635	2346.32122	0.24501216	2371.6013	2263.013	4.92945	0.5337	4.40830
Temperature (K)	298.15	298.15	298.149764	353.15	298.15	403.15	298.15	298.15	298.15	298.15	298.15	298.15	298.15
Pressure (N/m ²)	101325	101325	101325	3000	101325	101325	101325	101325	101325	101325	101325	101325	101325

Then the interacting hydroxyl group of glycerol captures the neighbouring isocyanate group producing a carbonate complex three. This group further converted to glycerol carbonate via Intracyclization releasing ammonia and regenerating the complex one. Only a small amount of Zn species was found to leach into the liquid phase and so the coexistence of glycerol and urea was required for Zn leaching. This synthesis of Glycerol carbonate from Glycerol and Urea in presence of Zn containing catalyst like ZnCl₂ under solvent free condition at 130°C and at 3 kpa pressure. Proceed homogeneously but not heterogeneously. The Zn species dissolved in the liquid phase by an action of both Glycerol and Urea [21-23]. So, compared to other Zn species ZnCl₂ give best result in manufacturing of Glycerol Carbonate from glycerol and urea. Streamwise simulation result using Aspen is shown in Table 3.1.

3.2 Manufacturing of Glycerol Carbonate (C₄H₆O₄) from Glycerol and CO₂:

Raw Materials:

- Glycerol
- CO₂
- Methanol
- Catalyst : n-dibutyltin oxide
- %Conversion of Glycerol: 35%

Reactor Condition:

- Temperature: 80°C
- Pressure: 3.5mpa

Chemical Reaction:



Process Block Diagram

The process flow diagram is shown in Figure 3.4 (with recycle) and 3.5 (without recycle)

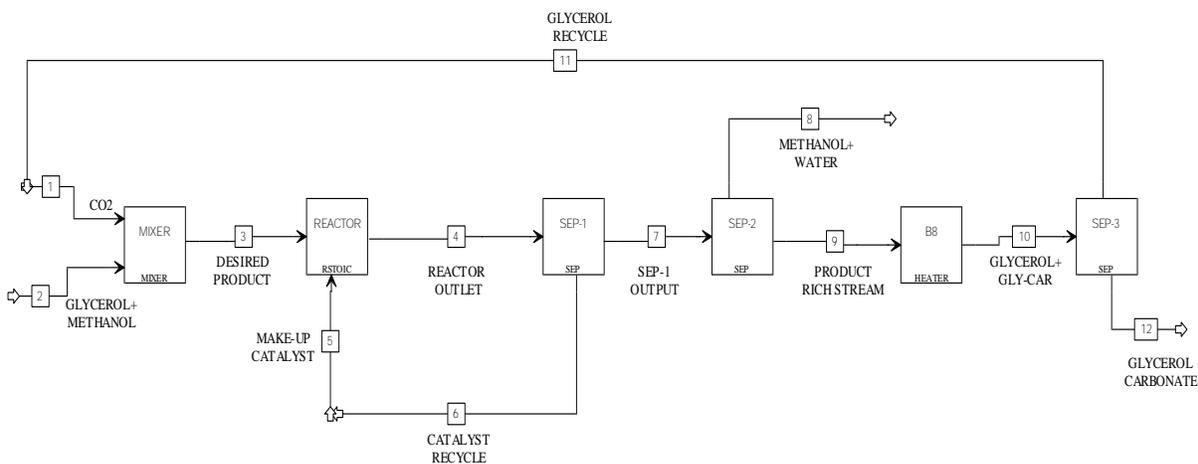


Figure 3.4 Manufacturing of glycerol carbonate from glycerol and CO₂ with recycle

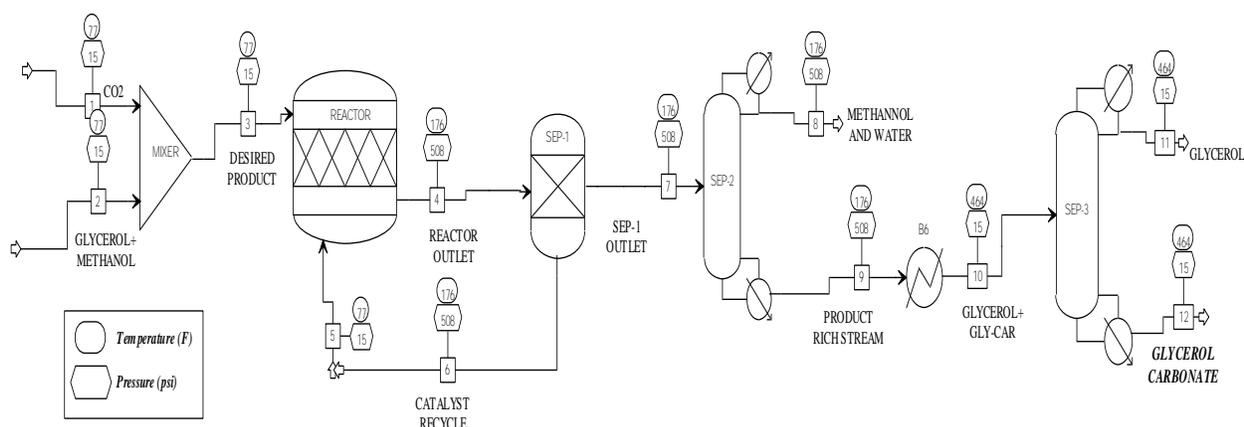


Figure 3.5 Manufacturing of glycerol carbonate from glycerol and CO₂ with recycle

Process Description:

Stream No.	Description
1.	Mixer Inlet Stream content CO ₂
2.	Mixer Inlet Stream content Glyceol+ Methanol
3.	Mixer Outlet Stream content Glycerol + Methanol + CO ₂ which is inlet for Reactor
4.	Reactor outlet stream content product and unreacted Glycerol, Methanol and CO ₂
5.	Make up catalyst n-Dibutyltin Oxide feed to the reactor
6.	Sep-1 outlet stream content only catalyst which is recycle back to reactor.
7.	Sep-1 product stream which content product + glycerol+ CO ₂ + methanol send to Sep-2
8.	Outlet from Sep-2 content Water+Methanol which is separated from Glycerol Carbonate and glycerol
9.	Sep-2 Product rich content high amount of Glycerol carbonate and some unreacted Glycerol
10.	Outlet of heat exchanger content Glycerol and Glycerol carbonate send to sep-3 for separation based on boiling point.
11.	Glycerol is obtained as a top product.
12.	Glycerol Carbonate final product obtained from bottom of column.

In this process Glycerol is reacted with CO₂ in presence of methanol as a solvent and ndibutyltin oxide as a catalyst to give one mole of glycerol carbonate and one mole of water. A conversion of 32.15 % can be achieved under supercritical

CO₂ in the presence of zeolites and ion exchange resins. 35% conversion is possible at 80 °C and 3.5 MPa using 1 mol% of ndibutyltin (IV) oxide (n-Bu₂SnO) and methanol as solvent. The best suited conditions for this process are 80°C and 35 bar temperature and pressure respectively. After completion of reaction the catalyst is recycle back to the process and remaining product content stream send for purification process. After separation of methanol and water the contaminant stream of glycerol and glycerol carbonate is sent to the distillation column. Glycerol Carbonate is separated from glycerol due to difference is boiling point remaining glycerol is recycling to the process.

Simulation Result

The market value of crude bioglycerol is low due to its excess production as a by-product of the biodiesel production. Purification of glycerol in a small to medium scale biodiesel production plant is not an option due to high investment in separation units and low rate of return. As a result, direct conversion of glycerol into a value-added chemical, glycerol carbonate, reduces over production of crude glycerol and may improve the economics of the biodiesel plant. The process also consumes carbon dioxide, which is a renewable feedstock. If we comparing two glycerol carbonate production plant based on profit then there is the 17% chance that the direct carboxylation plant will not be profitable, while there is approximately 2% chance that the glycerolysis plant will not be profitable [8-10]. The glycerolysis plant is about 15% more likely to be profitable compared to the direct carboxylation plant. If the median probability of 50% is considered, then the glycerolysis plant yields having higher value of Net profit value and the lowest values of NPV for the direct carboxylation.

Table 3.2 Simulation result for synthesis of glycerol carbonate from glycerol and carbon dioxide

Glycerol Carbonate from Glycerol and CO ₂												
Stream ID	1	2	3	4	5	6	7	8	9	10	11	12
Mole Flow (kmol/hr)												
GLYCEROL	0	20.848100	20.848100	14.622214	0	0	14.622214	0	14.622214	14.622214	14.622214	0
CO ₂	6.2258859	0	6.2258859	0	0	0	0	0	0	0	0	0
WATER	0	0	0	6.2258859	0	0	6.2258859	6.2258859	0	0	0	0
GLY-CAR	0	0	0	6.2258859	0	0	6.2258859	0	6.2258859	6.2258859	0	6.2258859
N-DIBUTY	0	0	0	0.0040173	0.0040173	0.0040173	0	0	0	0	0	0
METHANOL	0	237.81168	237.81168	237.81168	0	0	237.81168	237.81168	0	0	0	0
Molar Flow (kmol/hr)	6.2258859	258.65978	264.88566	264.88968	0.0040173	0.0040173	264.88566	244.03756	20.848100	20.848100	14.622214	6.2258859
Mass Flow (kg/hr)	273.99999	9539.9999	9813.9999	9814.4443	0.9999999	0.9999999	9813.4443	7732.1609	2081.2833	2081.2833	1346.6287	734.65454
Volume Flow (l/min)	2538.6064	179.81522	1268.7703		6.11e+32	4.87e+32	225.48863	176.48815	60.164801	64.531888	20.342887	43.831566
Temperature (K)	298.15000	298.15000	298.39944	353.15000	298.15000	353.15000	353.15000	353.15000	353.15000	513.15001	513.15001	513.15001
Pressure (N/m ²)	1.0000000	1.0000000	1.0000000	34.542315	1.0000000	34.542315	34.542315	34.542315	34.542315	0.9869233	0.9869233	0.9869233

Production of glycerol carbonate using direct carboxylation route suffers from low yield and costly separation units. In contrast, the glycerolysis route using CO₂ indirectly and urea as a CO₂ donor may simplify the glycerol carbonate production, and hence it leads to a more economical biodiesel-glycerol carbonate production process. The synthesis of Glycerol carbonate from glycerol and CO₂ without any catalyst in presence of Methanol as solvent at temperature of 80°C and 3.5 mpa pressure the reaction is carried out and obtained product is glycerol carbonate and water as a bi-product. Addition of glycerol carbonate production process directly uses of excess methanol as a solvent in the direct carboxylation reaction. This process shows that glycerol carbonate production not only results in a more environmentally friendly process as it consumes renewable feedstock of carbon dioxide obtained from biodiesel process plant but it is also an economical process as it converts two by-products into a value-added bio-product [10-11]. Streamwise simulation result using Aspen is shown in Table 3.2.

3.3 Manufacturing of Glycerol Carbonate from Glycerol and Dimethyl Carbonate

Raw Materials:

- Glycerol
- Dimethyl Carbonate
- Catalyst : KF/Al₂O₃ (KOH and KAlO₂)
- %Conversion of Glycerol: 96%

Reactor Condition:

- Temperature: 75°C
- Pressure: 1atm

Chemical Reaction:



Process Block Diagram:

The process flow diagram is shown in Figure 3.6 (with recycle) and 3.7 (without recycle)

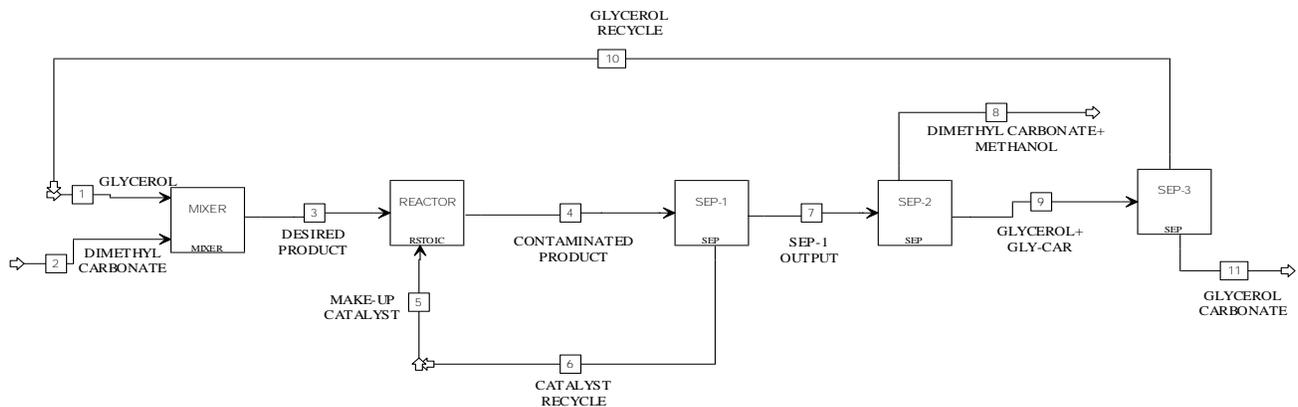


Figure 3.6 Manufacturing of glycerol carbonate from glycerol and dimethyl carbonate with recycle

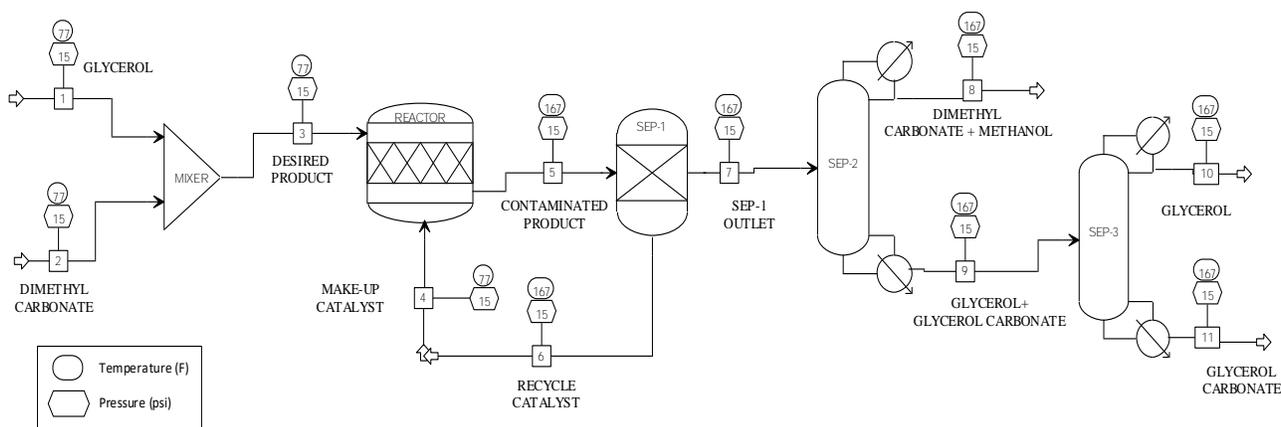


Figure 3.7 Manufacturing of glycerol carbonate from glycerol and dimethyl carbonate without recycle

Process Description:

Stream No.	Description
1.	Mixer Inlet Stream content Glycerol
2.	Mixer Inlet Stream content Dimethyl Carbonate (DMC)
3.	Mixer Outlet Stream content Glycerol + DMC which is reactor feed stream.
4.	Make-up catalyst KF/Al ₂ O ₃ fed to the reactor.
5.	Product content stream having product Glycerol Carbonate+ Methanol and unreacted reactant Glycerol+DMC+Catalyst.
6.	Sep-1 outlet stream content only catalyst KF/Al ₂ O ₃ which is recycle back to reactor.
7.	Sep-1 product stream which content product + glycerol+ DMC.
8.	Outlet from Sep-2 content DMC+Methanol which is separated from Glycerol Carbonate and glycerol.
9.	Sep-2 Product rich content high amount of Glycerol carbonate and some unreacted Glycerol
10.	Unreacted Glycerol recycle back to process.
11.	Glycerol Carbonate obtained as a final product.

Glycerol undergoes transesterification with a cyclic carbonate ester, DMC with KF/Al₂O₃ catalyst to give glycerol carbonate and methanol. The best suited condition for this process is temperature and pressures are 75 °C and 1atm respectively. Compared to other catalyst the KF/Al₂O₃(KOH and KAlO₂) give best result of % Conversion is 96%. The conversion of glycerol carbonate increased with increase in the temperature from 55 to 75°C and then remained almost constant with

further increase to 85⁰C. Selectivity for the transesterification product was 99.9 % at all temperatures indicating high efficiency of the catalyst for this reaction. The KF/γ-Al₂O₃ catalysts were prepared by a wet impregnation method KF·2H₂O were separately dissolved in distilled water to obtain several KF solutions and γ-Al₂O₃ was added into the above KF solutions. For the KF/γ-Al₂O₃ catalyst, solid state reactions between KF and γ-Al₂O₃ occurred during the calcinations process and several new phases such as KOH, KAlO₂ to be formed. After completion of reaction the catalyst is recycle back to the process and remaining product content stream send for purification process. After separation of Methanol and Dimethyl carbonate the contaminant stream of glycerol carbonate with glycerol is sent to the distillation column [7-11]. Here product Glycerol Carbonate is separated from glycerol due to difference in boiling points.

Simulation Result

The synthesized catalysts were characterized by various techniques and the properties were correlated to the catalyst performance based on the glycerol conversion and product yield (Figure 3.8). Potassium fluoride it is an efficient heterogeneous catalyst for transesterification. The KF impregnated catalysts were prepared by the commonly used procedure for the preparation of KF/Al₂O₃ except for the additional washing step after calcination. This additional step removes the weakly adsorbed KF from the catalyst. The remaining KF on the catalyst after water wash can be strongly adsorbed by the interaction with the support. The amount of KF on the support was determined by analyzing the concentration of potassium. KF content in the final catalyst depends on the nature of support because the interaction of KF varies with the type of support. It is observed that, even though different supports are treated with same amount of KF, KF content after water wash is different for different supports.

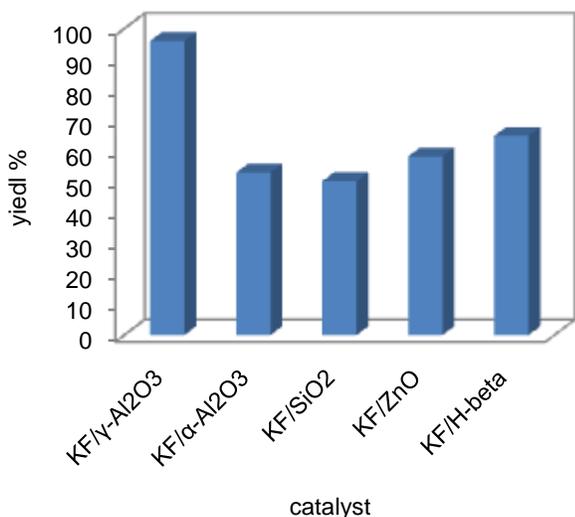


Figure 3.8 Characterisation of KF catalyst for synthesis of glycerol carbonate from glycerol and dimethyl carbonate

Glycerol undergoes transesterification with a cyclic carbonate ester, DMC to give glycerol carbonate and methanol. Different metal oxides, non-metal oxide (silica) and non-oxide (activated carbon) supports modified by KF were studied for the transesterification of glycerol with DMC in the liquid phase (Figure 3.9). The reaction was conducted at 75°C with glycerol: DMC: DMF mole ratio of 1:2:0.5. The 5 wt% catalyst with respect to the total reactant weight. Among those catalysts 3.8KF/Al₂O₃ showed the highest activity, producing glycerol carbonate with 95.8 % yield. The glycerol conversion linearly increased with increase in strong basic sites indicating that strong basicity generated by KF was necessary for

glycerol transesterification with DMC. The activity of 3.8KF/Al₂O₃ was compared with well-known conventional solid base catalysts such as MgO, CaO and HTc. Among these catalysts, KF/Al₂O₃ exhibited highest activity (95.8 % yield) followed by HTc (94 %), CaO (70.5 %) and MgO (68 %).

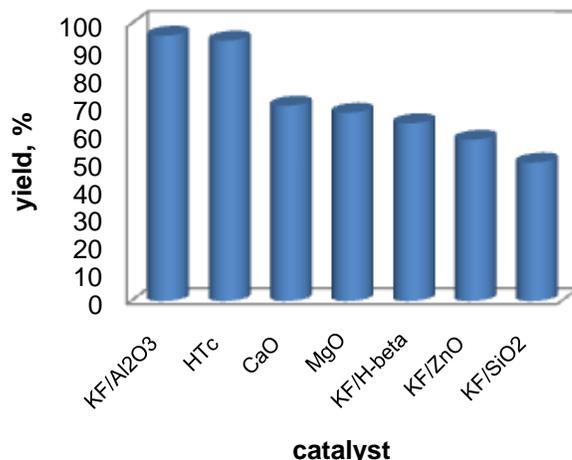


Figure 3.9 Comparison of KF/γ-Al₂O₃ with different catalysts for synthesis of glycerol carbonate from glycerol and methyl carbonate

The KF/Al₂O₃ catalyst with optimized amount of 3.8 mmol KF, gave the highest activity with 95.8% glycerol conversion and almost 100 % selectivity for glycerol carbonate. KF/Al₂O₃ was found to be an efficient and reusable solid base catalyst for the transesterification of glycerol to glycerol carbonate. Streamwise simulation result using Aspen is shown in Table 3.3.

Table 3.3 Simulation result for synthesis of glycerol carbonate from glycerol and methyl carbonate using KF/γ-Al₂O₃ catalyst

Glycerol Carbonate from Glycerol and DMC											
Stream ID	1	2	3	4	5	6	7	8	9	10	11
Mole Flow (kmol/sec)											
GLYCEROL	100	0	100	0	4	0	4	0	4	4	0
DMC	0	200	200	0	104	0	104	104	0	0	0
KOH	0	0	0	15	15	15	0	0	0	0	0
KAlO ₂	0	0	0	15	15	15	0	0	0	0	0
GLY-CAR	0	0	0	0	96	0	96	0	96	0	96
METHANOL	0	0	0	0	192	0	192	192	0	0	0
Mole Flow (kmol/sec)	100	200	300	30	426	30	396	296	100	4	96
Mass Flow (kg/sec)	9209.47	18015.7	27225.238	2311.8845	29537.123	2311.8845	27225.238	15520.293	11704.945	368.37886	11336.566
Volume Flow (m ³ /sec)	7.1172	16.4834	23.2217				27.7756	7656.0373	10.779570	0.2940769	10.498122
Temperature (K)	298.150	298.150	298.1500	298.1500	348.1500	348.1500	348.1500	348.1500	348.1500	348.1500	348.1500
Pressure (N/m ²)	101325	101325	101325	101325	101325	101325	101325	101325	101325	101325	101325

3.4 Manufacturing of Glycerol Carbonate from Oil and Dimethyl Carbonate (DMC):

Raw Materials:

- a. Oil (Triglyceride)
- b. Dimethyl Carbonate
- c. Catalyst : Absence
- d. % Conversion of Oil : 60%

Reactor Condition:

- a. Temperature: 350°C
- b. Pressure: 20Mpa

Chemical Reaction:



Triglyceride + DMC → Glycerol Carbonate + Citramalic Acid + FAME

(Linoleic Acid) (Methyl Stearate)

Process Block Diagram:

The process flow diagram is shown in Figure 3.10 (with recycle) and 3.11 (without recycle)

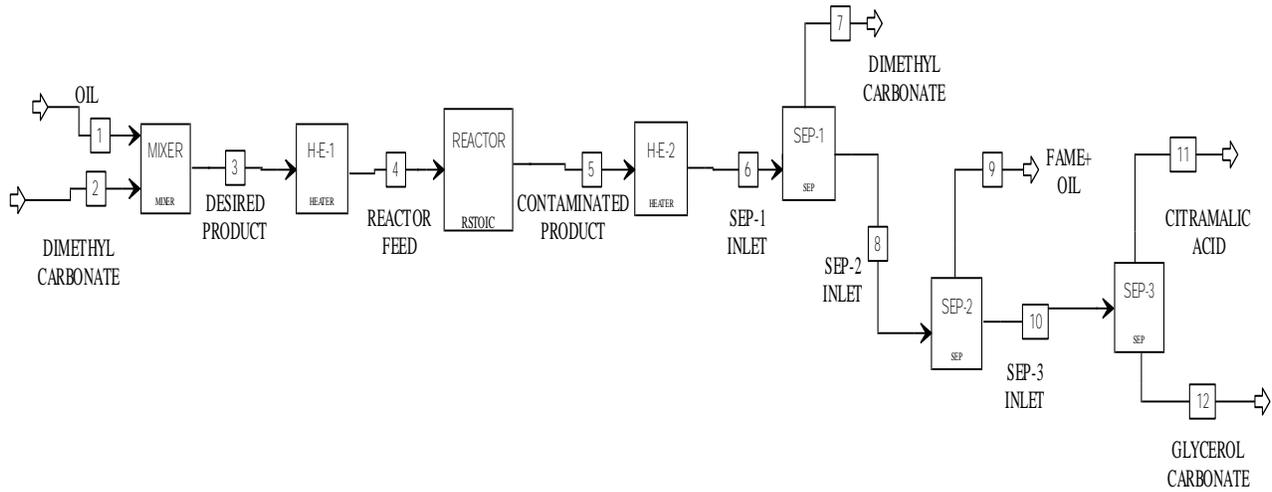


Figure 3.10 Manufacturing of glycerol carbonate from glycerol carbonate and oil without recycle

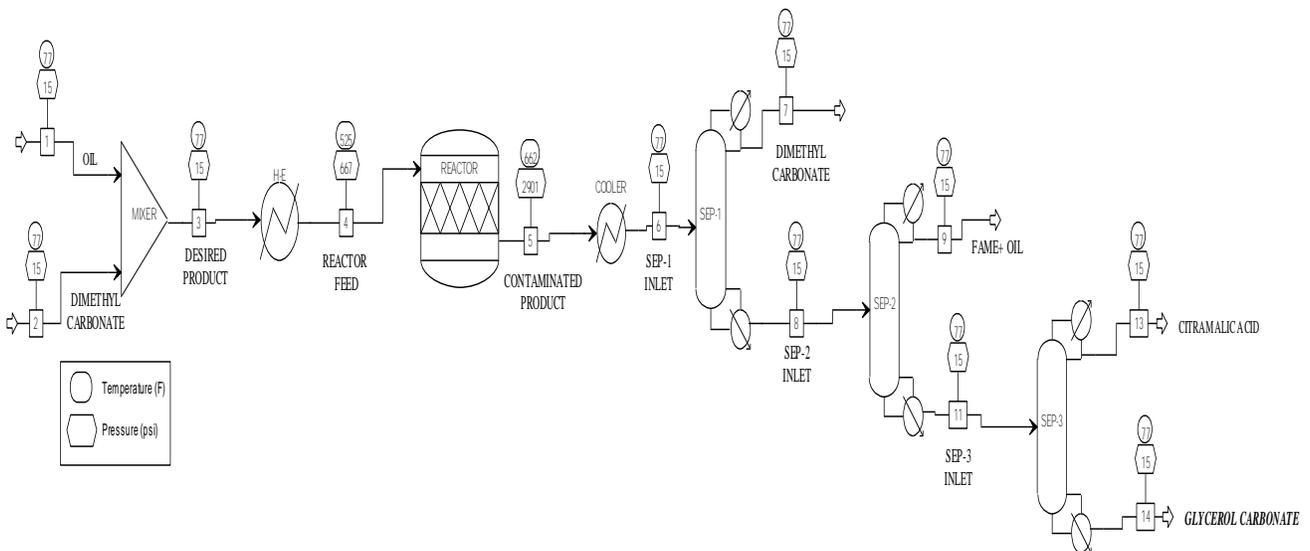


Figure 3.11 Manufacturing of glycerol carbonate from glycerol carbonate and oil with recycle

Process Description:

Stream No.	Description
1.	Mixer Inlet Stream content Oil.
2.	Mixer Inlet Stream content Dimethyl Carbonate (DMC)
3.	Mixer Outlet Stream content Oil+ DMC which is inlet stream of heat exchanger1.
4.	Reactor feed stream which is having high temperature than stream 3.
5.	Product content stream having product Glycerol Carbonate+ FAME + Citramalic Acid and unreacted reactant Oil+DMC which send to cooler to reduce temperature of product stream.
6.	Sep-1 inlet stream content contaminated product having low temperature.
7.	Sep-1 product stream which content only Dimethyl Carbonate.
8.	Outlet from Sep-2 content Glycerol Carbonate + FAME + Citramalic acid and some unreacted Oil.
9.	FAME and Oil are separated from product stream.
10.	Sep-3 inlet stream is product rich stream.
11.	Citramalic Acid is separated from Glycerol Carbonate.
12.	Glycerol carbonate obtained as final product.

Process Description:

The potential of non-catalytic supercritical Dimethyl carbonate process for the production of biodiesel has been studied in a one-step supercritical dimethyl carbonate method. Special focus is oriented towards the superiority of this process in producing higher value by-products, than the glycerol produced in the conventional process without tolerating the ability to produce high yield of fatty acid methyl

ester. Oil undergoes transesterification with a DMC in absence of catalyst to give Glycerol carbonate, FAME and Citramalic Acid. The best suited condition for this process is temperature and pressures are 350°C and 20Mpa respectively. The conversion of glycerol carbonate obtained in this process is 60%. This is the supercritical process so it is important to preheat reactant before entering in the reactor at a temperature of 274.9°C and Pressure 4.6 Mpa. After completing reaction Glycerol Carbonate product is formed with FAME and Citramalic Acid. After that it is cooled upto room temperature and send for purification process.

Simulation result

Dimethyl Carbonate as a green reagent for Glycerol Carbonate and biodiesel production. As we know Dimethyl carbonate has been useful compound having flexible reactivity which is non-toxic and biodegradable also. It has many applications but it has been now recently implemented in the supercritical process for Glycerol carbonate production. To achieve the designated supercritical condition, all reactions were done at temperature and pressure above the critical points of dimethyl carbonate ($T_c = 274.9^\circ\text{C}$ and $P_c = 4.63$ Mpa). Recognized that dimethyl carbonate could be really derived from biomass this green reagent could produce 100% biomass based biodiesel with clear Glycerol carbonate. This supercritical Non-Catalytic method is based on direct transesterification of triglycerides with dimethyl carbonate at the condition of temperature 350°C and pressure 20Mpa [4-8]. Without any catalyst uses triglycerides could be converted to Glycerol carbonate and FAME and more than 94wt% yield of FAME obtained after 12min reaction at 350°C and 20 Mpa pressure.

Table 3.4 Simulation result for synthesis of glycerol carbonate from triglyceride and methyl carbonate

Glycerol Carbonate from Oil and DMC												
Stream ID	1	2	3	4	5	6	7	8	9	10	11	12
Mole Flow (kmol/sec)												
OIL	100	0	100	100	66.6667	66.6667	0	66.6667	66.6667	5.438e-05	5.438e-05	0
DMC	0	100	100	100	1.421e-14	1.421e-14	1.421e-14	0	0	0	0	0
FAME	0	0	0	0	33.3333	33.3333	0	33.3333	33.3333	0	0	0
GLY-CAR	0	0	0	0	33.3333	33.3333	0	33.3333	0	33.3333	0	33.3333
C.A	0	0	0	0	33.3333	33.3333	0	33.3333	0	33.3333	33.3333	0
Mole Flow (kmol/sec)	100	100	200	200	166.6667	166.6667	1.421e-14	166.6667	100	66.6667	33.3333	33.3333
Mass Flow (kg/sec)	28045.086	9007.883	37052.970	37052.970	37049.811	37049.811	1.281e-12	37049.811	28179.463	8870.3482	4937.015	3933.333
Volume Flow (m ³ /sec)	31.201664	8.2417343	40.430386	53.588677			1.172e-15		31.656808			
Temperature (K)	298.150	298.150	298.150	547.150	623.150	298.150	298.150	298.150	298.150	298.150	298.150	298.150
Pressure (N/m ²)	101325.00	101325.00	101325.00	4600000	20000000	101325.00	101325.00	101325.00	101325.00	101325.00	101325.00	101325.00

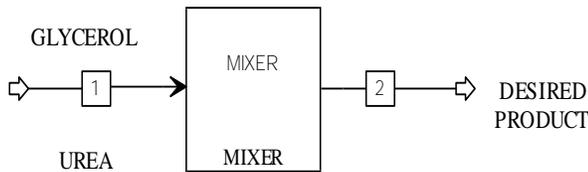
Stoichiometrically, 3 moles of dimethyl carbonate are required to react with 1 mole of triglycerides but in practical condition excess amount of dimethyl carbonate is required to achieve high yield. In this process ratio of dimethyl carbonate to oil should be high molar ratio which helps to facilitate the batch and flow type supercritical dimethyl carbonate process. Supercritical method is best to be operated at high temperature and high pressure with high molar ratio of dimethyl carbonate to oil to optimum required higher yield with the minimum reaction time [11-17]. As described this method is used to produce FAME and alternate value added Glycerol carbonate obtained from this supercritical method satisfied all requirement for international standards. Streamwise simulation result using Aspen is shown in Table 3.4.

IV. PROCESS DESIGN

4.1 Materia Balance :

Method 1: Manufacturing of Glycerol Carbonate(C₄H₆O₄) from Glycerol and Urea:

MIXER:



Feed Content,

Glycerol = 100 kmol/sec

Urea = 100 kmol/sec

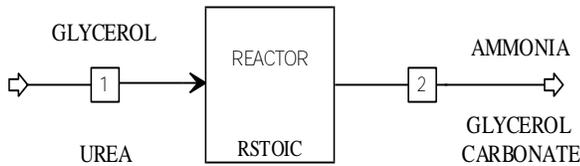
Overall material balance,

Glycerol in Kmol/sec + Urea in kmol/sec = Desired Product in kmol/sec

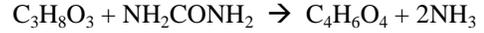
$$100 + 100 = 200$$

∴ Desired Product flow rate = 200 kmol/sec

REACTOR:



Chemical Reaction:



Moles of Glycerol fed = 50 kmol/sec

Moles of Urea fed = 50 kmol/sec

% Conversion of Glycerol = 85 %

$$\% \text{ Conversion of Glycerol} = \frac{\text{Glycerol reacted}}{\text{Glycerol charged}} * 100$$

$$\begin{aligned} \text{Moles of Glycerol reacted} &= \frac{\% \text{Conversion} * \text{Glycerol charged}}{100} \\ &= \frac{85 * 50}{100} = 42.5 \text{ kmol/sec} \end{aligned}$$

According to stoichiometric proportions (i.e from reaction),

1 kmol of Glycerol reacted = 1 kmol of Glycerol carbonate produced

42.5 kmol of Glycerol reacted = X

$$\therefore \text{Glycerol Carbonate Produced} = \frac{42.5 * 1}{1} = 42.5 \text{ kmol/sec}$$

Similarly,

1 kmol of Glycerol reacted = 2 kmol of Ammonia formed

$$42.5 \text{ kmol of Glycerol reacted} = x$$

$$\therefore \text{Ammonia produced} = 85 \text{ kmol/sec}$$

Similarly,

1 Kmol of Glycerol reacted = 1 kmol of Urea reacted

$$42.5 \text{ kmol of Glycerol reacted} = x$$

$$\therefore \text{Urea reacted} = 42.5 \text{ kmol/sec}$$

Unreacted streams:

Glycerol feed = Glycerol reacted + Glycerol Unreacted

$$50 = 42.5 + \text{Glycerol Unreacted}$$

$$\text{Glycerol Unreacted} = 50 - 42.5$$

$$= 7.5 \text{ kmol/sec}$$

Urea Feed = Urea reacted + Urea Unreacted

$$50 = 42.5 + \text{Urea Unreacted}$$

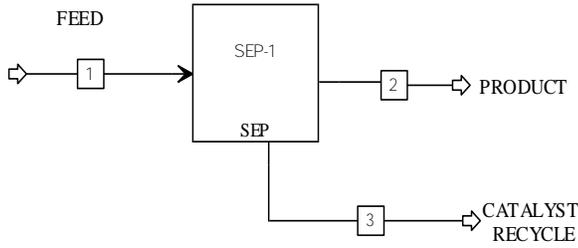
$$\text{Urea Unreacted} = 50 - 42.5$$

$$= 7.5 \text{ kmol/sec}$$

Table 4.1. Material balance Method I

Component	Quantity, kmol/sec	Mole%
Glycerol	7.5	5.26
Urea	7.5	5.26
Glycerol Carbonate	42.5	29.82
Ammonia	85	59.65
Total	142.5	100

SEPARATOR-1



Overall Material Balance,

$$\text{Feed} = \text{Product} + \text{Catalyst}$$

Feed Stream content,

$$\text{Glycerol} = 7.5 \text{ kmol/sec}$$

$$\text{Urea} = 7.5 \text{ kmol/sec}$$

$$\text{Glycerol Carbonate} = 42.5 \text{ kmol/sec}$$

$$\text{Catalyst (ZnCl}_2\text{)} = 1.86 \text{ kmol/sec}$$

CATALYST BALANCE:

$$\text{Catalyst in Feed} = \text{Catalyst in Product} + \text{Catalyst in Recycle stream}$$

$$\text{Catalyst in Recycle stream} = \text{Catalyst in Feed} - \text{Catalyst in Product}$$

$$= 1.86 - 0$$

$$= 1.86 \text{ kmol/sec}$$

GLYCEROL CARBONATE BALANCES:

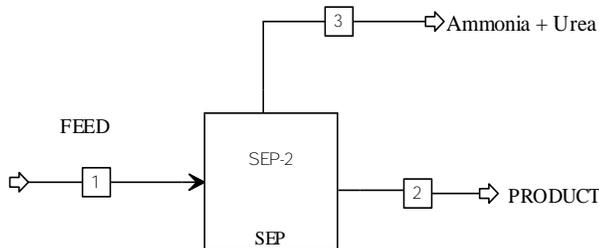
$$\text{Glycerol Carbonate} = \text{Glycerol Carbonate in Product stream} + \text{Glycerol Carbonate in recycle stream}$$

$$\text{Glycerol Carbonate} = \text{Glycerol Carbonate in Product stream} - \text{Glycerol Carbonate in Feed in recycle stream}$$

$$= 42.5 - 0$$

$$\text{Glycerol Carbonate} = 42.5 \text{ kmol/sec in Product stream}$$

SEPARATOR-2:



$$\text{Total Feed} = 142.5 \text{ kmol/sec}$$

Overall Material Balance,

$$\text{Feed Input} = \text{Product stream} + \text{Ammonia and Urea stream}$$

$$142.5 = \text{Product stream} + (85 + 7.5)$$

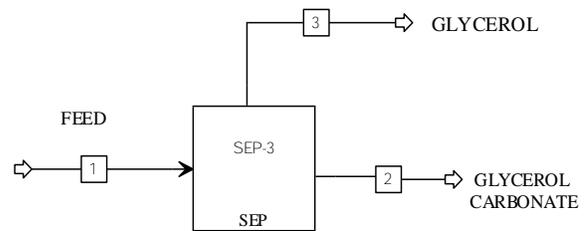
$$\text{Product stream} = 142.5 - 85 - 7.5$$

$$= 50 \text{ kmol/sec}$$

$$\text{Product stream content Glycerol} = 7.5 \text{ kmol/sec}$$

$$\text{and Glycerol Carbonate} = 42.5 \text{ kmol/sec}$$

SEPARATOR-3:



$$\text{Total Feed content} = 50 \text{ kmol/sec}$$

Overall Material Balance,

$$\text{Feed flow rate} = \text{Glycerol flow rate} + \text{Glycerol Carbonate flow rate}$$

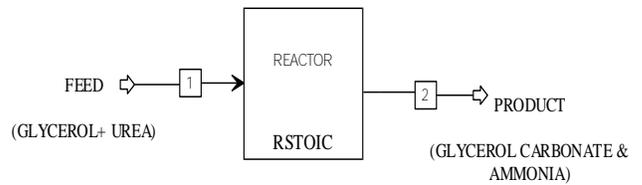
$$\text{Glycerol carbonate flow rate} = \text{Feed flow rate} - \text{Glycerol flow rate}$$

$$= 50 - 7.5$$

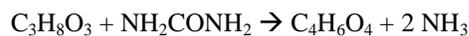
$$= 42.5 \text{ kmol/sec}$$

$$\therefore \text{Product Glycerol Carbonate obtained} = 42.5 \text{ kmol/sec}$$

4.2 ENERGY BALANCE:



Chemical Reaction:



Heat of Formation:

$$\Delta H_f^0 \text{ Glycerol} = -669.6 \text{ kJ/kmol}$$

$$\Delta H_f^0 \text{ Urea} = -333.0 \text{ kJ/kmol}$$

$$\Delta H_f^0 \text{ Glycerol carbonate} = -940.5 \text{ kJ/kmol}$$

$$\Delta H_f^0 \text{ Ammonia} = -46.1 \text{ kJ/kmol}$$

Standard Heat of Reaction:

$$\begin{aligned} \Delta H_R^0 &= [\sum \Delta H_f^0]_{\text{product}} - [\sum \Delta H_f^0]_{\text{Reactant}} \\ &= [1 * \Delta H_f^0 \text{ Glycerol carbonate} + 2 * \Delta H_f^0 \text{ Ammonia}] - [1 * \Delta H_f^0 \text{ Glycerol} + 1 * \Delta H_f^0 \text{ Urea}] \\ &= [1 * (-940.5) + 2 * (-46.1)] - [1 * (-669.6) + 1 * (-333)] \\ \Delta H_R^0 &= -30.1 \text{ kJ/mol} \end{aligned}$$

$$\text{Moles of Glycerol} = 50 \text{ kmol/sec}$$

$$\text{Mass of Glycerol} = 50 * 95 = 4600 \text{ kg/sec}$$

$$\text{Moles of Urea} = 50 \text{ kmol/sec}$$

$$\text{Mass of Urea} = 50 * 60 = 3000 \text{ kg/sec}$$

$$\text{Total Feed in Moles} = 50 + 50 = 100 \text{ kmol/sec}$$

$$\text{Total Feed on Mass} = 4600 + 3000 = 7600 \text{ kg/sec}$$

- Heat absorbed by Glycerol stream to rise temperature from 80°C to 130°C

$$\begin{aligned} Q_{\text{Glycerol}} &= m * c_p * \Delta T \\ &= 4600 * 2.3357 * (130-80) \\ &= 537211 \text{ kJ/sec} \\ &= 537211 \text{ kW} \end{aligned}$$

- Heat absorbed by Urea stream to rise temperature from 80°C to 130°C

$$\begin{aligned} Q_{\text{Urea}} &= m * c_p * \Delta T \\ &= 3000 * 1.5465 * (130-80) \\ &= 231975 \text{ kJ/sec} \\ &= 231975 \text{ KW} \end{aligned}$$

$$\begin{aligned} \text{Total heat to be supplied} &= Q = Q_{\text{Glycerol}} + Q_{\text{Urea}} \\ &= 537211 + 231975 \\ &= 769186 \text{ kJ/sec or KW} \end{aligned}$$

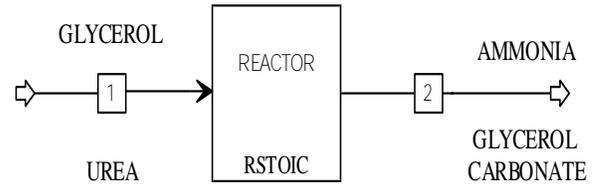
$$\text{Latent heat of steam } \lambda_s = 2257.92 \text{ kJ/kg}$$

$$\begin{aligned} Q &= m_s \lambda_s \\ m_s &= Q / \lambda_s \\ &= 769186 / 2257.92 \\ m_s &= 340.66 \text{ kg/sec} \end{aligned}$$

10% excess steam supplied for losses,

$$\therefore \text{ Steam supplied} = 374.726 \text{ kg/sec}$$

4.3 Process Design



$$\begin{aligned} \text{Glycerol Feed} &= 50 \text{ kmol/sec} \\ &= 50 * 95 = 4600 \text{ kg/sec} \end{aligned}$$

$$\begin{aligned} \text{Urea Feed} &= 50 \text{ kmol/sec} \\ &= 50 * 60 = 3000 \text{ kg/sec} \end{aligned}$$

$$\begin{aligned} \text{Total Feed} &= 100 \text{ kmol/sec} \\ &= 7600 \text{ kg/sec} \end{aligned}$$

Volumetric flow rate of Glycerol :

$$\begin{aligned} Q_{\text{Glycerol}} &= \frac{\text{Mass flow rate} \left(\frac{\text{kg}}{\text{sec}} \right)}{\text{Density} \left(\frac{\text{kg}}{\text{m}^3} \right)} \\ &= \frac{4600 \left(\frac{\text{kg}}{\text{sec}} \right)}{1260 \left(\frac{\text{kg}}{\text{m}^3} \right)} \\ &= 3.6507 \text{ m}^3/\text{sec} \end{aligned}$$

$$\begin{aligned} Q_{\text{Urea}} &= \frac{\text{Mass flow rate} \left(\frac{\text{kg}}{\text{sec}} \right)}{\text{Density} \left(\frac{\text{kg}}{\text{m}^3} \right)} \\ &= \frac{3000 \left(\frac{\text{kg}}{\text{sec}} \right)}{1320 \left(\frac{\text{kg}}{\text{m}^3} \right)} \\ &= 2.2727 \text{ m}^3/\text{sec} \end{aligned}$$

$$\begin{aligned} \therefore Q_{\text{total}} &= 3.6507 + 2.2727 \\ &= 5.9234 \text{ m}^3/\text{sec} \end{aligned}$$

$$\text{Residence time} = 3 \text{ hrs} = 10800 \text{ sec}$$

$$\text{Volume} = V$$

$$\begin{aligned} V &= \tau * Q \\ &= 10800 * 5.9234 \\ &= 63972.72 \text{ m}^3 \end{aligned}$$

$$\text{Volume} = V = (\pi/4) * D^2$$

$$D^2 = \frac{63972.72 * 4}{\pi}$$

$$D = 285.39 \text{ m} \approx 286 \text{ m}$$

4.3 Equipment Design

Mechanical Design

A) Reactor Design

Reactor Diameter	=	2000 (mm)
Reactor length	=	6000 (mm)
M.O.C	=	High Alloy Carbon Steel
Permissible Stress (f)	=	98 (N/mm ²)
Working Pressure	=	1.72 (N/mm ²)
Internal Design Pressure	=	1.1*0.3= 0.33 (N/mm ²)
Joint Efficiency	=	0.85

a) Thickness of Shell

$$(t_s) = \frac{(P * d_i)}{(2 f_j - P)} + c$$

$$= \frac{(0.33 * 2000)}{(2 * 98 * 0.85 - 0.33)} + 4$$

$$= 7.969 \text{ (mm)}$$

$$\text{Take } (t_s) \approx 8 \text{ (mm)}$$

Now, let's check if the resultant stress allows for thickness obtained from above calculation. Calculation for the resultant/ equivalent stress for cylindrical vessel is under combined loadings. Checking a thickness of 16mm for combined loading

1) Circumferential Stress:

$$(f_t) = \frac{P (D_i + t)}{(2 t)}$$

$$= \frac{0.33 * (2000 + 8)}{(2 * 8)}$$

$$= 41.41 \text{ (N/mm}^2\text{)}$$

2) Stress in axial Direction:

a) Due to internal pressure (fL₁)

$$(fL_1) = \frac{P (D_i + t)}{(4 t)}$$

$$= \frac{0.33 * (2000 + 8)}{(4 * 8)}$$

$$= 20.7075 \text{ (N/mm}^2\text{)}$$

b) Due to Wt of vessel & its content

$$(fL_2) = \frac{W}{(\pi * (D_i + t) * t)}$$

Let W be the weight of the vessel (take = 65000N).

Here, W is the total weight of the vessel along with its contents, fittings, auxiliary equipments etc, It is expressed in Newton's. Also W is obtained by increasing the weight of the

vessel and its contents by 10 to 25 % , to take care of the weight due to various fittings and auxiliary equipments.

$$fL_2 = \frac{65000}{(\pi * (2000 + 8) * 8)}$$

$$fL_2 = 1.2879 \text{ (N/mm}^2\text{)}$$

c) Due to Wind load

$$fL_3 = 0 \text{ (No wind Load)}$$

Thus Resultant stress in longitudinal Direction

$$f_{LR} = fL_1 + fL_2 + fL_3$$

$$= 20.7075 + 1.2879 + 0$$

$$= 21.99 \text{ (N/mm}^2\text{)}$$

1) Torsional stress

Torque due to offset piping (T) = 500 kNm

$$\text{Stress due to torque } (f_s) = 2 T / (\pi * D_i * t * (D_i + t))$$

$$= (2 * 500) / (\pi * 2000 * 8 * (2000 + 8))$$

$$f_s = 9.9075 * 10^{-6} \text{ N/mm}^2$$

Resultant stress i.e f_R=

$$\sqrt{(fT^2 - fT + fLR + fLR^2 + 3 f_s^2)}$$

$$f_R = \sqrt{41.41^2 - 20.7075 + 22 + (22 * 22) + 3 * (9.9075 * 10^{-6})^2}$$

$$= 22.86 \text{ N/mm}^2$$

$$\text{Hence, } f_R = 22.86 \text{ N/mm}^2$$

As this resultant stress is less than the permissible stress of 98 N/mm² that we utilized earlier, the thickness obtained is satisfactory and design is safe.

b) Design For Head:

$$\text{External Diameter} = D_i + 2t$$

$$= 2000 + 2 * 8$$

$$= 2016 \text{ mm}$$

For Torrispherical Head:

$$\text{Crown Radius } (R_c) = 2016/2 = 1008 \text{ mm}$$

$$\text{Knuckle Radius } (R_k) = 6\% \text{ of Internal radius}$$

$$= 0.06 (2000/2)$$

$$= 60 \text{ mm}$$

$$T_h = \frac{(P R_c W)}{(2 f_j)}$$

$$W = \left(\frac{1}{4}\right) * \left[3 + \sqrt{\frac{Rc}{Rk}} \right]$$

$$= \left(\frac{1}{4}\right) * \left[3 + \sqrt{\frac{1008}{60}} \right]$$

$$W = 1.77$$

$$J = 1 \text{ (for Head)}$$

Thus, we have $T_h = \frac{0.33 * 1008 * 1.77}{2 * 98 * 1} + c$

$$= 3.00 + 4 = 7 \text{ mm}$$

Take, $T_h \approx 8 \text{ (mm)}$

c) Design of Flange And Bolts

i. Design of gasket

Outer diameter of shell $Do = Di + 2t = 2000 + 2 * 8 = 2016 \text{ (mm)}$

Thus, Inner diameter of gasket

$$Gi = Do + 10$$

$$Gi = 2016 + 10$$

$$= 2026 \text{ (mm)}$$

Also, $(Go/Gi) = \sqrt{\frac{Y-Pm}{y-P(m+1)}}$

Where, $Go = \text{Outer Diameter of Gasket}$

$Y = \text{Gasket Seating Stress.}$

$$= 80 \text{ (N/mm}^2\text{)}$$

Thus, $Go = Gi * \sqrt{\frac{Y-Pm}{y-P(m+1)}}$

$$= 2026 * \sqrt{\frac{80 - (0.33 * 2)}{80 - 0.33(2+1)}}$$

$$Go = 2030.22 \text{ (mm)}$$

$$\approx 2031 \text{ (mm)}$$

Thus, width of the gasket $N = \left(\frac{Go - Gi}{2}\right)$

$$N = \left(\frac{2031 - 2026}{2}\right)$$

$$N = 2.5 \text{ (mm)}$$

Basic Gasket Seating width (b_o) = $\frac{N}{2}$

$$= \frac{2.5}{2}$$

$$b_o = 1.25 \text{ (mm)}$$

Now, as $b_o > 6.3 \text{ mm}$, Effective gasket seating width (b) is given as :

$$b = b_o$$

$$b = 1.25$$

$$\approx 1.5 \text{ (mm)}$$

Diameter of gasket at load reaction (G)

$$G = G_i + N$$

$$= 2026 + 2.5$$

$$G = 2028.5 \text{ (mm)}$$

ii. Design of Bolt

Bolt load under atmospheric condition :

$$W_{m1} = \pi G b y$$

$$= \pi * 2028.5 * 1.5 * 80$$

$$W_{m1} = 5.3826 * 10^5 \text{ (N)}$$

Bolt load under operating conditions :

$$W_{m2} = \pi G (2b) m p + \left(\frac{\pi}{4}\right) G^2 P$$

$$W_{m2} = 1.0705 * 10^6 \text{ (N)}$$

As $W_{m2} > W_{m1}$, we take this value.

Hence, Controlling Load is W_{m1}

Area of bolt required is $Ab_1 = \frac{W_{m1}}{fb}$

$$= \frac{5.3826 * 10^5}{5860}$$

$$Ab_1 = 91.8532 \text{ (mm}^2\text{)}$$

But, $Ab_2 = \frac{W_{m2}}{fb}$

$$= \frac{1.0705 * 10^6}{5860} = 182.67 \text{ (mm}^2\text{)}$$

Where, $n = \text{no. of bolts.}$

$$n = \frac{G}{25}$$

$$= \frac{2028.5}{25}$$

$$n = 81.14 \approx 82 \text{ bolts}$$

Take $n = 82$

Thus Diameter of Bolt

$$d_b = \sqrt{\frac{(4 * Ab_{max})}{(\pi * n)}}$$

$$d_b = 1.6842 \approx 5 \text{ (mm)}$$

Bolt circle diameter (B) = $Go + 2 db + 12$

$$B = 2031 + 2(5) + 12$$

$$B = 2053 \text{ (mm)}$$

Actual bolt spacing required

$$b_s = \frac{\pi B}{n}$$

$$= \frac{(\pi * 2053)}{82}$$

$$b_s = 78.65 \text{ (mm)}$$

$$\approx 80 \text{ (mm)}$$

iii. Design of Flange

$$k = \frac{1}{[0.3 + \frac{1.5 Wm h_G}{HG}]}$$

where, $Wm = \text{Max bolt load (Controlling Load)}$

$$= 1.0705 * 10^6 \text{ N}$$

$$h_G = \frac{(B - G)}{2}$$

$$= \frac{(2052 - 2028.5)}{2}$$

$$h_G = 11.75 \text{ (mm)}$$

$$H = \left(\frac{\pi}{4}\right) G^2 P$$

$$H = 1.06606 * 10^6 \text{ (N)}$$

Thus, $k = \frac{1}{[0.3 + \frac{1.5 * 1.0705 * 10^6 * 11.75}{1.06606 * 10^6 * 2028.5}]}$

$$k = 3.23$$

Thickness of flange $t_f = G \sqrt{\frac{P}{k f}}$

$$t_f = 2028.5 \sqrt{\frac{0.33}{3.23 * 98}}$$

Thus, $t_f = 65.48 \text{ (mm)}$

Outside diameter of the flange $D_{fo} = B + 2 d_b + 12$

$$= 2052.22 + 2(5) + 12$$

$$D_{fo} = 2074.22 \text{ (mm)}$$

Width of Flange $= \frac{D_{fo} - D_i}{2}$

$$= \frac{2074.22 - 2000}{2}$$

$$= 37.11 \text{ (mm)}$$

Nozzle Reinforcement Design

Design Pressure = 0.33 N/mm^2

Diameter of nozzle = 80 mm .

Material of nozzle is same as that of reactor.

Thickness of nozzle (t_n) = $\frac{P D_i}{(2 f J - P)}$

$$t_n = \frac{(0.33 * 80)}{(2 * 98 * 1 - 0.33)}$$

$$t_n = 0.13492 \text{ mm} \approx 1 \text{ mm.}$$

Horizontal diameter for compensation

$$AB = 2 D_i$$

$$= 2 * 80$$

$$= 160 \text{ (mm)}$$

Vertical Diameter for Compensation.

We take the greater value of the following:

i) $AD = 6 * t_n$

$$= 6 * 3$$

$$= 18 \text{ mm.}$$

ii) $AD = 3.5 * t_s + 2.5 t_n$

$$= 3.5 * 18 + 2.5 * 3$$

$$AD = 70.5$$

Take greater value, i.e. $AD = 70.5$

Area of Compensation = $80 * 8$

$$= 640 \text{ mm}^2$$

Area of compensation provided by head = $D_{in} * (t_s - t_s')$

$$A_h = 80 * (18 - 16)$$

$$= 800 \text{ mm}^2$$

Area of compensation provided by

Nozzle = $2 Ht * (t_n - t_n' - c)$

Where, $Ht = 2.5 * t_s$

$$= 2.5 * 18 = 45 \text{ mm.}$$

$$t_n = 3$$

$$t_n = 0.1349 \approx 1 \text{ mm}$$

Thus, $A_o = 2 * 45 * (3 - 0.1349 - 0)$

$$A_o = 257.86 \text{ mm}^2$$

Nozzle does not project inside the vessel. Thus, H_2 and $A_t = 0$.

Total area of compensation available = $A_n + A_o + A_t$

$$= 800 + 257.86 + 0$$

$$= 1057.86 \text{ mm}^2$$

$$A \approx 1058 \text{ mm}^2$$

B) Distillation Design:

a) Shell:

Internal Diameter (D_i) = 3000 mm

Shell height = 44 mm

Design Pressure (P) = 1.76 N/mm^2

Working Pressure = 1.6 N/mm²
Design Temperature = 200⁰C
Working Temperature = 195⁰C
Permiscible Tensile Stress = 95 N/mm²
Insulation Thickness = 100 mm
Density of Insulation = 120 kg/ m³
Material of Construction = Stainless Steel (IS-2002)

Hence, no Corrosion allowances.

i. Thickness of Shell

$$(t_s) = \frac{(P * di)}{(2 f J - P)} + c$$

$$= \frac{(1.76 * 3000)}{(2 * 95 * 1 - 1.76)}$$

$$= 28.04 \text{ (mm)}$$

Take (t_s) ≈ 28 (mm)

Let us assume height 'H' in 'm' from the top. We shall assume 28mm thickness prevails in this height. To check upto which height this thickness can be taken safely we have to do stress analysis of this thickness.

1) Stress in axial Direction:

a) Due to internal pressure (fap)

$$(fap) = \frac{P (Di + t)}{(4 t)}$$

$$= \frac{1.76 * (3000 + 28)}{(4 * 28)}$$

$$= 47.58 \text{ (N/mm}^2\text{)}$$

2) i) Compressive stress due to dead weight:

(fps) = weight of shell/ c/s area of shell

$$= (\sqrt{4}) (D_0^2 - D_i^2) * \text{density of shell} * H / \sqrt{4} * D_m * t$$

So,

Outside diameter = D₀ = Di + 2t

$$= 3000 + 2(28) = 3056 \text{ mm}$$

Mean Diameter = (D₀ - Di)/2

$$= (3056 + 3000)/2 = 3028 \text{ mm}$$

Density of Shell material = 7850 kg/m³

$$(fps) = (\sqrt{4}) (D_0^2 - D_i^2) * \text{density of shell} * H / \sqrt{4} * D_m * t$$

$$= (\sqrt{4}) (3056^2 - 3000^2) * 7850 * H / \sqrt{4} * 3028 * 28$$

$$= 7850 H * 9.807 * 10^{-6}$$

$$= 0.077H \text{ N/mm}^2$$

(Note: The factor 9.807 is convert to Kg into Newton)

ii) Compressive stress due to weight of Insulation :

The insulation thickness is 100mm

Outside diameter with Insulation is (D_{ins}) = D₀ + 2(100) = 3256 mm

f_d(ins) = Weight of insulation / Cross-sectional of Shell

$$= \frac{\sqrt{4} * D_{ins} * t_{ins} * \rho_{ins}}{\sqrt{4} * D_m * t}$$

$$= \frac{\sqrt{4} * 3256 * 100 * 120 * H * 9.807 * 10^{-6}}{\sqrt{4} * 3028 * 28}$$

$$= 0.0045 H \text{ N/mm}^2$$

iii) Compressive stress due to Liquid :

Weight in terms of height = (H/0.675) + (√4) * 3² * 92

∑ Liquid wt = 963.4 H kg

$$f_d = \frac{\sum \text{liquid wt}}{c/s \text{ of shell}}$$

$$= \frac{963.4H * 9.807}{\sqrt{4} * 3028 * 28} = 0.035 H \text{ N/mm}^2$$

iv) Compressive stress due to attachment:

(weight of ladders, top head, platforms etc. approximate = 150 kg)

$$f_{d(\text{ins})} = \frac{\sum \text{wt of attachment}}{c/s \text{ of shell}}$$

$$= \frac{(2670 + 150x)9.807}{\sqrt{4} * 3028 * 28}$$

$$= 0.098 + 5.52 * 10^{-3} H = 0.098 + 0.0055H$$

Total compressive dead wt stress = f_{dx}

$$f_{dx} = f_{ps} + f_{dins} + f_{liq} + f_d$$

$$= 0.077 H + 0.0045 H + 0.035 H + 0.098 + 0.0055H$$

$$= 0.122 H + 0.098 \text{ N/mm}^2$$

v) Stress due to Wind load:

$$f_{wx} = \frac{1.4 P_w H^2}{\sqrt{4} * 3028 * 28}$$

where,

P_w = wind pressure = 1300 N/mm²

$$f_{wx} = \frac{1.4 * 1300 * H^2}{\sqrt{4} * 3028 * 28}$$

$$= 6.83 * 10^{-3} H^2$$

Determination of Height :

$$\frac{1.4 P_w H^2}{\sqrt{4} * 3028 * 28} + \frac{P (Di + t)}{(4 t)} - \frac{\sum \text{liquid wt}}{c/s \text{ of shell}} + f = f_{max} + f_{wx} + f_{ap} + f_{dx}$$

$$0 = 6.83 * 10^{-3} (H^2) - 0.122 H - 47.902$$

$$H = 93.15 \text{ m}$$

Height of determination of 'H' is 93.15m is acceptable as the

actual column height is 95m.

The column of uniform shell thickness of 33mm is acceptable.

Heads : Elliptical welded to Shell

(Ratio of major to minor axis 2:1)

Material = Stainless steel IS-2002

Permissible tensile stress = 95 N/mm²

Weight of head = 2670 kg

Thickness of Head is given by,

$$t_h = \frac{PDv}{2fj}$$

$$= \frac{1.76 \times 3000 \times 1}{2 \times 95 \times 1} = 27.78 \text{ mm} \approx 28 \text{ mm}$$

Tray : Sieve Trays

1) No. of Trays = 41

2) Spacing = 675 mm

3) Hole Diameter = 5mm

4) Trays are made from stainless steel with thickness of 2 mm and with hole dia. 5mm

Height of Tower = 2.3 N

Where,

N = no. of trays

$$93.15 = 2.3 N$$

$$\therefore N = 93.15/2.3 = 40.5$$

Plate Specification :

$$\text{Area of Circular tray (a)} = (\pi/4) * D^2$$

$$= (\pi/4) * (0.005^2) = 1.963 * 10^{-5} \text{ (m}^2\text{)}$$

$$\text{Total no. holes} = \frac{0.117}{\text{Area of circular tray}}$$

$$= \frac{0.117}{1.963 * 10^{-5}} = 5960$$

V. CONCLUSIONS

The direct synthesis from glycerol and CO₂ is not currently industrially possible due to low CO₂ reactivity resulting in yields below 32%. Other manufacturing processes of Glycerol Carbonate from glycerol using various components like Urea, CO₂ and Dimethyl Carbonate (DMC) and different catalyst such as ZnCl₂, ZnSO₄, ZnBr₂, and KF/Al₂O₃ at different temperature and pressure conditions is analysed by using a chemical software ASPEN PLUS. Carbonation of glycerol with urea, transesterification of ethylene carbonate or dimethyl carbonate with glycerol and transesterification of triglyceride with dimethyl carbonate were analyzed. Our analysis proves that the supercritical dimethyl carbonate

process can convert triglycerides to fatty acid methyl esters (FAME) with higher value by-products like Glycerol Carbonate and Citramalic acid without producing glycerol. In addition, the use of neutral ester, dimethyl carbonate (DMC), can allow the reaction to be milder to avoid a corrosion problem in the reaction system.

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