

ACETIC ACID INDUSTRIES

INTRODUCTION

Acetic acid, CH_3COOH is an organic compound which also written as $\text{CH}_3\text{CO}_2\text{H}$ or $\text{C}_2\text{H}_4\text{O}_2$. It is a colourless liquid in undiluted form is called as glacial acetic acid. Andreas Libavius in the sixteenth century described a procedure for preparation of glacial acetic acid through the dry distillation of certain metal acetates like copper (II) acetate and compared the produced glacial acetic acid with vinegar. The presence of water in vinegar has such a profound effect on acetic acid's properties that for centuries chemists believed that glacial acetic acid and the acid found in vinegar were two different substances. Later on Pierre Adet proved that both are same. The very dilute form of acetic acid (8 – 10%) is known as vinegar and has a distinctive sour taste and pungent smell. Besides its production as household vinegar, it is mainly produced as a precursor to polyvinyl acetate and cellulose acetate. Although it is classified as a weak acid, while concentrated acetic acid is corrosive to the skin.

Due to the global present of acetic acid producing bacteria via air oxidation of beer and wine vinegar was first known to the society. In the 3rd century BC, Theophrastus described how vinegar acted on metals to produce pigments useful in art, including white lead (lead carbonate) and verdigris, a green mixture of copper salts including copper (II) acetate. Ancient Romans boiled soured wine in lead pots producing lead acetate rich highly sweet syrup called as sapa or sugar of lead or sugar of Saturn, which contributed to lead poisoning among the Roman nobility.

Hermann Kolbe synthesized acetic acid first time from inorganic compounds in 1847. The reaction sequence consisted of chlorination of carbon disulfide to carbon tetrachloride, followed by pyrolysis to tetra chloro ethylene and aqueous

chlorination to trichloro acetic acid, and finished with electrolytic reduction to acetic acid.

In the first decade of twentieth century most glacial acetic acid was obtained from the "pyro ligneous liquor" from distillation of wood. The acetic acid was isolated by treatment with milk of lime, and the resulting calcium acetate was then acidified with sulfuric acid to recover acetic acid.

The formation of acetic acid furnishes an excellent example of liquid-phase oxidation with molecular oxygen. Acetic acid may be obtained by the direct oxidation of ethanol, but the concentrated acid is generally obtained by oxidation methods from acetaldehyde that may have been formed by the hydration of acetylene or the oxidation of ethanol. The oxidation usually occurs in acetic acid solution in the presence of a catalyst and at atmospheric or elevated pressures. Temperatures may range, up to 100 °C, depending upon conditions, but are usually lower.

USES

- As monomer in the production of vinyl acetate
- Used in synthesis of wood glue, synthetic fibres, fabrics and cellulose acetate
- Esters of acetic acid used as solvent in coatings, inks and paints industry
- 20% of acetic acid is used as solvent in terephthalic acid production
- As a stop bath in development of photographic films
- As a household vinegar to clean indoor climbing holds of chalk
- As solvent for recrystallization to purify organic compounds
- As wart and verruca remover
- As a food additives

PROPERTIES

- Molecular formula : $C_2H_4O_2$
- Molecular weight : 60.05gm/mole
- Appearance : Colourless liquid
- Odour : Pungent
- Boiling point : 118-119 $^{\circ}C$
- Melting point : 16-170 $^{\circ}C$
- Density : 1.049gm/cm³
- Solubility : Miscible with water

MANUFACTURE

Acetic acid can be manufactured by following methods

1. Methanol carbonylation
2. Acetaldehyde oxidation
3. Ethylene oxidation
4. Oxidative fermentation
5. Anaerobic fermentation

1. Methanol carbonylation

Raw material

Basis: 1000kg acetic acid by methanol carbonylation (95% yield)

- Methanol 510kg
- Carbon monoxide 445kg

Reaction



Manufacture Process

Rhodium catalyzed carbonylation of methanol is carried out in presence of iodine as activator. Methanol and carbon monoxide were charged into carbonylation reactor at partial pressure between 10 – 15 bar while the temperature is maintained at 175 °C. The exhaust gas from the reactor is coming out from the top and introduced into gas scrubber where gases coming out from purification section are also scrubbed using methanol and then recycle to reactor.

Reactor used in carbonylation of methanol is bubble column reactor. This reactor provides excellent mass and heat transfer. In this reactor gas is sparged from the bottom of the reactor. Design of the sparger controls the bubble size distribution in the column.

While remaining mixture from the reactor is heated in flash tank where vapour is transferred to crude column for distillation while liquid coming out from bottom is recycled to reactor. In crude acetic acid column, light end are vaporized and send to light ends column where they are removed. Liquid coming out from bottom is again heated in flash tank and acetic acid–water mixture is taken out from side cut and charged in to dehydration column where methanol is introduced. After dehydration, liquid mixture from bottom of column is charged into acetic acid column where acetic acid is obtained as product. Waste acid are removed using stripping operation.

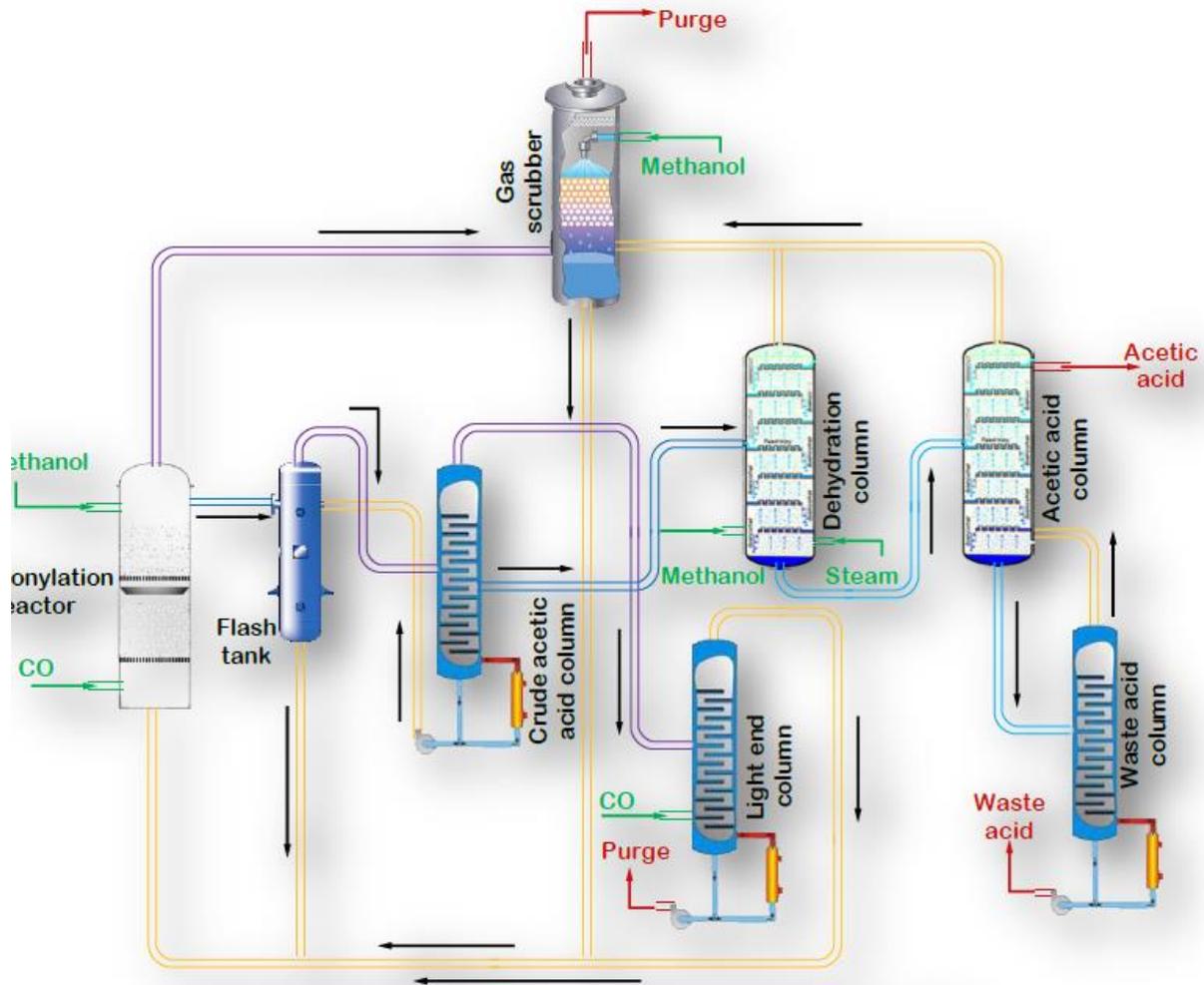


Figure: Manufacture of acetic acid by methanol carbonylation

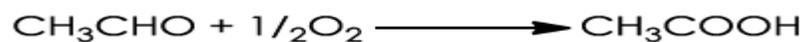
2. Acetaldehyde Oxidation

Raw material

Basis: 1000kg acetic acid by acetaldehyde oxidation (87% yield)

- Acetaldehyde 845kg
- Oxygen 615kg

Reaction



Acetaldehyde from acetylene hydration was preheated in heat exchanger and purified in acetaldehyde still by distillation. Purified acetaldehyde was stored in refined aldehyde storage tank. Then refined

aldehyde was charged in to oxidation vessel from top in counter current direction of air as a source of oxygen from bottom.

The reaction vessel consists principally of aluminum-lined steel vessel fitted with air distributor. In operation, previously cooled acetaldehyde at 0-5 °C was introduced, and then manganese acetate is added either in the form of saturated acetic acid solution or as a powder ground to pass 200 mesh sieve. At the same time air was introduced through the distributor head and temperature was raised by steam by passing through the aluminum coils. The heat of reaction must be removed by cooling water, which is substituted for the initial steam. Temperature plays an important role for the oxidation reaction. It should be maintained 27 °C for 1st hrs. Then increase of 1 to 2 °C for 2hrs and gradually increased up to 60 °C after 4hrs. The most satisfactory operating temperature is about 60 °C. The reaction takes 12-14 hrs for completion. The pressure was kept below 5 kg/cm².

The nitrogen being vented through a series of condensers attached to the dome. Condensed aldehyde was returned to the kettle. The nitrogen was passed through water scrubbers to remove the last traces of the aldehyde, which is later recovered. Acetic acid, exceeding 96% strength was obtained. Distillation is carried out for final concentration and purification of acid. The yield varied from 88-95% of the theoretical.

3. Ethylene Oxidation

Raw material

Basis: 1000 kg of acetic acid by ethylene oxidation

Ethylene 470 kg

Oxygen 530 kg

Reaction



Vapour phase oxidation of ethylene was carried out using palladium supported on alumina as catalyst. Ethylene and oxygen was charged into a reactor in vapour phase. The reaction temperature and pressure was 215 – 250 °C and 150-300psi respectively. Unreacted ethylene from product stream was separated in separator. The crude liquid containing acetaldehyde and acetic acid was separated in a distillation column. Acetaldehyde and ethylene obtained from distillation and separation respectively, where recycled to the process for increasing yield and conversion.

4. Oxidative Fermentation

Raw material

Basis: 1000kg of acetic acid by oxidative fermentation

- Ethanol 770kg
- Oxygen 530kg

Reaction



Dilute solution of alcohol was first sterilized in autoclave and then charged into the fermenter. Oxygen in the form of air was supplied by bubbling through the solution of alcohol in the fermenter. An aerobic bacterium like acetobacter was added into the fermenter for aerobic fermentation. Oxidation of ethanol was carried out at 26 – 36 °C temperature.

Nitrogen was removed from the product stream in a scrubber, by scrubbing with cooled water. Liquid mixture coming out from the bottom of the scrubber containing acetic acid and water was separated in an acetic acid still. Vinegar of 15% and 20% acetic acid was manufactured in 24 hrs and 60 hrs process respectively.

5. Anaerobic fermentation

Raw material

- Sugar
- Anaerobic bacteria (Genus Clostridium)
- Nitrogen

Reaction



Manufacture Process

The species of anaerobic bacteria, including members of the genus clostridium are used which are capable to convert sugars to acetic acid directly, instead of using ethanol. At an actual 85% yield, the anaerobic process offers 60% reduction in raw material. The mechanism of anaerobic fermentation of sugar is quite complex.

Anaerobic Fermentation of sugar was carried out in fermenter. An anaerobic bacterium like clostridium was added to initiate the fermentation process. Nitrogen is supplied by bubbling during the fermentation process.

The mixture was then charged in to scrubber where it is scrubbed with cooled water to remove excess nitrogen present in system. Mixture coming out from bottom of scrubber contains acetic acid and water which was then separated in acetic acid still.

The most important method for producing acetic acid in modern industries is carbonylation of methanol.

Chlorine Industry

Introduction

Chlorine is a chemical element and having atomic number 17. It is denoted as Cl. It belongs to the halogen family and is the second lightest halogen after fluorine. Under standard conditions, it is appear as a yellow-green gas, where it forms diatomic molecules. It has the highest electron affinity. Chlorine is a strong oxidizing agent as having the third highest electronegativity of all the elements. Due to direct or indirect oxidation by oxygen, free chlorine results which are rare on earth.

Sodium chloride is the most common compound of chlorine and has been known since ancient times. Chlorine gas was first synthesized in a chemical reaction around 1630, but not recognized as a fundamentally important substance. In 1774, characterization of chlorine gas was made by Carl Wilhelm Scheele, who supposed it an oxide of a new element. Chemists suggested that the gas might be a pure element in 1809 and Sir Humphry Davy was confirmed this in 1810, who named it from Ancient Greek: *χλωρός* *khlôros* "pale green".

In various ionic compounds, all chlorine in the Earth's crust occurs as chloride, including table salt. In Earth's crust, it is the second most abundant halogen and 21st most abundant chemical element. By electrolysis method elemental chlorine is commercially produced from brine. Due to the high oxidizing potential, chlorine led commercially to free chlorine's bleaching and disinfectant uses.

Chlorine is necessary in the form of chloride ions for all known species of life. While other types of chlorine compounds are rare in living organisms. Artificially produced chlorinated organic compounds are inert and toxic.

Chlorine-containing organic molecules such as chlorofluorocarbons have been implicated in ozone depletion in the upper atmosphere. By oxidation of chloride

small quantities of elemental chlorine are generated, as part of the immune response against bacteria. For all living organisms, elemental chlorine at high concentrations is extremely dangerous and poisonous. It was historically used as the first gaseous chemical warfare agent in World War I.

Manufacture

Chlorine is manufactured by following methods

1. Electrolysis of salt
2. From salt and nitric acid
3. Mercury cell process
4. Diaphragm cell process
5. Membrane cell process

1. Electrolysis of salt

Raw material

Basis: 1000 kg chlorine plus 470 kg sodium hydroxide plus 25 kg hydrogen

Salt 1660 kg

Sodium carbonate (58%) 26kg

Sulfuric acid (660Be) 10kg

Steam 10365kg

Electricity 3000kwhr

Refrigeration 935kg

Graphite 5kg

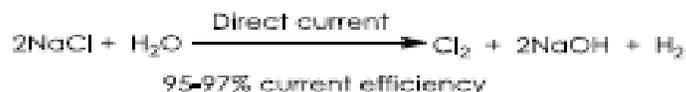
Manufacture Process

Purified brine was first charged into the electrolytic cell where electrolysis of brine was carried out using direct current. Hot chlorine gas containing considerable water vapour was evolved from the anodes of the electrolytic cell. The wet chlorine was then charged to the cooler, where the temperature of the gas was reduced to 12–14 °C to avoid the formation of solid chlorine hydrate. Generally almost all water vapour was condensed in these coolers, which may be of the following types such as chemical stoneware chlorine lines submerged in water in trenches, water-cooled glass pipes and rubber lined steel pipes. Depending upon the available water temperature refrigeration was used.

The chlorine gas containing water was trapped and partially dried chlorine gas was passed to drying tower, where the remaining water was removed by scrubbing with 660Be sulfuric acid. After drying, the chlorine can be handled in iron steel equipment. Otherwise the dried gas was charged into the compressors to withdraw the chlorine. Most of the plants use a carbon-ring non lubricated compressor which operates at about 40 psi gauge.

After compression, mixture was passed from expansion drum where sulfuric acid separated out and chlorine was condensed using refrigerants. Different refrigerant such as ammonia, carbon dioxide and freon are commonly employed. A temperature between -30 and -450C was achieved using single-stage or multiple-stage refrigeration. The resulting liquid chlorine from condenser was stored and filled into cylinders or into tank cars.

Reaction



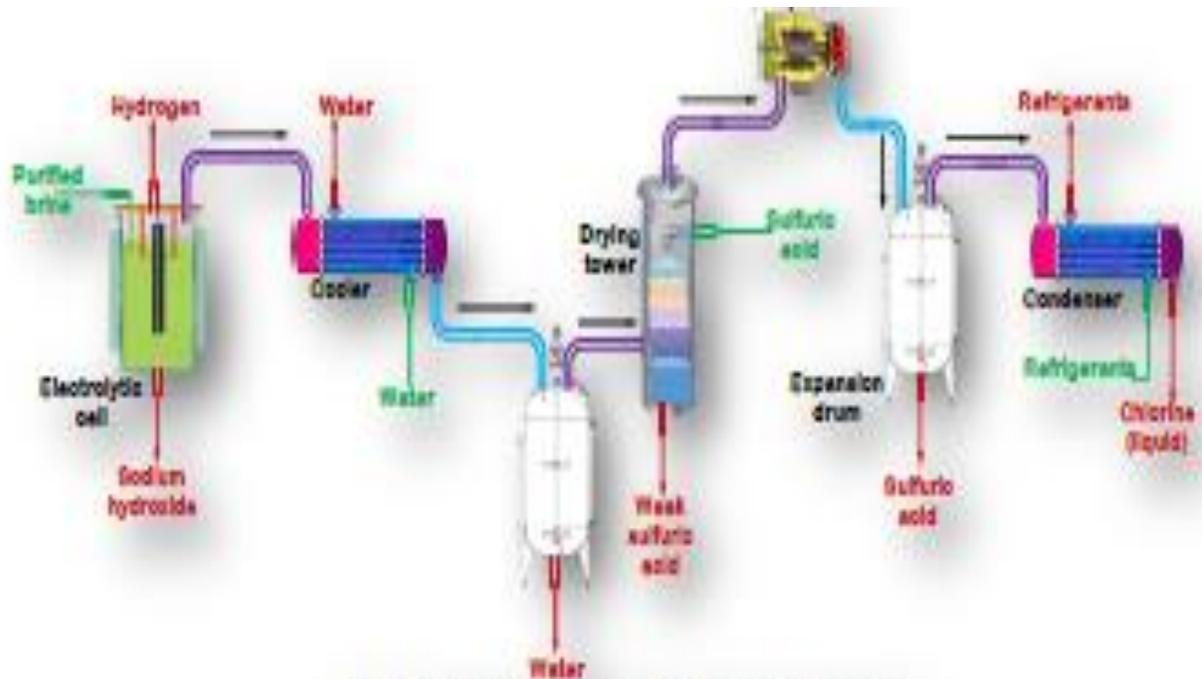


Figure: Manufacture of chlorine from salt by electrolysis

2. From Salt and Nitric Acid

Raw material

Basis: 1000kg chlorine plus 232kg sodium nitrate

Salt 1500kg

Nitric acid (as 100%) 1610kg

Oxygen 275kg

Reaction



Manufacture Process

The gases leaving the drying column were liquefied by cooling with brine at -15 to 20°C in a digester-condenser which was made of chrome-alloy steel. The condensed liquid was then fed to a column where chlorine gas goes overhead and nitrosyl chloride was removed as a bottoms end. The liquid nitrosyl chloride was passed from the vapourizer and heated again along with oxygen from 100 – 200°C. The hot mass was sent to an oxidizer where the nitrosyl chloride was converted into nitrogen dioxide and chlorine at 200 – 400°C.

After cooling the gaseous effluent to 25 – 35°C the cooled liquid was run into the fractionating column where it was fractionated at 15 – 60°C. So, chlorine gas obtained as overhead product and nitrogen dioxide coming out as the bottom end. Remaining nitrogen dioxide may be converted into the nitric acid by conventional methods.

Hydrogen peroxide solution was sprayed on nitrogen dioxide, into the exhaust gas stream which produced the nitric acid. In addition nitrogen dioxide was oxidized to nitric acid.

3. Mercury Cell Process

Raw material

Basis: 1000kg of Chlorine

Raw salt 1820kg

Sodium carbonate 35kg

Sulfuric acid 115kg

Steam 11445kg

Electricity 1365kJ

Refrigeration 1035kg

Direct labour 22work-h

The solution of raw salt was mixed with sodium chloride in saturator. Sodium chloride contains sulfate of magnesium, calcium impurities. The mixture from saturator was charged into purification tank where it was purified using caustic soda, soda ash and barium chloride. Muds containing calcium carbonate, magnesium hydroxide, barium sulfate and sodium chloride were removed.

Purified brine was charged into the electrolytic cell. Electrolysis of brine was carried out using direct current. During electrolysis process hot chlorine gas containing water vapour and hydrogen gas was evolved from the electrolytic cell. Then wet chlorine from the cell was charged to the cooler. The temperature of the chlorine gas was reduced to 12 °C to avoid the formation of solid chlorine hydrate.

The stream from cooler was passed to drying and purification section, where the sulfuric acid was charged. Chlorine was obtained from the top and 70 – 80% acid was obtained from bottom. Unwanted caustic and waste mixture from cell was filtered where caustic was separated out while other waste was charged to waste treatment plant to obtained solid waste and waste water.

Dimethyl Sulfoxide

INTRODUCTION

Dimethyl sulfoxide, denoted as DMSO, is an organosulfur compound with having the formula $(\text{CH}_3)_2\text{SO}$. It is a colourless liquid and an important polar aprotic solvent that dissolves both polar and nonpolar compounds. It is miscible in a wide range of organic solvents as well as water. As it penetrates in the skin very readily, it gives the unusual property for many individuals of being secreted onto the surface of the tongue after contact with the skin and causing a garlic-like taste in the mouth. DMSO was first synthesized in 1866 by Alexander Zaytsev. But the use of DMSO as a pharmaceutical was began in 1961, when Stanley Jacob discovered that it penetrated the skin quickly and deeply without damaging it.

Kraft pulping is the conversion of wood into wood pulp which consisting of pure cellulose fibres, where DMSO was obtained as by-product. Oxidation of dimethyl sulfide with oxygen or nitrogen dioxide produced DMSO.

It also has significant known side effects although it has some medicinal uses. It is promoted as a fake cure for cancer and other conditions.

MANUFACTURE

Raw Material

Basis: 2000kg of $(\text{CH}_2)\text{S}$ or 1000 kg of $(\text{CH}_3)_2\text{S}=\text{O}$

Black liquor (45% solids) 66000-100000kg

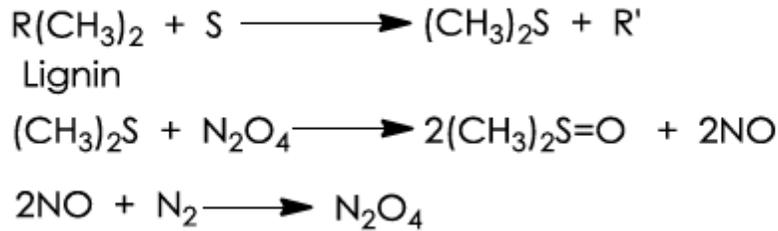
Sulfur 2200-2500kg

NaOH make-up 25kg

Plant capacities: 15000kg/day of DMS

7500kg/day of DMSO

Reaction



Sulfate pulp black liquor was concentrated to 45 – 50% solids and then pumped to a high pressure reactor along with molten sulfur. To raise the temperature up to 230°C, steam was sprayed in the reactor. Black liquor is an industrial by-product of the pulp and paper industry.

Demethylation of liquor occurs via reaction with the sulfur to form dimethyl sulfide (DMS) and methyl mercaptan (MM). Then reaction mass was charged to flash tank where sulfur-containing products were removed overhead while the demethylated black liquor was returned to the pulp mill

for digestion chemicals. The DMS and MM overheads were condensed and then separated out from water.

Using 10% caustic washings, mercaptan and remaining water was removed in MM scrubber and returned to the pulp plant. Mercaptans can be separated and purified as a major by-product with a maximum yield of about 5% of dimethyl sulfide (DMS). The overheads from the scrubber were again washed with 50% caustic and then run to the DMS column where dimethyl sulfide was purified by distillation and sold as a co-product or converted to dimethyl sulfoxide (DMSO).

Manufacture process

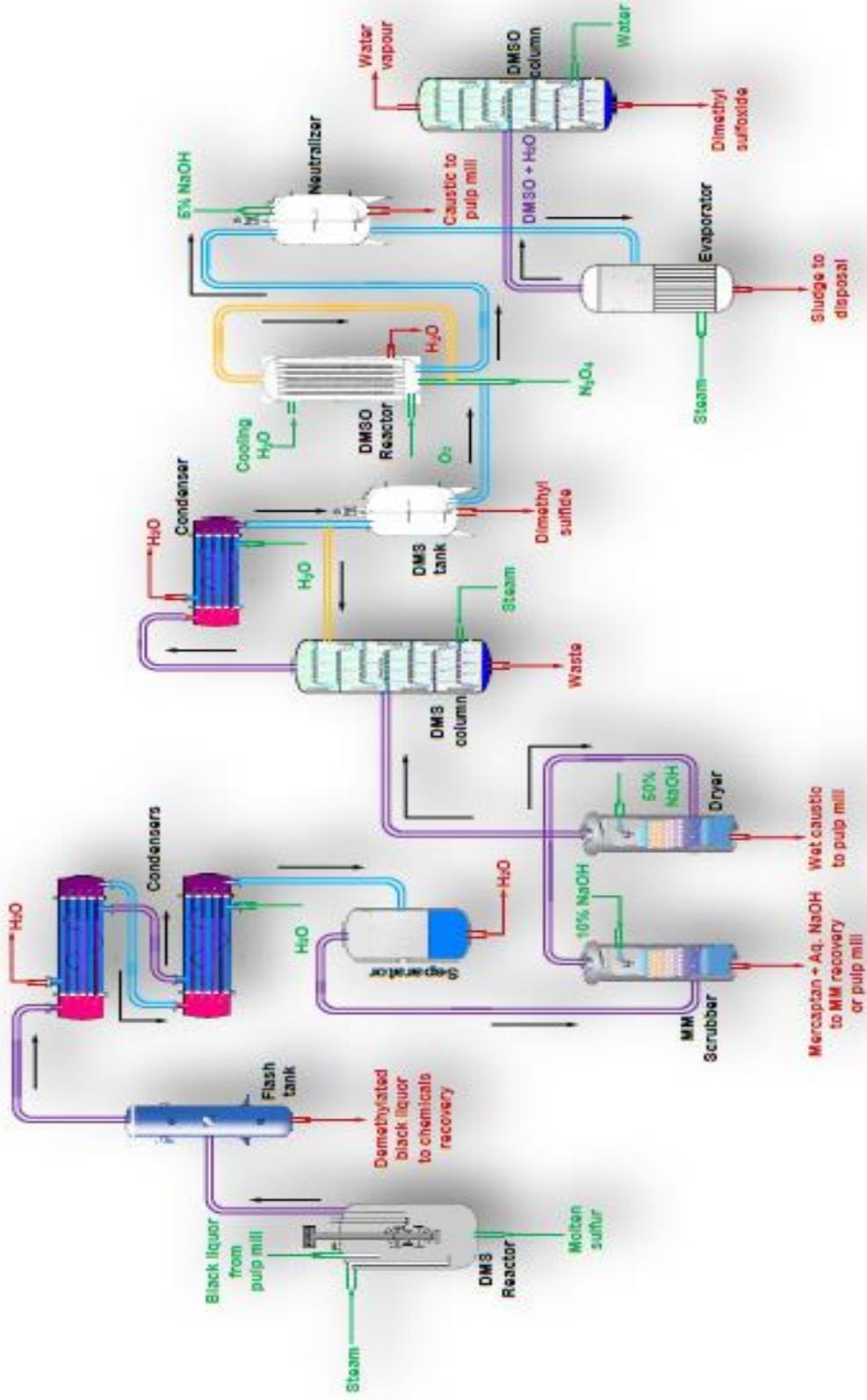


Figure: Manufacture of Dimethyl sulfoxide from wood liquor

To produce dimethyl sulfoxide (DMSO), the DMS was line-blended with nitrogen tetra oxide (N_2O_4) and fed into the bottom of the liquid-phase oxidation reactor (DMSO reactor) where, the oxidation of DMS was carried out using nitrogen tetra oxide and converted into the dimethyl sulfoxide. The oxygen was added to reoxidize the nitrogen oxide. The crude liquid DMSO was separated from gases and washed with 5% NaOH solution. Then washed liquid mixture was run into the evaporator where the overhead was sent to the DMSO column for final purification. In DMSO column, dimethyl sulfoxide was separated from water.

Engineering Aspects

Optimization of Yield of Dimethyl Sulfide (DMS)

The cleavage of methoxyl groups and conversion of the methyl groups to DMS depend on the time and temperature of the lignin-sulfur reaction. The conditions represent a compromise between completeness of demethylation and undesirable condensation of lignin and DMS to produce insoluble products which occur at extreme conditions.

Materials of Construction

The high temperature level in many parts of the plant coupled with presence of sulfur required use of stainless steel for these conditions.

Explosion Hazards in the Oxidation Step

N_2O_4 catalyzed oxidation of DMS in vapour phase is explosive. A large plant using vapour phase was completely demolished in 1959. A method for avoiding this hazard has been developed in which a solution of DMS in DMSO is oxidized in liquid phase with a mixture of NO and oxygen. Process was controlled by the presence of excess DMSO and a low temperature of operation (650C maximum).

Health and safety factors

Dimethyl sulfoxide is relatively stable solvent. It has a low toxicity. The LD50 for single dose oral administration to rats is 17,400 – 28,300mg/kg. This solvent itself presents less hazards compared to the other solvents and chemicals used in the industry. Sometimes it penetrates into the skin as it combined with some other chemicals in certain conditions. Regular protective measures should be taken while handling in the laboratory. While handling large quantities special protecting clothing is recommended including eye protectants and suitable gloves. Generally gloves made of butyl rubber have to be recommended.

Now days it has been applied in the medicine field also. In 1981, in the USA, DMSO as a drug was examined under the FDA but this agency has not released DMSO for human as drug.

PROPERTIES

- Molecular formula : C_2H_6OS
- Molecular weight : 78.13gm/mole
- Appearance : Colourless liquid
- Odour : Garlic or spirit odour
- Boiling point : 189.0 °C
- Melting point : 19.0 °C
- Flash point : 89.0 °C
- Density : 1.100 gm/cm³
- Refractive index : 1.479
- Solubility : Miscible with water, diethyl ether

USES

- As solvent in NMR studies as its having ability to dissolve a wide range of analytes
- As a mild oxidant in organic synthesis
- As a cryoprotectant, added to cell media to reduce ice formation and thereby prevent cell death during the freezing process
- As a drug vehicle in in-vivo and in-vitro experiments
- DMSO is metabolized to dimethyl sulfone and dimethyl sulfide which is subjected to renal and pulmonary excretion
- In embolisation, the therapeutic occlusion of blood vessels as embolic agent
- In veterinary medicine as a liniment for horses alone or combination with other ingredients and other function of DMSO is as solvent to carry the other ingredients across the skin
- As an odourant in natural manufactured gas
- As an intermediate in preparing many S-containing derivatives
- As a solvent for spinning synthetic fibres such as polyacrylonitrile

FERMENTATION INDUSTRIES

INTRODUCTION

The word fermentation comes from the Latin “fermentare” means to boil. Fermentation stood for the decomposition of foodstuff, generally accompanied by evolution of gas e.g. fermentation of sugars to alcohols and carbon dioxide by yeast. Now a days the term fermentation is applied to changes brought about by microorganisms. Evolutions of gas are not an essential criterion. In daily life many complex chemical reactions are brought about by the agency of living organisms e.g. souring and curdling of milk, putrefaction of meal, production of indigo dye from the compound indicate in the food, curing of tobacco, the development of benzaldehyde or oil of bitter almonds from the amygdaline contained in the almond seed, conversion of fruit juice into wines etc. All these processes are called fermentation processes, in which complex organic material is broken down into smaller substances and decomposition it brought about by the action of living organisms, which secretes the enzyme catalyst, suitable to the process.

Fermentation of fruits to alcohol and making of beverage out of fruits and grain have been practiced for centuries. Now man is directing the life process of microorganisms, yeasts, bacterial and moulds to the production of large number of chemicals, like alcohol, acetone, acetic acid, lactic acid citric acid and many antibiotics which are of great synthetic as well as industrial important.

Microorganism

The organism having microscopic dimension is called as micro-organism. In other words the organism cannot be seen by naked eyes but required microscope are micro-organism e.g. pseudomonas, bacillus species, e – coli etc.

Aerobe

An organism that can use oxygen as an electron acceptor at the terminus of an electron-transport chain can grow at a level of O₂ equivalent to or higher than that present in an air atmosphere (21 %) and has a strictly respiratory type of metabolism.

Anaerobe

An organism that does not use O₂ to obtain energy that cannot grow under air atmosphere. O₂ is toxic for this class of organism.

Facultative Anaerobe

An organism that can use oxygen but also has anaerobic methods of energy production. It can survive in either environment.

Sterilization

Sterilization is the process of killing of all forms of life including transmissible agents such as fungi, bacteria, viruses, spore forms, etc. present on a surface, contained in a fluid, in medication, or in a compound such as biological culture media. Sterilization can be achieved by applying heat, chemicals, irradiation, high pressure, and filtration or combinations of two or more.

Medium

The substances used to provide nutrients for the growth and multiplication of organisms is called as medium or media.

Culture

It is the population of microorganisms cultivated in a medium.

Inoculation

The artificial introduction of microorganisms or other substances into the body or into the culture medium is called as inoculation. It can also be used to refer to the communication of a disease to a living organism by transferring its causative agent into the organism, the implanting of microorganisms or infectious material into a culture medium such as a brewers vat or a petri-dish, or the placement of microorganisms or viruses at a site where infection is possible

Inoculum

The substance containing microorganism or other material that is introduced in inoculation is called as inoculums.

Incubation

The subjecting of cultures of microorganisms to conditions favourable to their growth is called as incubation e.g. temperature.

Agar

A dried polysaccharide extract of red algae, used as a solidifying agent in microbiological media.

Lyophilisation

The preservation of biological specimens by rapid freezing and rapid dehydration in a high vacuum is called as lyophilisation.

FERMENTATION PROCESS

Prerequisites

The good fermentation process shall have the following prerequisites.

- Selection of microorganism that formed a desired end product. The organism must be readily propagated and be capable of maintaining biological uniformity, thereby giving predictable yield

- Economical raw materials for the substrate e.g. starch
- Acceptable yield
- Rapid fermentation
- A product that is readily recovered purified

Nutrients for Microorganisms

Microorganisms may or may not require certain type of complex carbon containing compounds as nutrients as in the case of Human and other animals. All living organisms, microorganisms are the most versatile and diversified in their nutritional requirements. Some microbes can grow with just a few inorganic substances as their sole nutritional requirements, while other microorganisms are like higher organisms in their need for complex organic compounds. But all living organisms share some common nutritional needs, like the need for carbon, nitrogen, and water.

Water is particularly important to microorganisms, besides most of microorganisms can absorb nutrients only when the chemicals are dissolved in water.

Classification of nutrients

Nutrients are frequently classified as

- Essential nutrients
- Non essential nutrients

Essential Nutrients

Essential nutrients which are not synthesized internally either at all, or in sufficient quantities. There so, they must be consumed by an organism from its environment. For humans, these include essential fatty acids, essential amino acids, vitamins, and certain dietary minerals. Oxygen and water are also essential for human survival, but are generally not considered "food" when consumed in isolation. Humans can derive

energy from a wide variety of fats, carbohydrates, proteins, and ethanol, and can synthesize other needed amino acids from the essential nutrients.

Non-essential Nutrients

Nonessential nutrients are those nutrients that can be made by the body, they may often also be absorbed from consumed food. The majority of animals ultimately derive their essential nutrients from plants, though some animals may consume mineral-based soils to supplement their diet. Non-essential substances within foods can still have a significant impact on health, whether beneficial or toxic. For example, most dietary fiber is not absorbed by the human digestive tract, but is important in digestion and absorption of otherwise harmful substances.

Chemical elements as nutrients

All the microorganisms need a variety of chemical elements as nutrients. These elements are necessary for both the synthesis and the normal functions of cellular components.

The main nutrient elements for cell growth are

1. Carbon
2. Nitrogen
3. Hydrogen and oxygen
4. Sulfur
5. Phosphorous

1. Carbon

Carbon is one of the most important chemical elements required for microbial growth. Carbon forms the backbone of three major classes of organic nutrients e.g.

carbohydrates, lipids and proteins. Such compounds provide energy for cell growth and serve as building blocks of cellular material.

2. Nitrogen

Elemental nitrogen in the atmosphere cannot be used directly by either plants or animals, and must be converted to a reduced (or 'fixed') state to be useful for higher plants and animals. All organisms also require nitrogen in some form. Nitrogen is an essential building block of amino and nucleic acids, essential to life on the Earth.

3. Hydrogen and oxygen

Hydrogen and oxygen form part of many organic compounds. Water is one of the important compounds of hydrogen and oxygen. Water has many distinct properties from biological point of view that are critical for the proliferation of life. All known forms of life depend on water. Water is vital both as a solvent in which many of the body's solutes dissolve and as an essential part of many metabolic processes within the body.

4. Sulfur

Sulfur is needed for the biosynthesis of amino acids cysteine, cystine and methionine.

5. Phosphorous

Phosphorous is essential for the synthesis of nucleic acid and adenosine triphosphate (ATP), a compound that is extremely important for energy storage and transfer.

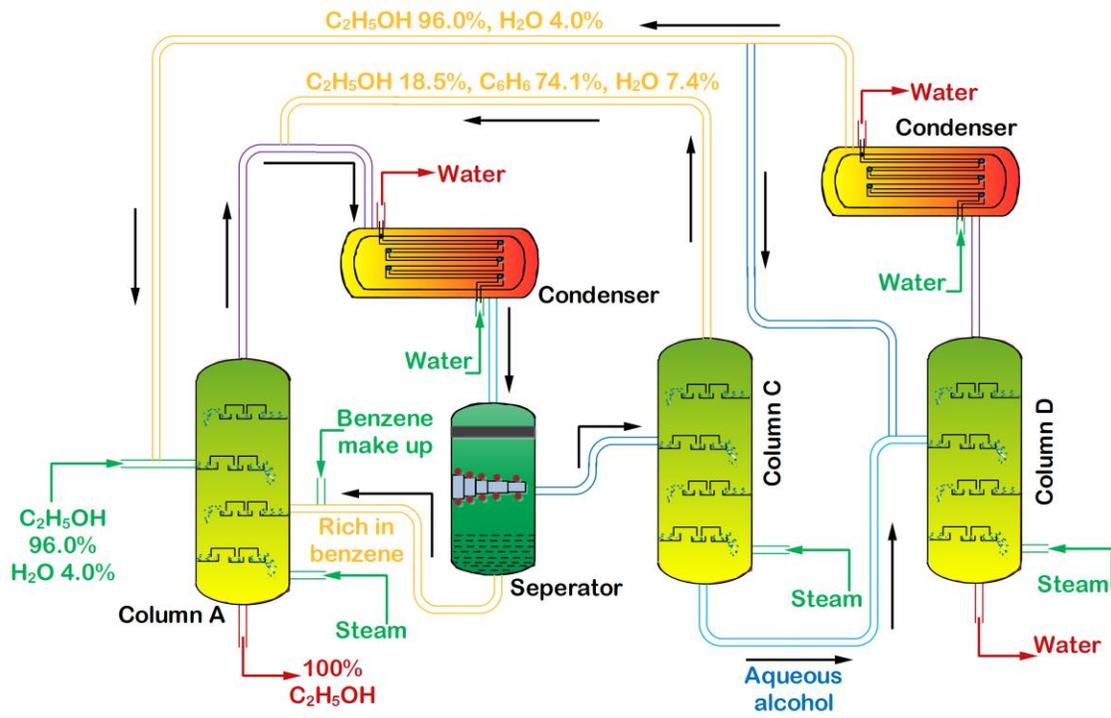


Figure: Manufacture of Absolute alcohol from 96% alcohol

Glass Industries

This technology covers the whole range of manufacturing process for glassware, which breaks down to bottles, tableware and crystal glassware.

Included in glass bottles are food containers, liquor bottles, soft-drink bottles and pharmaceutical bottles, while tableware include cups, kitchenware, ashtrays and the like. Crystal glassware include cups, kitchen-ware, ashtrays and other accessories.

The licensor of these products is rich in experiences of erecting manufacturing plants with its own technology which is already officially authorized by Coca cola and Pepsi Cola. It places particular emphasis on further developing new products on the basis of accumulated production Know-how coupled with highly-skilled technical personnel over the past 25 years since starting its business in this field .

Process Description

After removing foreign matters and pieces of iron contained in the raw material, it is weighed in proportional mixing ratio with auxiliary material.

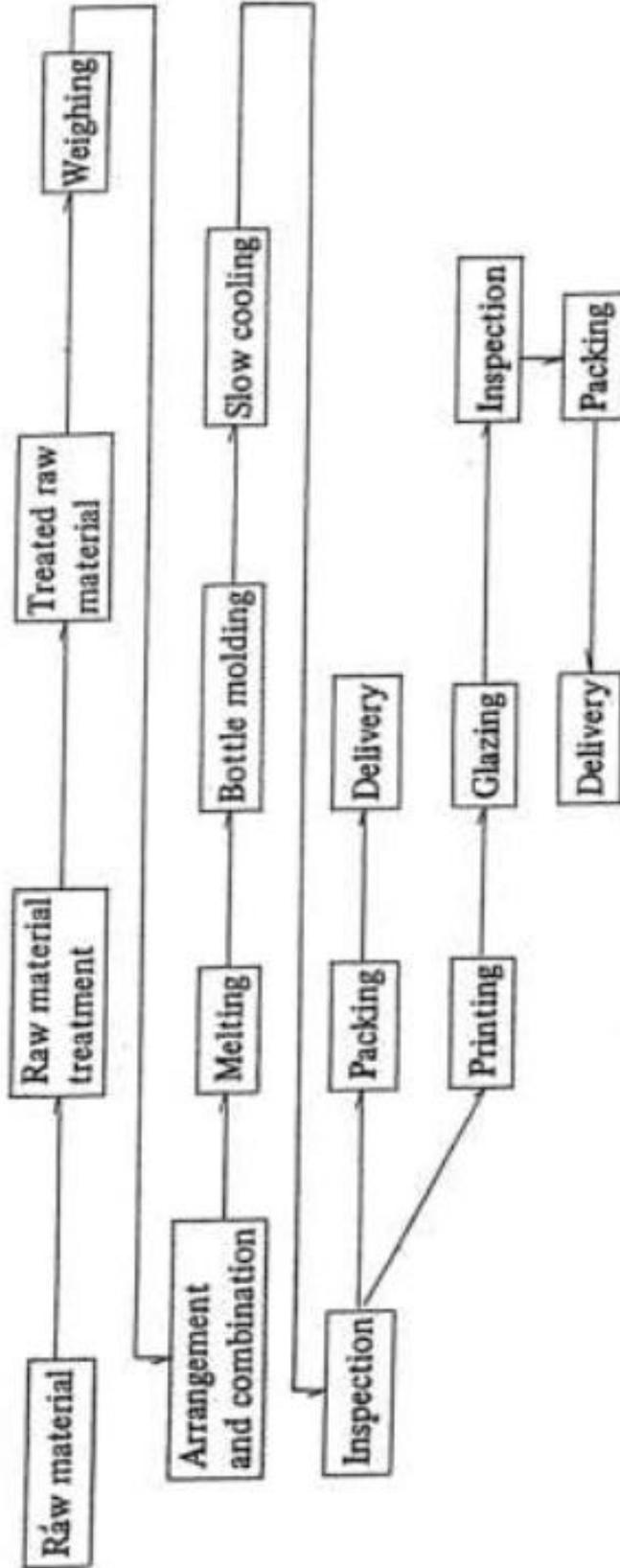
Then the mixture is processed into molten, refined glass in the furnace at the temperature of approximately 500 C . It is molded by bottle forming machine and cooled slowly and uniformly in annealing furnace.

Going through inspection, the annealed product is packed and delivered. when necessary, the bottle is automatically printed in ceramic colors by multi-color decorating machine . After glazing, it is inspected for delivery.

Raw Materials and Utilities

Raw materials and Utilities	Requirement (per ton of product)
Silica	610 Kg
Limestone	168 Kg
Soda ash	192 Kg
Broken glass	170 Kg
Additive materials	32 Kg
Ceramic color	0.5 Kg
LPC	30 Kg
Bunker - Coil	150 L
Electric power	200 Kwh
Steam	350 Kg
Water	2 ton
Compressed air	25 m ³

Bottles and Tableware Manufacturing Process Block Diagram



Glass Sheet Plant

The sheet glass plant to be introduced here is based on Pittsburg process, which is most suitable when having in mind the first sheet glass production or a small or medium plant in scale. It is characterized by a long life of machinery and quick production speed to ensure high productivity. It also facilitates production of thick heavy-duty sheet glass as well as high – quality glass.

Products and Specifications

In this plant, the clear sheet glass, tempered glass and heat-absorbing glass on the basis of soda – lime glass products are manufactured.

Products and It's Uses

Items	Special features and uses
Clear sheet glass	2 m m to 12 mm, windows, green house cases, mirrors, etc.
Tempered glass	Free from fragility and hazard. For safety uses in automobiles, steamships. Aquariums, larger windows, etc .
Heat absorbing glass	Suitable for colorful and comfortable interior conditioning. For modern buildings, patio doors, hospital windows, ships, high-grade cars, etc.

The tempered glass is produced by heating a superb quality sheet glass first to its softening point and quenching both sides to strengthen with

cooling air, having the strength several times greater than that of ordinary sheet glass against a strong shock, heavy load or sudden change in temperature.

Should it be broken, it is shattered momentarily to extremely small particles with no edge due to its strong cracking energy, thus preventing damages to be caused by pieces of broken glass.

The heat - absorbing glass is manufactured by adding some additives to the soda - lime glass and is stained whitish or bronzy. Absorbing more visible rays, infrared rays and ultraviolet rays than ordinary glass, the heat-absorbing glass assures pertinent temperature, lighting and comfortable state.

When used, it plays the role of reducing air-conditioning load in summer and preventing the drop of room temperature in winter.

Process description

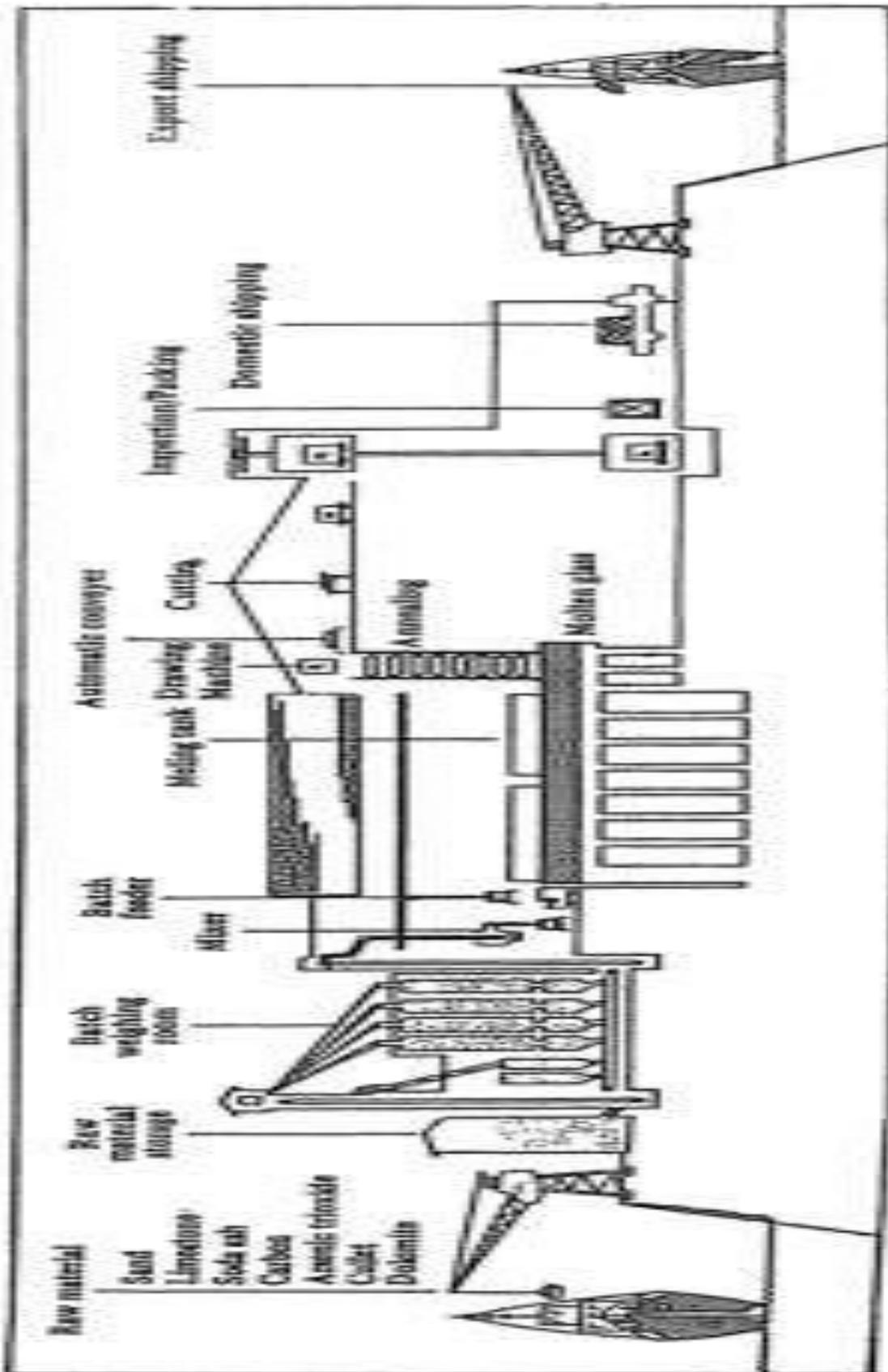
Clear sheet and heat absorbing glass

The ordinary sheet glass is produced by the vertical drawing method . Its manufacturing process consists of appropriately weighing respective specified raw materials and feeding uniformly the mixed batch into the furnace by appropriate means.

The batch is melted by heating system, and the molten glass is homogenized as it slowly flows through the refining vessel, and then its

viscosity gradually drops, and the molten glass, with pertinent viscosity suited for drawing, reaching a tank .

This molten glass is drawn by a drawing machine installed at the end of the tank. From one to four drawing machines are installed depending upon production scale.



GLYCEROL INDUSTRIES

INTRODUCTION

Glycerol is the common name for 1,2,3-propantriol ($C_3H_8O_3$), having a molecular weight of 92.1 gm/mole. It was discovered in 1779, during saponification of olive oil with lead oxide by Scheele. In 1811, Chevreul give the name 'glycerol', which was derived from the Greek word "glycos" means sweet. Pelouze announced the empirical formula as $C_3H_8O_3$. In 1883, Berthelot and Lucea was established the structural formula as $C_3H_5(OH)_3$.

Glycerol is found in all fats and oils, in the form of a fatty acid ester, so it means that it is distributed widely in Nature. Tallow oil, coconut oil, palm oil and soya oil contain 17%, 11%, 10% and 10% glycerol, respectively, making this substance part of our daily dietary intake. It founds as a lecithin in egg yolk, brain tissue, blood cells, bile and neural tissue. During alcoholic fermentation, small quantity of glycerol is produced.

Friedel synthesize glycerol from acetone, via isopropanol, propene, 1,2-dichloropropane a 1,2,3-trichloropropane. Glycerol is obtained as a by-product during fat saponification. Back in the 1940s, when synthetic detergents dominated the market, particularly in the USA, there was no longer enough fatty acid-based glycerol to meet demand, so synthesizing processes were developed. Currently, petrochemical-based glycerol production has peaked in many countries.

The great Swedish scientist Alfred Nobel discovered the value of nitroglycerine as an explosive. Glycerol can protect cells and tissues against frost burn.

Since last 150 years microbial production of glycerol was known. Later it was subsequently declined as the low glycerol yields and the difficulty in extraction and purification of glycerol from broth.

As the cost of propylene was increased especially in developing countries, glycerol became an attractive feedstock for production of various chemicals.

MANUFACTURE

1. Byproduct from soap manufacture

Raw material

Basis – 1000kg Glycerine (plus 2200kg salt)

Spent lye (5% glycerine) 22000kg

Sodium hydroxide 90kg

Ferric chloride 50kg

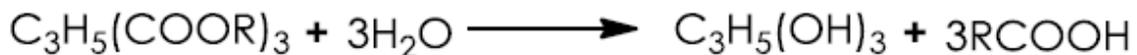
Aluminium sulfate 10kg

Activated carbon 3-5kg

Steam 3600 kg

Electricity 10Kw hr

Reaction



75% Yield (hydrolysis or saponification and recovery)

90% recovery (from spent soap lye)

Manufacture Process

The manufacture of free fatty acids and soap by hydrolysis or saponification of fats and oils yields glycerine as by-product.

In the hydrolysis process, splitting of the mixed glycerides of various fatty acids (the main constituents of fats and oil) occurs to give free fatty acids and glycerine.

This may be accomplished by several process.

- Twitchell Process (the hydrolysis by water at ordinary pressures with the aid of a catalyst)
- Autoclave process (the high-temperature-high-pressure hydrolysis with or without a catalyst)
- Ittner process (the continuously counter current hydrolysis at high temperature and pressures with or without the aid of a catalyst)

The saponification method generally operated as batch by batch or continuously, which utilized sodium hydroxide as the alkali to give soap and glycerine. In the older, more common batch processes, the saponified product was separated into a soap and mixture called spent soap lyes by graining with sodium chloride. The continuous process was operated at high temperatures and pressures to give a reaction mixture, which may be separated by mechanical means into powdered soap and vapours of aqueous glycerine.

The hydrolysis and continuous saponification process yields aqueous salt free solutions containing 15% glycerol. These solutions require very little chemical treatment (neutralization with lime or barium hydrate) and are concentrated by evaporation to give crude glycerine known as “88% saponification crude”. In the batch spent soap lyes were contained 3 – 8% glycerine 5 – 15% sodium chloride water and small quantities of alkali, soap fatty acids and other organic impurities. After chemical treatment the spent lyes were concentrated to yield the crude glycerine is known as “80% soap lye crude” since the recovery of glycerine from spent soap lye is a major source of supply and entitled a more involved procedure. Spent lye, which has been allowed to cool and settle to remove much of the impurities, was pumped in to an open steel tank fitted with an agitator. Ferric chloride solutions was added to form insoluble precipitates with the soap and carbonated alkali impurities. Aluminium sulphate was used for low grade lye to obtain a more complete removal of impurities. Hydrochloric acid was added to cause precipitation of the metallic soaps the slightly acid lyes were filtered and run into a second tank where enough aqueous.

Sodium hydroxide was added to bring them over to the alkaline side after filtration the lye contains 4 – 10% glycerine and 10 – 18% salt, which was concentrated in a double effect evaporator provided with salt catchers. Most of the salt crystallized out during evaporation and was periodically dropped from the evaporator cone into the salt chambers. The salt was removed, centrifuged or filtered on a nutsch filter, washed and returned to the soap plant for reuse. The evaporation was stopped when the glycerine content of liquor was reached to 80%. The crude product, 80% soap lye, contains 43% salt, 0.1% soap and smaller amount of organic impurities.

The crude soap-lye glycerine or crude saponification glycerine (from the hydrolysis plants) was refined by steam distillation under vacuum. The crude material was made strongly alkaline to hold back fatty acid impurities and then charged into a

direct-steam still. The vapours were condensed by passage through a series of air condensers and finally through water-cooled condenser. Most of the glycerine was removed by the air-cooled condensers as 85% refined glycerine; the water containing about 1 – 2% glycerine was collected in the water-cooled condenser, which is known as sweet water.

In many modern plants, various sweet waters, and sometimes crude glycerine stocks, were purified by ion-exchange treatment. This process not only removes dissolved salts but also odour and colour bodies.

glycerine solution was then concentrated by conventional vacuum distillation. The 85% refined glycerine was concentrated to give the 99% dynamite grade. By decolorizing with activated carbon, a pale-yellow high gravity or industrial grade may be obtained. The water-white product contains 95 – 98% glycerine; the rest is water. The recovery yield of C.P. glycerine from spent soap lye is approximately 90%.

2. From propylene via allyl chloride

Raw material

Basis-1000kg glycerine (99%)

Propylene 565kg

Sodium hydroxide 405kg

Chlorine 1800kg

Hydrated lime 405kg

Manufacture process

The allyl chloride was produced by high temperature continuous chlorination of propylene, which was converted to dichlorohydrins by reaction with hypochlorous acid. Reaction of the dichlorohydrins with milk of lime yield epichlorohydrin which was converted to glycerine by hydrolysis with aqueous sodium hydroxide.

Dry propylene gas was passed through a preheater maintained at about 400°C and was mixed in ratio of 4:1 mole of chlorine:propylene. The chlorine was previously vapourized by passing the liquid through hot-water heaters. The vapourized chlorine reaches the mixing jet at 60psi and 200°C. The mixed gases were passed from the jet into a steel tube reactor which was insulated. Due to the exothermic reaction the reaction temperature was increased from 400 – 500°C. The residence time of the gases in the reaction zone is in the range of 2 – 3sec. The reactor was maintained at a pressure of about 15psig. Over 99% chlorine in the reactor was utilized.

For the cleanout of carbon two reactors are run alternately, which is done once in every 2 weeks. Based on the moles of chlorine fed to the reactor, approximately 80%, allyl chloride, plus varying amounts of chloropropenes, mixed dichlorides, trichlorides, and heavier residues were obtained. Among these by-products, the cis- and trans-1,3-dichloropropenes and 1,2-dichloropropane were produced in largest quantities. One mole of hydrogen chloride was formed with each mole of allyl chloride.

The reaction products were recovered and an excess propylene and hydrogen chloride were separated from the organic chlorides continuously by passing through a cooler into a fractionating column. Liquid propylene (from storage) was used as reflux, and the top of the fractionator were passed and cooled to about 400C by self-refrigeration of propylene in a flash drum. The heads from the fractionator were passed into an absorber, where hydrogen chloride was recovered as hydrochloric acid of commercial concentration (32% by weight HCl). Liquid propylene was injected into the absorber to remove the heat of absorption, and the propylene leaving the top was scrubbed with aqueous sodium hydroxide. The propylene then compressed and returned to storage for reuse.

The crude allyl chloride from the bottom of the fractionating column was distilled in two columns. Light ends (mostly 2-chloropropene) and traces of propylene were taken as vapours from the first column, and refined allyl chloride was taken overhead from the second. The bottoms, containing mostly dichloropropens, was sent to storage.

Allyl chloride was fed to a stirred tank where it was reacted with hypochlorous acid to form a mixture of dichlorohydrins. The reaction takes place in the aqueous phase so the concentration of allyl chloride in the tank was held to a minimum to avoid side reaction in the non-aqueous phase. Reaction temperature was held 26 – 370C.

By using water as azeotrope epichlorohydrin was removed by steam distillation of the product. It was then purified (to 98% purity) by distillation.

Glycerine was produced from epichlorohydrin by hydrolysis with 10% caustic soda solution in a stirred reactor. Complete conversion was achieved in 30min at 150°C temperature. The product, a dilute glycerine solution containing sodium chloride, was purified and concentrated by evaporation and distillation in the conventional manner.

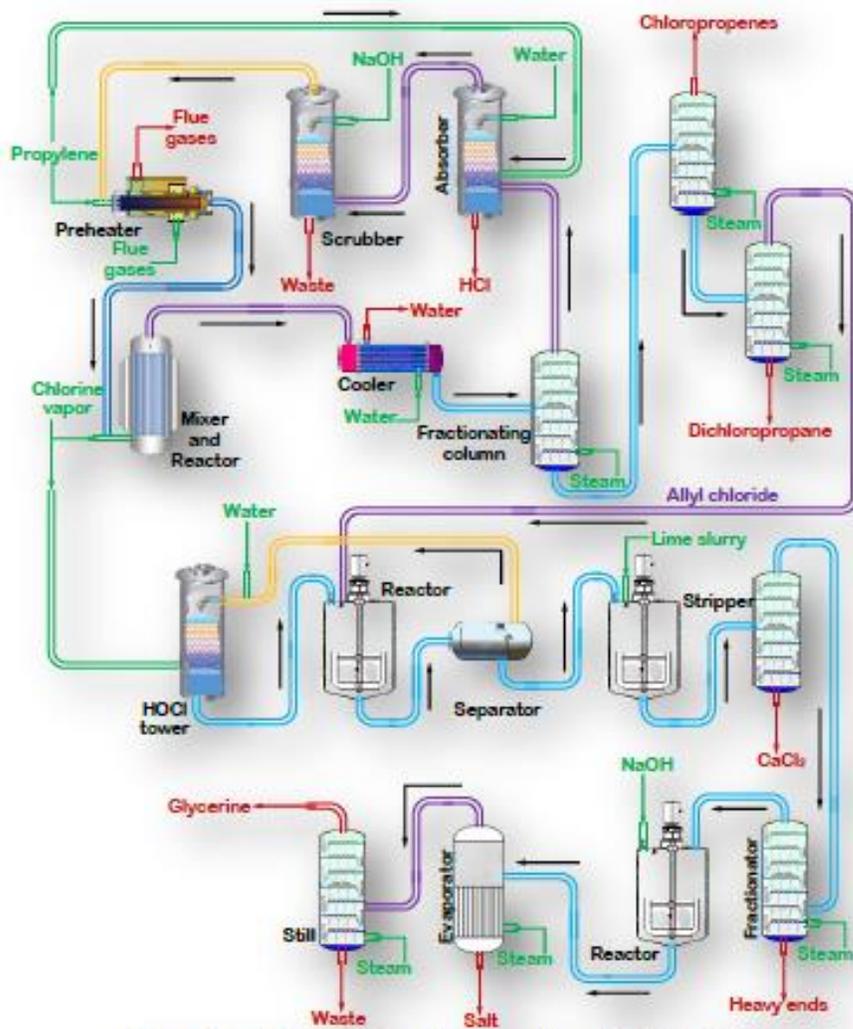


Figure: Manufacture of Glycerol from propylene via allyl chloride

INDUSTRIAL ALCOHOL

INTRODUCTION

Industrial alcohol is ethanol which is also called as ethyl alcohol, pure alcohol, grain alcohol, or drinking alcohol. Ethanol is a volatile, flammable, colourless liquid. The intoxicating effects of ethanol consumption have been known since ancient times. It is also used in thermometers, as a solvent, and as a fuel. In common usage, it is often referred to simply as alcohol or spirits.

Ethanol is synthesized by the fermentation of sugar which is one of the oldest biotechnologies employed by humans. Although distillation was well known by the early Greeks and Arabs, School of Salerno alchemist's first synthesized alcohol from distilled wine in the 12th century. In 1796, Raymond Lull and Johann Tobias Lowitz mentioned the distillation of industrial alcohol to absolute alcohol with an excess of anhydrous alkali and then distilling the mixture over low heat. Antoine Lavoisier described ethanol as a compound of carbon, hydrogen, and oxygen. The chemical formula was determined by Nicolas-Théodore de Saussure in 1807, which was later published by Archibald Scott Couper.

MANUFACTURE

Industrial alcohol was an outgrowth of alcoholic beverages. Now a days it is economically useful as a solvent and for synthesis of other chemicals.

1. Bymalt fermentation

Raw material

Corn

Water

Manufacture process

Manufacture process

Manufacturing Sequence of industrial alcohol by fermentation is as follows

- Transplantation of corn or molasses to the plant
- Storage of corn or molasses
- Grinding of corn
- Hydrolysis by beating of cornmeal with acid to make mash
- Growth of culture
- Fermentation of diluted inverted molasses or of corn mash
- Distillation of alcohol from beer
- Rectification and purification of alcohol
- Recovery of by-product, e.g. CO₂, feed, potash salts

The various operations involved in changing corn to alcohol were listed as above. The corn is degerminated, dehulled and milled, either in wet or dry. The milled corn mass was conveyed to the cooker. Cooking was gelatinized the ground grain so that the barley malt amylases can be converted the starch to fermentable sugars. The cookers may be batch or continuous and are operated under pressure.

In the continuous process the grain was precooked for 1 – 5min with water and stillage. The dealcoholized, fermented beer was discharged from the bottom of the beer still. The mash was continuously fed to a steam heater.

Time in the cooker was about 1.5min and pressure was maintained at 60 – 100kPa gages. The temperature of the mash was dropped to about 60°C in the flash chamber. The water and malted barley mixed with gelatinized grain mash. The mix was pumped through pipeline for 2min at 60°C and then it was sent to fermenters through pipe coolers. The starch was hydrolyzed to about 70% maltose and 30% dextrin in

the short time in the converter. To lower the pH, providing nutrition to yeast and provide buffering action stillage (20 – 25% of the final mash volume) from the beer still was. The initial pH was adjusted to 4.8 – 5.0 with sulfuric acid and/or stillage. As the reaction indicated, fermentation is exothermic, so cooling may be necessary to ensure that maximum temperature does not exceed 320C. The time of the fermentation may vary from 40 – 72hr.

The liquors in the fermenter, after the action was finished are called beer. The alcohol was separated by distillation. The beer containing 5.5 – 11% alcohol by volume was pumped to the upper section of the beer still. As the beer passes down the column, it loses its lighter boiling constituents. The liquid discharged from the bottom of the still through heat exchanger was known as Stillage. The overhead containing alcohol, water, and aldehydes passes through heat exchanger to the partial condenser, or dephlegmator, which condensed 50% alcohol, containing volatiles or aldehydes. The condensate was conducted into the aldehyde column, from which the low boiling impurities were separated as an overhead. The effluent liquor from bottom of the aldehyde column flows into the rectifying column. In this third column the alcohol was brought to the strength and finally purified to 95 – 95.6%.

2. By esterification and hydrolysis

Raw material

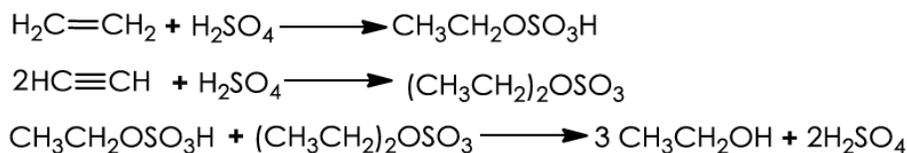
Basis: 1000kg of Industrial alcohol by esterification and hydrolysis

Ethylene 610kg

Water 390kg

Reaction

Reaction



Ethylene was passed in to the bottom of an absorption tower under 150 – 200psi pressure. Sulfuric acid (90 – 95%) was charged from the top of the tower. The temperature was maintained by controlling the rate of feed of ethylene and sulfuric acid. Catalyst like oxide of iron or copper was added for better absorption. Due to ethylene absorption in sulfuric acid, ethyl hydrogen sulfate and diethyl sulfate were formed. The unabsorbed gas escaped from top of the tower and can be used for fuel. The mixtures of ester were discharged from the bottom of the tower and diluted with water by 2times and charged into hydrolyzer. In hydrolyzer, the mixture was heated at 700C for 4hrs. During this time ester were converted into alcohol along with diethyl ether (5 – 10%). The mixture of crude ethanol, dilute sulfuric acid and diethyl ether passed through stripping column where dilute sulfuric acid was withdrawn from bottom of the column and concentrated in evaporator and was reused.

While the remaining mixture passes into scrubber where sodium hydroxide solution was sprayed which neutralized the traces of acid and withdrawn from bottom. The mixture of ethanol, water and ether vapours were first condensed then sent to the ether column where, from bottom steam was passed. Ethyl ether was escaped from the top while alcohol obtained at bottom of the ether column, is purified in fractionating column. In fractionating column 95% pure alcohol was obtained from the top which was then condensed. 95% ethanol is also known as rectified spirit and ordinary rectified spirit is known as industrial alcohol.

3. By catalytic hydration

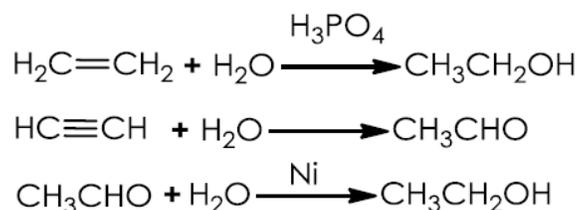
Raw material

Basis: 1000kg of Industrial alcohol by catalytic hydration

Ethylene 580kg

Water 390kg

Reaction



This is the latest method to obtain ethanol. Compressed 95% ethylene was first mixed with recycle ethylene and mixed with water. The ethylene water mixture was charged to a heat exchanger where it was converted into vapours. The vapours were again heated at 300°C in a heater. Hot vapours were transferred into a reactor where they passed over the inert diatomaceous earth soaked with phosphoric acid. Ethylene was hydrated to form ethanol. The mixture was then passed to a high pressure separator so that unreacted ethylene gas was separated out from the alcohol mixture. Unreacted ethylene was scrubbed to remove traces of alcohol and then recycled to the process. As acetylene is present in trace amounts in ethylene, acetaldehyde is also formed along with ethanol. Ethanol, water, and acetaldehyde were passed through a stripping column where water was removed from the bottom and the remaining mixture escapes from the top of the column, which was then hydrogenated with hydrogen gas in the presence of a nickel catalyst.

Acetaldehyde was converted into ethanol due to catalytic hydrogenation. Excess hydrogen was separated from the separator and reused while the liquid from the bottom was purified by fractional distillation where 95% alcohol, known as industrial alcohol, is obtained.

Engineering aspects

Major engineering problems

Malt fermentation process

- Maintenance of sterile and specific yeast culture conditions should be carried out
- Collection and storage of molasses
- Continuous molasses dilution and continuous distillation are introduced to save the equipments, space and operating costs
- During waste disposal if uneconomic to concentrate for cattle feed, trickling filters, activated sludge or anaerobic digestion must be used to lower biological oxygen demand before discharging to water run-off
- For fuel economy in the series of distillations preheat exchangers are used

Improvement in fermentation alcohol yields

Generally in Indian plants 80 – 82% yield is obtained which is lower than U.S. plant. Control of yeast culture and conditions are important. Alcohol should be recovered from CO₂ off gas via activated-carbon adsorption to increase the yield of alcohol.

PROPERTIES

- Molecular formula : C₂H₆O
- Molecular weight : 46.07gm/mole
- Appearance : Colourless liquid
- Odour : Mild and pleasant odour
- Boiling point : 78.00C
- Melting point : -1140C
- Flash point : 13-140C

- Autoignition temperature : 3630C
- Density : 0.789gm/cm³ at 200C
- Vapour pressure : 5.95kPa at 200C
- Refractive index : 1.361
- Solubility : Miscible with water.

USES

- The largest use of ethanol is as motor fuel and fuel additive and currently it is used in lightweight rocket-powered racing aircraft
- It is main psychoactive constituent in alcoholic beverages with depressant effects on the central nervous system
- Alcohol dissolves hydrophobic flavour compounds so alcoholic beverages are used in cooking for their flavours
- As base chemical for organic compounds like diethyl ether, ethyl esters, ethyl halides, acetic acid and ethyl amine
- As an antiseptic in wipes and antibacterial hand sanitizer gels at concentration of 62% v/v
- To treat poisoning by other toxic alcohol particularly ethylene glycol and methanol
- As solvent in paints, tinctures, markers and personal care products such as deodorants and perfumes
- In cooking such as in vodka sauce as a solvent or solute
- As lamp fuel, but a tax levied on industrial alcohol during the Civil War made this use uneconomical. It remains a common fuel for spirit lamps.

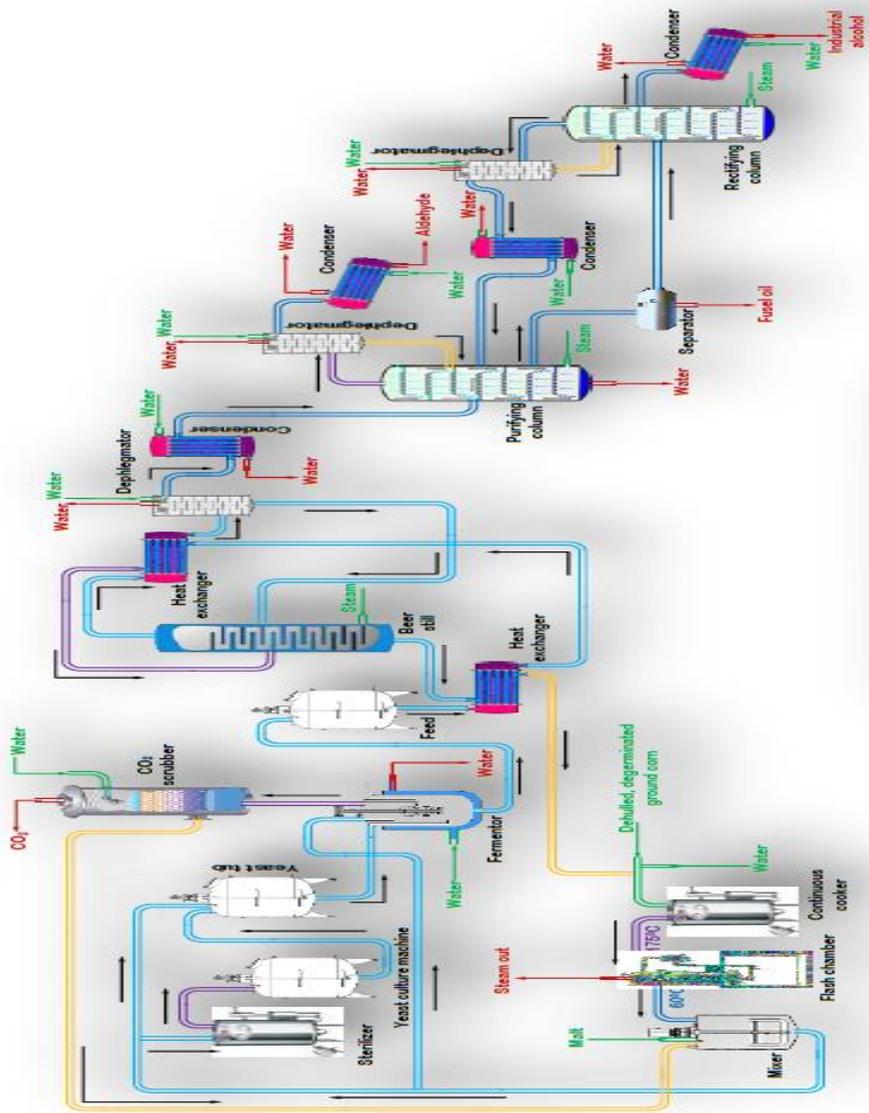


Figure: Manufacture of industrial alcohol by malt fermentation

SILICON CARBIDE

INTRODUCTION

Silicon carbide known as carborundum, it is a compound of silicon and carbon with chemical formula SiC. It occurs in nature as the rare mineral moissanite. Silicon carbide powder has been mass-produced since 1893.

Silicon carbide is the most important abrasive and was first discovered by Acheson in 1891 while he was attempting to harden clay in a homemade electric furnace. When carbon was dissolved in molten clay, it was assumed to be mixture of carbon and fused alumina called corundum and hence the name carborundum comes.

Silicon carbide powder has been mass-produced since 1893 for use as an abrasive. Grains of silicon carbide can be bonded together by sintering to form very hard ceramics

The first LED action was demonstrated in 1907 using SiC and also first commercial LEDs were based on SiC, yellow LEDs made from 3C-SiC were manufactured in the Soviet Union in the 1970s and blue ones from 6H-SiC in the 1980s.

Large single crystals of silicon carbide can be grown by the Lely method; they can be cut into gems known as synthetic moissanite. Silicon carbide with high surface area can be produced from SiO₂ contained in plant material.

Manufacture Process

Silicon carbide (SiC) is now manufactured from silica and carbon. The sources of carbon are coke, pitch, petroleum cokes and anthracite. The sand contains pure silica (98 – 99.5%).

1. The Acheson Process

Special type of open top indirect heating resistance furnace is used for manufacture of SiC. The furnace was consisting of a movable side wall with opening for gases, electrode, heating core and permanent bed of cast iron pieces lined with fire brick on which the charge was placed. The charge was built up in the furnace around a heating core of granular carbon. The 30 – 50ft long furnace was provided with about 60 carbon electrodes which were 1metre long and 8cm. in diameter and the central core of iron connects these electrodes. The ends of the furnace were permanent and the sides were built up every time with the charge. The outside unreacted charge acts as an insulator. There so, excessive heat loss cannot occurred.

The mixture of 53.5% SiO₂, 40% coke, 5% saw dust and 1.5% salt was charged to furnace until the furnace is fully charged. Saw dusts were added because it increases the porosity of the charge to permit the circulation of vapours. A typical initial current was passed between the two electrodes which were initially 6000amp at 250volts, but its resistance gradually decreased as the reaction proceeds and the final current becomes 20000amp at 75volts. After about 2hr, the current increased rapidly from 6000 to 20000amps and remains steady during the whole run of 36hr. The temperatures at the core are 22000C and remain steady for the whole 36hr until the reaction was completed. During the reaction CO was generated which was burned at the top of the furnace and escape through a movable side walls.

The product was then cooled for 24hr. The side walls were pulled down after as the process was completed. Crystals of silicon were removed from the furnace. The yield is about 6000 – 8000kg per furnace.

The black crystals were broken and then treated successively with sulfuric acid and sodium hydroxide solution. It was dried in a kiln and graded

through a screening or sieving system into, the powders of various degrees of fitness. The graphite formed in this manner is called artificial graphite. The outer unreacted part of the charge was combined with the next charge for the furnace and next to the core some graphite formed as a result of decomposition of SiC was obtained. After complete run, which taken about 36+24=60hrs, the graphite can be separated as a by-product from silicon carbide and converted to desired shapes.

Effect of temperature

It should be noted that the temperature of the core should not exceed 2200 °C otherwise silicon carbide was decomposed into graphite with the volatilization of silicon.

2. The ESK process

A major disadvantage of the Acheson furnace is loss of by-product CO and even SO₂ and dust contains in the waste gases leads to pollution. These disadvantages of Acheson process leads to the development of ESK process.

The ESK furnace consists of floor electrode, gas-permeable furnace bed, gas collector, plastic sheet and heating core. Heating core used for this ESK furnace was horizontal as same in case of Acheson furnace. The mixture of coke and sand was charged by wheel loaders into reaction zone, until the zone was full of raw material or charge reached the top of the graphite columns. Graphite was placed on each electrode of furnace. ESK furnace is considerably larger than Acheson furnace.

As the reaction mixture was reached to top of the column level, horizontal heating core which is linear or U shaped, put in the position and connected to a graphite column. Then heating core was covered with remaining

reaction mixture from wheel loaders, so it forms a mound shape. Further this mound has to be covered with plastic sheet to trap the evolved gases. Furnace has no walls while electrodes are located in floor.

The initial current was passed, which was initially 6000 amp at 250 volts, after that was increased to 20000amp. The CO evolved as by-product which was trapped through plastic sheet and collected in gas collection tube continuously. After completion of reaction, switch off the power and then plastic sheet was pulled off. Unconverted or remaining reaction mixture was removed first and lumps of silicon carbide were taken out of the furnace and broken down with hydraulic equipment. Finally, the crystalline outer zone was further size reduction was carried out in jaw crusher and recycled to the process. The coarsely crystalline from the inner zone of the SiC roll were sorted. The top-grade material formed the largest fraction of silicon carbide yield.

Engineering aspects

Steps for improvement in yield

- Silica or sand should be of 98% pure
- The carbon used may be petroleum coke, metallurgical coke, anthracite etc. having low ash and sulfur contents
- Fe_2O_3 and Al_2O_3 in silica should be as low as possible as they catalyzed the decomposition of SiC. The carbide undergoes decomposition at 2830°C
- The temperature of formation of silicon carbide is about $1840^\circ\text{C} \pm 30^\circ\text{C}$
- 100 parts by weight of finest grade sand, 60parts by weight of coke and 19parts by weight of saw dust is the charge composition for a good yield of SiC
- Saw dust increases the porosity of the charge or escape of CO and other volatile matter during SiC formation

Purity

The impurities from the reaction zone were removed by introducing chlorine gas. Depending on the amount of impurities colour of product crystals varies from pale yellow or green to black. Addition of boron, titanium or zircon in small amount to the furnace charge reduces the product sensitivity to oxidation at 900 – 1100 °C. As described earlier in Acheson process, the reduction of silica was carried out at temperature in excess of 2100 °C resulting in SiC grains.

PROPERTIES

- Molecular formula : SiC
- Molecular weight : 40.10gm/mole
- Appearance : Colourless crystals
- Odour : Odourless
- Boiling point : 2815 °C dissociates
- Melting point : 2730 °C (decomposes)
- Density : 3.21gm/cm³ (all polytypes)
- Refractive index : 2.55 (infrared, all polytypes)

USES

- Silicon carbide is a popular abrasive in modern lapidary due to the durability and low cost of the material
- In composite armour
- As a support and shelving material in high temperature kilns such as for firing ceramics, glass fusing or casting
- In automobile industry
- In a sintered form for diesel particulate filters

- Used in LED
- Low thermal expansion coefficient, rigidity, high hardness and thermal conductivity make silicon carbide a desirable mirror material for astronomical telescopes
- Silicon carbide fibres are used to measure gas temperatures in an optical technique called thin filament pyrometry
- Important material in TRISO-coated fuel particles, which is found in high temperature gas cooled reactors and layer of silicon carbide gives structural support and is the main diffusion barrier to the release of fission products
- Used to produce epitaxial graphene by graphitization at high temperatures
- In steel manufacturing
- Used in applications requiring high endurance, such as car brakes, car clutches and ceramic plates in bulletproof vests
- Used in high-temperature and high-voltage semiconductor electronics equipments

SODIUM SULFATE

INTRODUCTION

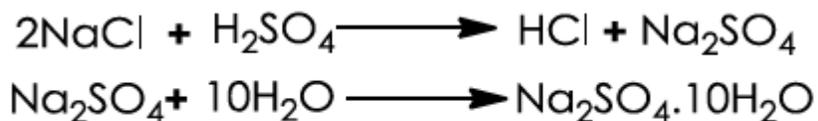
Sodium sulfate (Na_2SO_4) is the sodium salt of sulfuric acid. Anhydrous sulfate is a white crystalline solid also known as the mineral thenardite, while the decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ has been known as Glauber's salt or mirabilis. $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ is transformed to mirabilite when it is cooled. Mirabilite is the natural mineral form of the decahydrate. About two-thirds of the world's production of sodium sulfate is obtained from mirabilite. It is also produced from by-products of chemical processes such as hydrochloric acid production.

In 1625, Johann Rudolf Glauber discovered the sodium sulfate from Austrian spring water, therefore the hydrate form is known as Glauber's salt. Due to its medicinal properties he named it as sal mirabilis (miraculous salt). The crystals were used as a general purpose laxative, until 1900s.

By reaction with potassium carbonate or potash, Glauber's salt was used as a raw material for the industrial production of soda ash in the 18th century. In the nineteenth century the demand of soda ash was increased, so the large scale Leblanc process which produced synthetic sodium sulfate, became the principal method of soda ash production.

Manufacture Process

1. From salt and sulfuric acid



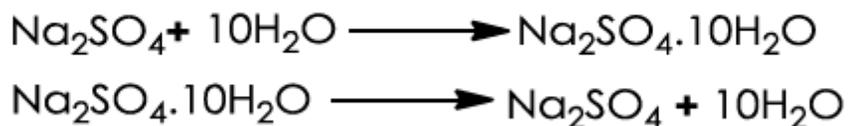
Salt and 600Be sulfuric acid in an excess were charged to the Mannheim furnace. It is equipped with a rake agitator, where the reacting mass was slowly heated to a temperature just below fusion temperature 843 °C. During process hydrogen chloride was evolved from the furnace. Salt cake contains crude sodium sulfate was then continuously discharged from the periphery of the furnace.

To produce Glauber's salt, the salt cake was charged in to the solution tank where it was dissolved in hot water to form the 32 °Be solution. Also soda ash or lime was then added to neutralize excess sulfuric acid present in the system and to precipitate iron and alumina. The precipitate was allowed to settle for a layer separation. The clear supernatant liquor was pumped to the crystallizer where crystallization take place and the muddy bottom layer was filtered and also charged into the crystallizer while the filtered mud cake was discarded.

After crystallization, to prevent desiccation, the Glauber's salt was stored in closed bins. The mother liquor from crystallizer was returned to the solution tank for reused. In order to obtain colourless crystals, the crystallizer liquor must be maintained on the acid side of neutral.

2. From Natural Brines

Reaction



Natural brines contains with very high to extremely high concentrations of dissolved constituents elements, ions and molecules. Brines are commonly considered to be those waters more saline, or more concentrated in dissolved

materials, than sea water. Salt content of brine can be five times greater than the salt content of average sea water.

Natural brines are a secondary source of sodium sulfate. About 60% of the natural sodium sulfate of the market is a by-product.

The natural brines contain 7 – 11% Na_2SO_4 , NaCl and MgSO_4 was charged into the salt depositor. For lowering the solubility of the sodium sulfate in the brine, sodium chloride was added from the top of salt depositor. The salt enriched brine from the bottom of the tank was chilled to -9 to -6 $^{\circ}\text{C}$ in a chiller using ammonia. The chilled mass was sent to the crystallizer where crystallization took place. Mixture from crystallizer was then filtered where Glauber's salt crystals were separated from their mother liquor. The mother liquor was returned to the process. The Glauber's salt crystals were charged to a submerged combustion evaporator where they were melted and most of the water was removed by evaporation. The wet sodium sulfate product was then passed from the rotary kiln dryer where it was dried.

Sources

The recovery of natural sodium sulfate was dependent upon the composition of the brine. Half of the sulfates was came directly from nature as a mineral or from salt deposits while half of the sulfate was produced as by-product in different industrial processes. e.g. in the production of rayon, chromates, phenol or boric acid, sulfate was produced as by-product. A small quantity of sodium sulfate was manufactured by synthesis from sodium chloride and sulfuric acid.

PROPERTIES

- Molecular formula : Na_2SO_4
- Molecular weight : 142.04 gm/mole (anhydrous), 322.20gm /mole (decahydrate)
- Appearance : White crystalline solid
- Odour : Odourless
- Boiling point : $1429\text{ }^\circ\text{C}$ (anhydrous)
- Flashpoint : $800\text{ }^\circ\text{C}$
- Melting point : $884\text{ }^\circ\text{C}$ (anhydrous), $32.4\text{ }^\circ\text{C}$ (decahydrate)
- Density : 2.664 gm/ml (anhydrous), 1.464 gm/ml (decahydrate)
- Refractive index : 1.468 (anhydrous), 1.394 (decahydrate)
- Solubility : Soluble in water, glycerol and hydrogen iodide and insoluble in ethanol

USES

- Sodium sulfate is used to dry an organic liquid
- As filler in powdered home laundry detergents
- As a fining agent which removes small air bubbles from molten glass
- Glauber's salt, the decahydrate was used as a laxative which removes the certain drugs such as acetaminophen from the body
- For de-frosting windows, in carpet fresheners, starch manufacture
- As additive to cattle feed
- In the manufacture of detergents and in the Kraft process of paper pulping

Sulfur and its Component Industries

Introduction

Sulfur is one of the few elements that is found in its elemental form in nature. Typical sulfur deposits occur in sedimentary limestone/ gypsum formations, in limestone/anhydrite formations associated with salt domes, or in volcanic rock. A yellow solid at normal temperatures, sulfur becomes progressively lighter in color at lower temperatures and is almost white at the temperature of liquid air. It melts at 114 to 119°C (depending on crystalline form) to a transparent light yellow liquid, becoming deep orange as the temperature is increased. The low viscosity of the liquid begins to rise sharply above 160°C, peaking at 93 Pa·s at 188°C, and then falling as the temperature continues to rise to its boiling point of 445°C. This and other anomalous properties of the liquid state are due to equilibria between the various molecular species of sulfur, which include small rings and chains.

Sulfur also is found as sulfide minerals in combination with iron or base metals (e.g., pyrites) and as sulfates in combination with alkali metals and alkaline earths (e.g., gypsum). Hydrogen sulfide with its "rotten egg" odor is the primary sour component of sour gas. Crude oil and coal contain a variety of complex sulfur-containing organic species. These sulfur compounds are removed from the liquid fuels by treatment with hydrogen to convert the sulfur to hydrogen sulfide, which is taken off in the gas stream. The recovery of sulfur values from sour fuels for environmental reasons is the largest source of sulfur today. World sulfur production in 1989 was 40 million tons. Over 99 percent of the sulfur that is marketed is sold as crude sulfur. The two primary grades are "bright," which is bright yellow and at least 99.5 percent (typically 99.9 + %) pure, and "dark," which can contain upwards of 0.25 percent carbonaceous material. Recovered sulfur generally is bright, whereas

mined sulfur often is dark owing to traces of crude oil, which is associated with salt-dome sulfur deposits. Volcanic sulfur deposits yield bright sulfur, but it often is contaminated with toxic metal oxides. Sulfuric acid production accounts for 93 percent of the elemental sulfur used in the United States. Small quantities of several specialty sulfurs are produced for a wide variety of other applications, including fumigation, bleaching, pharmaceuticals, pyro-technics, rubber making, and cutting oils.

Development of the Sulfur Industry

Early humans doubtless found elemental sulfur in volcanic craters, encrusting the edges of hot sulfur springs, and embedded in limestone formations. They discovered that it would burn and used it for medicinal purposes, as a bleach, as a fumigant, as a colorant, and as incense. Its use for these purposes is mentioned in ancient writings. The Romans produced incendiary weapons from sulfur. In the thirteenth century, the Chinese invented gunpowder using sulfur, nitrate, and charcoal. The earliest commercial sulfur came from limestone deposits, of which those in Sicily and the Italian mainland developed world markets in the eighteenth and nineteenth

production rate and efficiency. Italian mono-poly of the sulfur markets continued until the early 1900s when the Frasch process brought previously unrecoverable sulfur deposits on the North American Gulf Coast into production. Oil exploration efforts in Texas and Louisiana in the late 1800s uncovered sulfur deposits in limestone at depths of 200 to 300 meters. Mining was complicated by intervening layers of quicksand and the presence of hydrogen sulfide gas. Numerous conventional mining attempts at Sulphur, LA, proved disastrous. Finally, in December 1894, Hermann Frasch demonstrated the hot water process for mining underground sulfur deposits. With its favorable economics, the Frasch process

completely displaced the Italian sulfur industry. Ready availability of low-cost sulfur opened the way for commercial sulfuric acid production by burning sulfur. This process largely supplanted the long-standing iron pyrite combustion process for sulfuric acid production by eliminating its extensive gas-cleaning operations.

In 1883 C. F. Claus patented a process for producing sulfur from hydrogen sulfide through partial combustion over an iron oxide catalyst. A number of improvements on the Claus process were made over the next 50 years, but it enjoyed limited success as a method for producing sulfur. Its primary driving force was, and remains, the need for a means to remove the sour component of sour gas for processing reasons and for environmental compatibility. Since the 1950s the demand for larger quantities of cleaner natural gas to meet increasingly more stringent environmental standards has caused a proliferation of the family of Claus processes. The processing of sour gases has increased to the extent that the production of recovered sulfur now exceeds that of mined sulfur.

Sulfur has been produced from sulfide ores (pyrites) by thermal decomposition in the absence of air, by roasting/smelting under reducing conditions, or by reaction of the ore with SO_2 . Hydrometallurgical processes have produced sulfur from metal pyrites as a by-product. These processes do not contribute significant quantities of sulfur to the world markets.

Production of Sulfur

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is produced by increasingly more industrial processes, for instance, when calcium carbonate or lime is used to neutralize sulfuric acid containing effluents or when apatite ($\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2 \cdot \text{CaCO}_3$), the raw material used in phosphoric acid manufacture, is attacked by sulfuric acid. The precipitated toxic metals which are often contained in this gypsum (mercury, lead, arsenic, zinc,

cadmium, etc.) and the large amounts of gypsum produced (hundreds of millions of tons produced yearly throughout the world) imply that there is, so far, no convenient method for its disposal without causing damage to the environment. Apart from some local opportunities such as its inclusion in plasters or in cements, gypsum (as industrial by-product) is usually disposed of in controlled sites or discharged in the seas, threatening to pollute soils and waters.

The biotechnological process reported here takes advantage of the so called dissimilatory sulfate-reducing bacteria (SRB) which can produce sulfide from sulfate and oxidize an organic substrate into carbonate containing a majority of carbonate and impurities precipitated as sulfides, could be recycled repeatedly in neutralization in order to concentrate the toxic metals. Alternatively, the sulfide could be recycled in the manufacture of sulfuric acid, after chemical transformation into sulfur (derivatives of the Claus process using catalysts).

Production of Sulfur Dioxide

Sulfur dioxide has been produced commercially from the following raw materials: elemental sulfur; pyrites; sulfide ores of non-ferrous metals; waste sulfuric acid and sulfates; gypsum and anhydrite; hydrogen sulfide-containing waste gases; and flue gases from the combustion of sulfurous fossil fuels. It is most commonly produced by burning sulfur but can also be produced by burning pyrites in a special furnace or by purifying and compressing sulfur dioxide gas from smelting operations.

Sulfur dioxide has been produced by burning molten sulfur in a special burner with a controlled amount of air. The burner gas, free of dust

and cooled, is dissolved in water in a series of two towers. In a third tower, the solution is sprayed at the top and flows down while steam is injected at the base. The gas issuing from the third tower is then cooled to remove most moisture and passed up a fourth tower against a countercurrent of sulfuric acid. The dried gas is liquefied by compression.

Sulfur dioxide can also be recovered commercially by liquefying gas obtained during smelting of non-ferrous metals such as lead, copper, and nickel. Much of this smelter by-product is recovered and oxidized to sulfur trioxide for producing sulfuric acid. Sulfur dioxide recovery, however, usually occurs only for environmental reasons

Uses

Sulfur dioxide has numerous commercial uses which are based on its function as an acid, as a reducing or oxidizing agent, or as a catalyst. Sulfur dioxide is used in large quantities as a captive intermediate in the production of sulfuric acid and in the pulp and paper industry. Other common uses of sulfur dioxide include the following: fumigant, preservative, bleach, and steeping agent for grain in food processing; catalyst or extraction solvent in the petroleum industry; flotation depressant for sulfide ores in the mining industry; intermediate for bleach production; and reducing agent in several industrial processes.

