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Manufacture of 40% Glyoxal Based on Oxidative Dehydrogenation using Silver Catalyst

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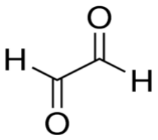
***Abstract*—Glyoxal is provided generally as a four-hundredth solution. it's oftentimes used for condensation and cross-linking reactions owing to the reactivity of its organic compound teams towards polyfunctional compounds with group or amino teams, e.g. with organic compound and its derivatives, or with starch, cellulose, cotton, casein, or animal product. It acts as a biologically active compound, inhibits corrosion, and aids in solidifying rubber and in animal skin tanning. it's associate intermediate within the preparation of dyes, prescription drugs, polymers and textile auxiliaries. industrial glyoxal is ready by either the gas section reaction of ethanediol within the presence of a silver or copper catalyst or by the liquid section reaction of ethanal with acid. The potential of manufacturing glyoxal from the ethanediol is encouraging and may be any explored particularly within the country with the high ethanediol productivity**

Keywords— Oxidation of ethylene glycol, Condensation and cross linking reactions.

I. INTRODUCTION

Glyoxal is Associate in Nursing compound with the statement OCHCHO. it's the tiniest dialdehyde (a compound with 2 organic compound groups). Pure glyoxal isn't usually encountered as a result of it forms hydrates, that oligomerize. for several functions, these hydrous oligomers behave equivalently to glyoxal. it's made industrially as a precursor to several product. Glyoxal is provided generally as a four-hundredth solution. Like different little aldehydes, glyoxal forms hydrates. moreover, the hydrates condense to relinquish a series of oligomers, a number of that stay of unsure structure. Glyoxal or ethanedial is often used for condensation and cross-linking reactions due to the reactivity of its organic compound teams towards poly purposeful compounds with chemical group or amino teams, e.g. with carbamide and its derivatives, or with starch, cellulose, cotton, casein, or mucilage. It acts as a biologically active compound, inhibits corrosion, and aids in solidification rubber and in animal skin tanning. it's Associate in Nursing intermediate within the preparation of dyes, prescription drugs, polymers and textile auxiliaries.



Structure of Glyoxal

Glyoxal, the only organic compound was initial ready and named by the German-British chemist Heinrich Debus (1824–1915) by reacting ethyl alcohol with acid. The HNO_3 technique remains used commercially, alongside metal-catalyzed gas-phase oxidization of ethanediol. At low temperatures, glyoxal forms yellow crystals; it melts at 15 °C and boils at 51 °C. Its low flash purpose (–4 °C) makes its inexperienced vapor explosive in air. It’s used principally in paper coating and textile finishing processes. industrial glyoxal is ready either by the gas-phase oxidization of ethanediol within the presence of a silver or copper catalyst or by the liquid-phase oxidization of ethanal with acid. the primary industrial glyoxal supply was in LaMotte, France, started in 1960. The only largest industrial supply is BASF in Ludwigshafen, Germany, at around sixty,000 tons p.a. different production sites exist additionally within the United States of America and China. industrial bulk glyoxal is created and reported as a 40%-strength answer in water.

II. PROPERTIES &APPLICATIONS

Physical characteristics of glyoxal such as boiling point, melting point, density, and chemical characteristics such as can affect the use of such substance and render its suitability for specific applications.

Physical Properties:

IUPAC Name	: Oxoaldehyde
Chemical Formula	: $C_2H_2O_2$
Appearance	: Pale Yellow
Odor	: Weak sour odor
Melting Point	: 15 °C
Boiling Point	: 51 °C
Auto ignition temperature	: 285 °C
Heat capacity	: 1.044 J/(Kg)
Solubility	: Miscible with
water	

Applications:

- Textile industry- Physical characteristics of glyoxal like boiling purpose, freezing point, density, and chemical characteristics like will have an effect on the utilization of such substance and render its quality for specific applications.
- Paper business - It's used as building block for cross linker. It will increase paper wet strength (e.g. rest room paper). It will increase paper dry strength (e.g. recycled paper). it's used as economical paper coating additive for high-quality papers.
- Oil and gas business - It’s used as H_2S scavenger and crosslinking polymers (hydro colloids). it's Anti-corrosive, perishable and it supports safety work. It improves body in oil drilling fluids.
- Leather business - It's used as crosslinking agent in tanning method. It helps to preserve the animal skin quality.

III. METHODOLOGY

The various process and technologies required for the manufacture of 40% Glyoxal are as follows

- **Oxidation of Acetaldehyde to Glyoxal By Nitric Acid:** The liquid section oxidisation of aldehyde or aldehyde by binary compound acid to glyoxal was investigated during a chrome steel autoclave maintained underneath autogenous pressure. The presence of acid was necessary for the reaction. ethanoic acid and glyoxylic acid were the main by-products. the results of concentration of acid, acid and aldehyde in addition as temperature and amount of reaction on the conversion and yield of glyoxal were studied with a read to getting the foremost appropriate conditions for the assembly of glyoxal.
- **Glyoxal From Ozonolysis of Benzene:** Glyoxal is produced when benzene is treated with ozone in the presence of Zn/H2O.This process is called ozonolysis.
- **Microbial Catalysis of Ethylene Glycol to Glyoxal:** The production of glyoxal from glycol has been incontestable with the utilization of glycerine enzyme and enzyme as catalyst from Aspergillus versicolor. glycerine enzyme was fashioned within the mycelia of the fungi grownup on glycol because the sole carbon supply. enzyme activity is actually vital as co-catalyst to decompose by-product oxide, therefore limiting peroxide-dependent methanolate production and glycerine enzyme deactivation. the initial strain of Aspergillus versicolor possess high glycerine enzyme and enzyme activities. throughout additional screening of the enzymes, we've got found that glycerine enzyme from A versicolor change glycol to glyoxal.
- **Enzymatic Production of Glyoxal From Ethylene Glycol Using Alcohol Oxidase from Methanol Yeast:** A new oxidative reaction of ethylene glycol was found with two alcohol oxidases from methanol yeast, Candida boidinii and Pichia pastoris. Both alcohol oxidases oxidize ethylene glycol to glyoxal via glycolaldehyde. These alcohol oxidases were specific for short-chain linear aliphatic alcohols such as methanol, ethanol, n-propanol, and n-butanol, which were oxidized to the respective aldehydes, formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde.
- **Glyoxal By Oxidative Dehydrogenation Using Silver Catalyst:** Glyoxal was obtained by the oxidative dehydrogenation of ethylene glycol. After a series of experiments, it was found that the best reaction conditions obtained at a residual pressure of 400-600 mm with the use of a silver catalyst in the form of spirals. A mixture of the vapor of 40% aqueous ethylene glycol (0.78 mole/h) and a 1:1 air-nitrogen mixture was passed through the previously described reactor containing 7 ml of catalyst. The air was passed at a rate of 180 litres/h. Oxygen was therefore taken in 150% of the theoretical amount. The condensate contained 0.25 g/ml of glyoxal (II), which corresponds to a yield of 63.2%.

IV. PROCESS SELECTION

Of all the feasible processes available for the manufacture of Glyoxal, **oxidative dehydrogenation using silver catalyst** method is selected. The process selection criteria are:

- Complexity of the process
- Availability of the catalyst
- Yield of the product
- Efficiency of the process
- Reusability of catalyst
- High selectivity
- Low operating cost

V. PROCESS DESCRIPTION

Glyoxal was obtained by the aerophilous dehydrogenation of glycol. once a series of experiments it absolutely was found that the simplest reaction conditions obtained at a residual pressure of 400-600 millimetre with the utilization of a silver catalyst within the variety of spirals. a combination of the vapor of four-hundredth binary compound glycol (0.78 mole/h) and a 1:1 air-nitrogen mixture was knowledgeable the antecedental represented reactor containing seven metric capacity unit of catalyst. The air was passed at a rate of a hundred and eighty litres/h. atomic number 8 was thus taken in

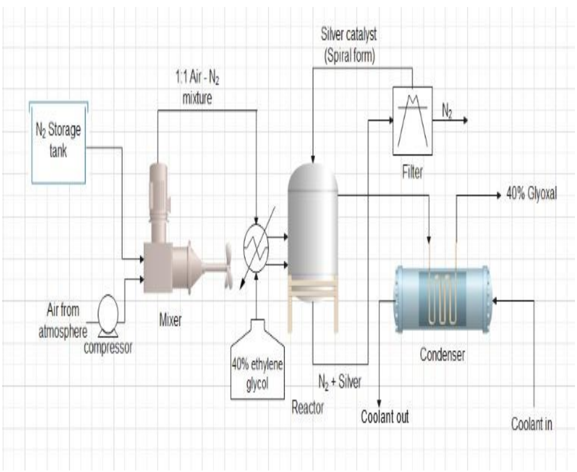


Fig: 1 Process flowsheet for the manufacture of glyoxal a hundred and fiftieth of the theoretical quantity. The atmospheric phenomenon contained 0.25 g/ml of glyoxal (II), that corresponds to a yield of 63.2%. technique involves vapor-phase chemical {process chemical change chemical action} process of partial aerophilous dehydrogenation of glycol with atomic number 8 diluted with steam and gas within the mole magnitude relation from 1/6.5 to 1/13.0 at temperature 400-700°C on carrier Ag-contacts and big Ag-catalysts fabricated from materials of electrolytic origin of particles size 0.1-4.0 mm. Then the method, involves continuous the vat-less separation of vapor-gaseous oxidate for liquid fractions and vaporific part whereby ready binary compound organic compound solutions contain 4-40% of glyoxal, 6.2% of glycolic organic compound, not above, 4.6% of gas, not above, 4.0% of glycol, not above, at the entire acidity index a pair of the top product contains 39.8% of glyoxal, 5.5% of glycolic organic compound and 0.4% of gas.

The method of continuous the vat-less separation of synthesis merchandise for glyoxal-containing liquid fractions and depleted vaporific part is meted out unceasingly within the vary of temperature 10-400°C as results of sub contact cooling together with three-step combined condensation of parts of vapor-gaseous oxidate in a very cascade block-unit in fragmental isolation of liquid and vaporific merchandise of synthesis, and in regulation of warmth programme of the combined condensation and alter of magnitude relation of the liquid fractions gift invention relates to never-ending technique of manufacturing glyoxal by reaction of glycol with atmospherically atomic number 8 in a very mixture with recirculating argonon on a catalyst containing silver. Recirculating gas used as an agent and glycol resolution coming into reactor square measure in turn preheated by heat generated throughout reaction of glycol at catalyst, and cooling of reaction merchandise is performed in turn by their irrigation with cooled resolution of glyoxal in a very zone lying like a shot behind catalyst layer and in cannular sub-contact 2-sectional device, in lower section of that glycol is heated, and within the higher section- heating of the recirculating gas used as an agent.

VI. MATERIAL BALANCE

Basis:

Production of 40% glyoxal of capacity 60,000TPA.
Number of plants working days = 300 days.
So, Mass flow rate of glyoxal = (60000*1000)/(300*24)
= 8333.333 kg/hr
Molar flow rate of glyoxal = 8333.333/58.04
= 143.57914 kmol/hr

COMPONENT	INPUT (kg/hr)	OUTPUT (kg/hr)
$(CH_2OH)_2$ ETHYLENE GLYCOL	3564.78289	--
AIR O_2 N_2	4594.24532 4022.13988	-- 4022.13988
$(CHO)_2$ GLYOXAL	--	3333.3332
H_2O	--	4825.69501
TOTAL	12181.16809	12181.16809

Table 1: Overall material balance for the process

VII. ENERGY BALANCE

As we know that according to the law of conservation of energy, "Energy can neither be created nor destroyed but it can be transformed from one form to another." So, according to this we have,

Heat in – heat out + Generation – consumption = accumulation

We assume that the system is in steady state (accumulation = 0).

Equation of heat capacity,

$$Cp = A + BT + CT^2 + DT^{-2}$$

General equation, $Q - Ws = \Delta H + \Delta Ek + \Delta Ep$

However, based on the assumption made, the above equation is reduced to the form of:

$$Q = \Delta H = mCp\Delta T$$

Energy Balance for Reactor column:

Inlet temperature of reactants=823.15 K (550°C)
Outlet temperature of products=873.15 K (600°C)
Reference temperature=298.15 K

$Cp_{glyoxal} = 1.079$ KJ/Kg.K; $Cp_{ethylene\ glycol} = 2.85$ KJ/Kg.K

$Cp_{O2} = 3.78$ KJ/Kg.K; $Cp_{N2} = 1.122$ KJ/Kg.K,

$Cp_{H2O} = 4.184$KJ/Kg.K

- Enthalpy in:

$$\Delta H_{in} = m_{EG,in} \times C_{pEG} \times (T_{in} - T_{ref}) + m_{O2,in} \times C_{pO2} \times (T_{in} - T_{ref}) + m_{N2,in} \times C_{pN2} \times (T_{in} - T_{ref})$$

$$= 16820.32773 \text{ MJ/hr}$$

- Enthalpy out:

$$\Delta H_{out} = m_{gly,out} \times C_{pgly} \times (T_{out} T_{ref}) + m_{H2O,out} \times C_{pH2O} \times (T_{out} - T_{ref}) + m_{N2,out} \times C_{pN2} \times (T_{out} - T_{ref})$$

$$= 16499.27069 \text{ MJ/hr}$$

Now,

$$Q_{net} = \Delta H_{in} - \Delta H_{out}$$

$$\Rightarrow \quad Q_{net} = 321.05704 \text{ MJ/hr}$$

Energy Balance for Condenser:

Cold fluid(coolant): Water (3,800 kg/hr)
Inlet temperature of hot fluid=873.15 K (600oC)
Inlet temperature of cold fluid=298.15 K (25oC)
Outlet temperature of hot fluid= 313.15 K (40oC)
Outlet temperature of cold fluid =683.15 K (410oC)
Reference temperature=298.15 K

Enthalpy of hot fluid in:

$$\Delta H_{HF,in} = m_{gly,in} \times C_{pgly} \times (T_{HF,in} - Tref) + mH_2O,in \times CpH2O \times (T_{HF,in} - T_{ref})$$

$$= 15561.81154 \text{ MJ/hr}$$

Enthalpy of cold fluid in:

$$\Delta H_{CF,in} = mCF,in \times CpCF \times (TCF,in - Tref) = 0 \text{ MJ/hr}$$

Enthalpy of hot fluid out:

$$\Delta H_{HF,out} = m_{gly,out} \times C_{pgly} \times (T_{HF,out} - T_{ref}) + mH_2O,out \times Cp_{H2O} \times (T_{HF,out} - Tref)$$

$$= 355.0606 \text{ MJ/hr}$$

Enthalpy of cold fluid out:

$$\Delta H_{CF,out} = mCF,out \times CpCF \times (TCF,out - Tref) + mCF,out \times \lambda$$

= 15605.2845 MJ/hr

Total heat in = 15561.81154 MJ/hr
Total heat out = 15960.3451 MJ/hr
Net Heat, $Q = \Delta Hin - \Delta Hout$
$Q = -398.53356$ MJ/hr

The "-" indicates heat is released to the atmosphere.

VIII. SPECIFIC EQUIPMENT DESIGN

For the production of 40% glyoxal we generally prefer batch process in the industry.

Design of reactor

H – height of the reaction mixture

D_a – diameter of impeller

h – Height of the impeller from the bottom

D_r – Diameter of the reactor

Reaction time = 0.00833hr = 30 sec

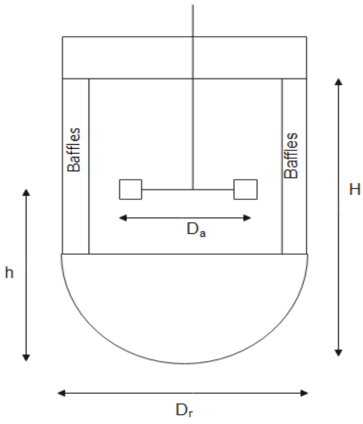


Fig 2 Batch reactor design

Volumetric flow rate = $\sum m_i / \rho_i$
=3564.78289/1142.6+4594.24532/1.273 + 4022.13988/1.065
= 7416.8442 m^3/hr

Volume of reactor = volumetric flow rate * reaction time

= 7416.8442*0.00833 = 61.782m^3

Volume of reactor = volume of cylindrical part + volume of tori spherical head

Volume of cylindrical part = $(\pi/4) * D_r^2 * H$

Volume of tori spherical head = $(\pi/24) * D_r^3$

Based on optimum design considerations,

$H/D_r = 1.3$ hence $H = 1.3 * D_r$

Height of baffles from the base h = H/3

Diameter of agitator $D_a = D_r/3$

Diameter of each baffle, $D_b = D_r/10$

Volume of reactor = $(\pi/4) * D_r^2 * H + (\pi/24) * D_r^3$

$61.782 = (3.14/4) * D_r^2 * 1.3 * D_r + (3.14/24) * D_r^3$

$61.782 = D_r^3 * (1.025 + 0.1308)$

$D_r^3 = 61.782 / 1.1558$

$D_r = 3.767$

Diameter of reactor = 3.767 m

$H = 1.3 * D_r$
$H = 1.3 * 3.767 = 4.897$

Height of reactor = 4.897 m

h = H/3
h = 4.897/3 = 1.622

Height of impeller from bottom = 1.622 m

$D_a = D_r/3$
$D_a = 3.767/3 = 1.256$

Diameter of impeller = 1.256 m

$D_b = D_r/10$
$D_b = 3.767/10 = 0.377$

Diameter of each baffle = 0.377 m

Calculation of heat transfer area:

Heat transfer area:

Heat transfer area = area of cylindrical part + area of tori spherical head

Area of cylindrical part = $\pi * D_r * H$

= 3.14 * 3.767 * 4.897

= 57.924 m^2

Area of tori spherical head = $0.1 * \pi * D_r * H$

= 0.1 * 3.14 * 3.767 * 4.897

= 5.792 m^2

Heat transfer area = 57.924+5.792

= 63.716 m^2

IX. MATERIAL OF CONSTRUCTION

Materials of construction square measure sometimes designated supported their strength, elasticity, hardness, toughness, sensitive to wear, corrosion and fatigue resistance, simple fabrication, availableness worth and value} price. Metals square measure sometimes characterized on the premise of their chemical and physical properties within the solid state. several factors need to be thought-about once choosing engineering materials except for natural action plant the predominant thought is typically the power to resist corrosion. the method designer is liable for recommending materials which will be appropriate for the method conditions.

Table 2: For the instrumentation in four-hundredth Glyoxal plant, the well-liked materials of construction square measure as follows-

Equipment	Material
Reactor	Stainless steel
Condenser	Aluminium or cast iron
Storage tank	Carbon or stainless steel
Mixer	Stainless steel
Filter	Carbon steel

X. HEALTH SAFETY AND ENVIRONMENTAL ASPECTS

The goal of factory isn't solely to supply chemicals, however conjointly to supply them safely. within the plant's chain of processes and operations, loss of management anyplace will cause accidents then losses of life and property from hazards. tries ought to be created to forestall troubles from the review whereas planning, fabricating and operational. Safety usually involves:

- Controlling machine hazards
- Procedural and body controls
- Electrical maintenance
- Periodic medical analysis
- Hazard identification

XI. INSTRUMENTATION AND PROCESS CONTROL

Instruments are providing to observe the key method variables throughout plant operation. they'll be incorporated in automatic management loops or used for the manual observance of the method operation. they'll even be a part of AN automatic laptop information work system. Instrument's observance crucial method variables are fitted with automatic alarms to alert the operators to crucial and dangerous things. Instrumentation and management include the subsequent

- Instrumentation & management objectives
- Components of the system
- Safety and environmental laws
- Control within a reactor
- Alarms and safety tips
- Pressure gauges and transmitters
- Temperature controllers
- Level sensors and flow controllers

XII. PLANT LOCATION AND LAYOUT

The geographical location of the ultimate plant will have sturdy influence on the success of an industrial venture. considerable care should be exercised in choosing the plant web site, and plenty of various factors should be thought-about for the plant came upon. Plant location depends upon the subsequent factors:

- Raw materials accessibility
- Markets
- Energy accessibility
- Climate
- Transportation facilities
- Water offer
- Waste disposal
- Labor offer
- Taxation and legal restrictions
- Site characteristics
- Flood and fireplace protection

After the method flow diagrams square measure completed and before careful piping, structural, and electrical style will begin, the layout of method units in an exceedingly plant and therefore the instrumentality among these method units should be planned. This layout will play a crucial half in decisive construction and producing prices, and therefore should be planned fastidiously. Some necessary factors that square measure to be thought-about square measure

- New {site|website|web web site} development or addition to antecedently developed site
- Possible future enlargement
- Economic distribution of utilities and services
- Health and safety concerns
- Waste-disposal necessities

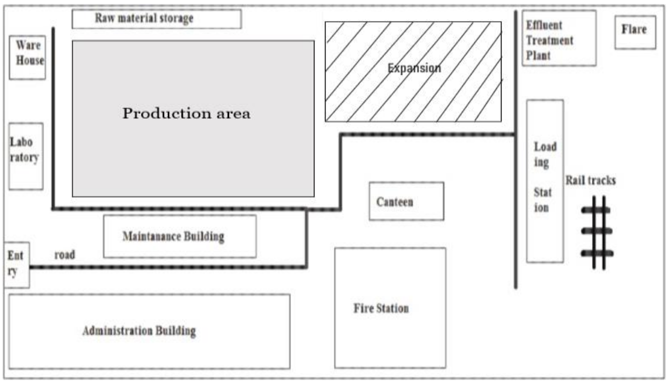


Fig.3: Typical plant layout for manufacture of Glyoxal

XIII. COST ESTIMATION

Evaluation of costs in the preliminary design phase is sometimes called guess estimations. A plant design obviously must present a process that is capable of operating under condition which will yield a profit.

Estimation of plant cost:

This chapter includes the detailed study of cost calculations done for the whole plant and finding the rate of return per annum based on 40% Glyoxal sales.

All the values are in US$.

Cost of 1 tonne of 40% Glyoxal : 780
No of tonnes produced per year : 60000
Gross annual sales : 60000 * 780 = 46800000
Total direct costs : 32760000
Total indirect costs : 14040000
Total production cost : 34304400
Gross profit : 12495600
Net profit : 3748680
Payout time : 5.35 years
Percentage returns : 18.69 %

XIV. CONCLUSION

The main objective of the paper is to supply the four-hundredth glyoxal from glycol in presence of Air/N2 mixture in autoclave batch reactor mistreatment silver spirals catalyst. four-hundredth Glyoxal is employed in big variety of applications thanks to its distinctive properties. the method of manufacture of four-hundredth Glyoxal from glycol by vapor section aerobic dehydrogenation is studied.

Material and energy balance are distributed for the plant taking 60,000TPA production. the planning for every instrumentation is distributed and therefore the materials of construction area unit instructed. because the chemical change involves safety as a very important facet, study concerning safety and varied controllers is completed. Plant location is recommended supported the material availableness and transportation because the necessary criteria and therefore the plant layout is recommended. the whole value to setup the plant is calculated and therefore the payout time and rate of come area unit calculated.

XV. ACKNOWLEDGMENT

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