

GATEFLIX

**CHEMICAL
TECHNOLOGY**

**For
CHEMICAL ENGINEERING**

CHEMICAL TECHNOLOGY

SYLLABUS

Inorganic chemical industries (sulfuric acid, phosphoric acid, chlor-alkali industry), fertilizers (Ammonia, Urea, SSP and TSP); natural products industries (Pulp and Paper, Sugar, Oil, and Fats); petroleum refining and petrochemicals; polymerization industries (polyethylene, polypropylene, PVC and polyester synthetic fibers).

CONTENTS

| Topics | Page No |
|---|---------|
| 1. INORGANIC INDUSTRIES | |
| 1.1 Sulfuric Acid | 1 |
| 1.2 Chlor Alkali Industry | 2 |
| Gate Questions | 4 |
| 2. FERTILIZER | |
| 2.1 Ammonia Production | 9 |
| 2.2 Urea | 10 |
| 2.3 Single Super Phosphate & Triple Phosphate | 11 |
| 2.4 Ammonia Phosphate | 11 |
| 2.5 Nitric Acid | 11 |
| Gate Questions | 12 |
| 3. NATURAL INDUSTRY | |
| 3.1 Paper & Pulp Industry | 15 |
| 3.2 Oils & Fat Industry | 16 |
| 3.3 Soap Industry | 17 |
| 3.4 Glycerin | 18 |
| 3.5 Detergents | 18 |
| 3.6 Sugar Industry | 18 |
| Gate Questions | 20 |
| 4. POLYMER INDUSTRY | |
| 4.1 Polymers | 23 |
| 4.2 Fibers | 23 |
| 4.3 Polyamides | 23 |
| 4.4 Polyester | 23 |
| 4.5 Acrylic Fibers | 26 |
| 4.6 Cellulosic Fiber | 26 |
| 4.7 Thermoplastic Polymer | 26 |
| 4.8 Thermosetting | 26 |
| Gate Questions | 29 |
| 5. PETROLEUM REFINING | 34 |
| 5.1 Classification of Crude | 34 |

| | | |
|-----------|----------------------------------|----|
| 5.2 | Properties of Petroleum Products | 35 |
| 5.3 | Petroknock | 36 |
| 5.4 | Calorific Value | 37 |
| 5.5 | Cracking | 37 |
| 5.6 | Reforming | 38 |
| 5.7 | Sweeting Process | 39 |
| | Gate Questions | 42 |
| 6. | PETROCHEMICAL | |
| 6.1 | Introduction | 46 |
| 6.2 | Formation of HCHO in Two steps | 46 |
| | Gate Questions | 49 |

1.1 SULFURIC ACID

Manufacturing of sulfuric acid is done by two processes:

- I. Contact Process
- II. Lead Chamber Process

CONTACT PROCESS

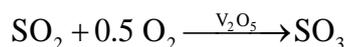
Firstly Sulfur and oxygen from moisture free air enters burner. Moisture is removed with H_2SO_4 or other dehydrating agents. Dry air is required to avoid corrossions. The sulphur which enters the burner is generally obtained by either **Frasch process** (sulphur obtained by mining process) or **Claus process** (sulphur obtained from hydrotreating). In the burner the sulphur and oxygen are burned and converted to sulphur dioxide.



The mixture containing 7-10 % SO_2 & 11-15 % O_2 is sent to multi stage catalytic converter. The active catalyst in multi stage catalytic converter is Vanadium pentaoxide (V_2O_5). Multi stage catalytic converter consists of 2 stages. First is high temperature stage followed by inter-stage cooling and enters low temperature stage.

1ststage-500-600 °C ; 80% conv.

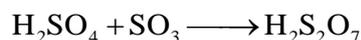
2ndstage-400-450 °C ; 97% conv.



SO_3 product is cooled down and absorbed by oleum in oleum tower followed by absorption to desire

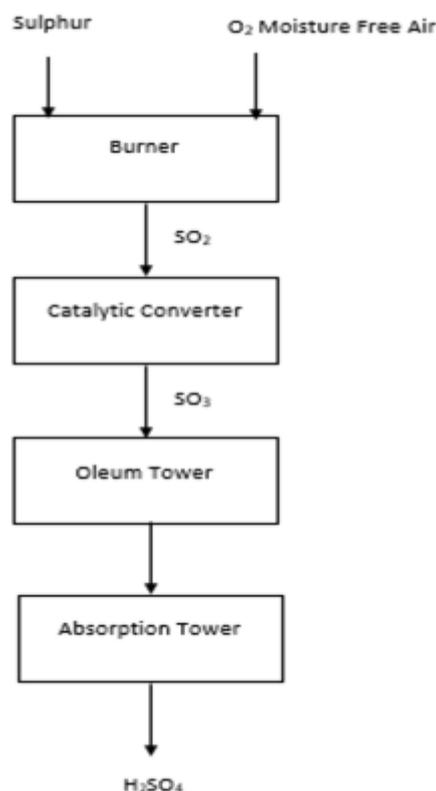
concentration is done with 97% H_2SO_4 in absorption column.

Oleum tower reaction:



Note : Oleum is mixture of H_2SO_4 & SO_3 . 20% Oleum means 20 kg SO_3 & 80 kg H_2SO_4 .

The overall process is exothermic & the moles of product is less than the moles of reactants so low temperature and high pressure favours the process.



Most commonly contact process is only used for sulfuric acid rather than Chamber process because conversion in Chamber process is less than 78% only.

In place of V_2O_5 ; Platinum (Pt) can also be used as catalyst but it is more expensive than V_2O_5 .

| Diaphragm | Mercury | Membrane |
|-------------------------------------|---------------------------------|--------------------------------------|
| Less purified brine is required | More purified brine is required | Most purified brine is required |
| 10-12% NaOH is produced | 70% NaOH is produced | % NaOH is between both of them |
| It uses asbestos | It uses mercury | It uses membrane |
| Produces Cl_2 that contains O_2 | Produces pure Cl_2 | Produces Cl_2 that contains O_2 |
| Energy consumption is less | Energy consumption is more | It consumes 77% of electrolytic cell |

1.2 Chlor alkali industry

Electrolytic process for NaOH

Brine solution flows through pipelines to a storage reservoir and then through a brine treatment system. Caustic soda, soda ash, and barium carbonate removes calcium, magnesium and iron salts which would clog up diaphragms. This purified saturated brine is heated and electrolyzed in a diaphragm cell.

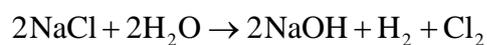
The cell operating at 45-55% decomposition efficiency, discharges a 10-12 % solution of caustic soda with about an equal concentration of NaCl.

Multiple effect evaporation concentrates the cell liquor to 50 % NaOH solution. The precipitated salt is separated, centrifuged, washed and then slurried with treated brine. Salt separator overflow is 50%

caustic soda product containing 2% NaCl and 0.1-0.5% NaClO on a dry basis. Commercial grade caustic can be obtained by evaporating the solution to produce saturated 73% NaOH liquor, fused to flake, granular or stick caustic. In the process we can use other cells as well instead of diaphragm cell. The difference between them are mentioned below.

Faraday law of electrolysis

One gram of equivalent weight of matter (NaOH) is deposited in electrode for 96500 coulombs of electricity passed through the electrode.



Decomposition efficiency

$$\eta_{De} = \frac{(\text{Gm. Eq. weight of NaOH produced})}{(\text{Gm. Eq. weight of NaCl Charged})} \times 100$$

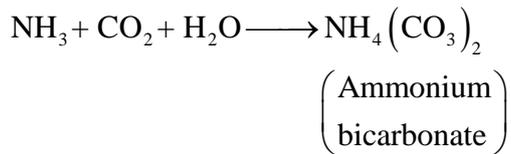
Current efficiency

$$\eta_c = \frac{\left(\begin{array}{l} \text{Theoretical amount of current required to} \\ \text{produce 1 gram equivalent of NaOH} \end{array} \right)}{\left(\begin{array}{l} \text{Actual amount of current required to} \\ \text{produce 1 gram equivalent of NaOH.} \end{array} \right)} \times 100$$

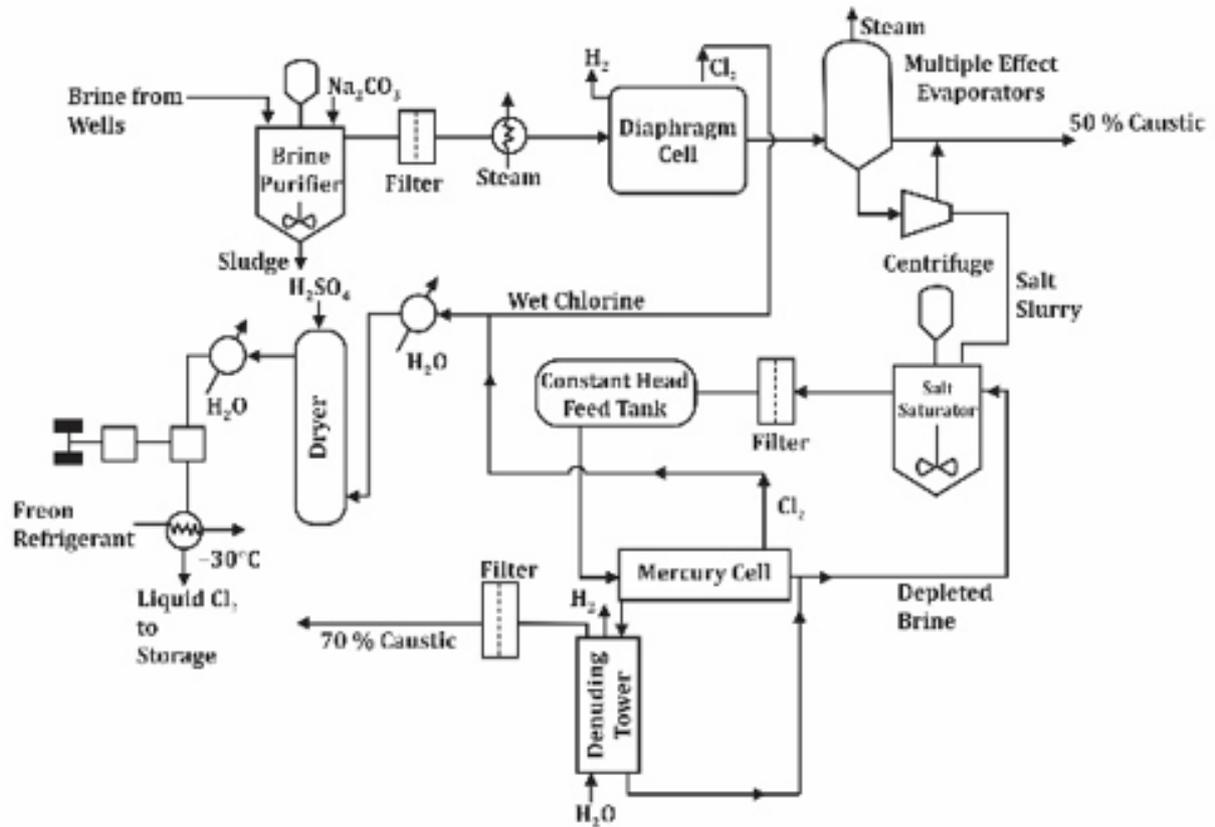
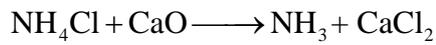
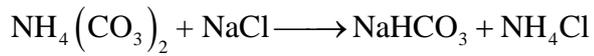
Soda ash (Na_2CO_3)

Soda ash is generally manufactured using **Solvay process** as compared to earlier days where its production took place by **Leblanc process**. Soda ash is sold on basis of Na_2O content which is generally 58%. Raw materials for Solvay process are limestone, brine, ammonia and coke/natural gas.

Reactions



CaCl₂ is the major pollutant in this process.



GATE QUESTIONS

Q.1 In the converter of the contact process for the manufacturing of H_2SO_4 , the equilibrium conversion of SO_2 (A) ... with increase in the temperature and... (B).... with increase in mole ratio of SO_2 to air.

[GATE-2001]

- | A | B |
|---------------|-----------|
| (a) increases | decreases |
| (b) decreases | increases |
| (c) increases | increases |
| (d) decreases | decreases |

Q.2 In the manufacturing of sulphuric acid from elemental sulphur, which of the following sequences of major operations is following?

[GATE-2002]

- (a) Furnace "Converter "Absorber
 (b) Furnace "Evaporator "Absorber
 (c) Furnace "Converter "Evaporator
 (d) Converter "Furnace "Absorber

Q.3 The catalytic converter for conversion of SO_2 to SO_3 by contact process should have a feed with SO_2 content between

[GATE-2003]

- | | |
|------------|------------|
| (a) 2-5% | (b) 7-10% |
| (c) 12-15% | (d) 20-25% |

Q.4 Match the items in Group I with the items in Group II.

| Group I | Group II |
|-----------------------------|----------------------------|
| P. Calcium ammonium nitrate | 1. Fertilizer industry |
| Q. $CaCl_2$ -NaCl liquor | 2. Paper and pulp industry |
| | 3. Soda ash industry |

[GATE-2003]

- | | |
|--------------|--------------|
| (a) P-1, Q-3 | (b) P-1, Q-2 |
| (c) P-3, Q-1 | (d) P-2, Q-3 |

Q.5 Match the processes in Group I with the products in Group II.

| | Group I | | Group II |
|---|--------------|---|------------------|
| P | DCDA process | 1 | Sodium hydroxide |
| Q | Mercury cell | 2 | Sulphuric acid |
| | | 3 | Sodium carbonate |
| | | 4 | Nitric acid |

[GATE-2004]

- | | |
|--------------|--------------|
| (a) P-1, Q-4 | (b) P-1, Q-3 |
| (c) P-2, Q-3 | (d) P-2, Q-1 |

Q.6 Match the process in Group I with the catalysts used in Group II.

| | Group I | | Group II |
|---|-----------------------------|---|--------------------|
| P | Sulphuric acid manufacture | 1 | Platinum |
| Q | Vegetable oil hydrogenation | 2 | Vanadium pentoxide |
| | | 3 | Iron |
| | | 4 | Raney Nickel |

[GATE-2004]

- | | |
|--------------|--------------|
| (a) P-3, Q-1 | (b) P-2, Q-1 |
| (c) P-2, Q-4 | (d) P-4, Q-2 |

Q.7 Match the products in Group I with the catalysts used for its production in Group II.

| | Group I | | Group II |
|---|--------------|---|------------------|
| P | Nitric acid | 1 | Silver oxide |
| Q | Formaldehyde | 2 | Raney nickel |
| | | 3 | Activated carbon |
| | | 4 | Pt-Rh |

[GATE-2005]

- | | |
|--------------|--------------|
| (a) P-1, Q-2 | (b) P-2, Q-3 |
| (c) P-3, Q-4 | (d) P-4, Q-1 |

Q.8 Match the products in Group I with the raw materials in Group II.

| | Group I | | Group II |
|---|--------------|---|----------------------------------|
| P | Caustic soda | 1 | Ammonia and sulphuric acid |
| Q | Soda ash | 2 | Sodium carbonate and slaked lime |
| | | 3 | Salt and limestone |
| | | 4 | Salt and sulphuric acid |

[GATE-2005]

- (a) P-2, Q-3 (b) P-1, Q-2
(c) P-3, Q-4 (d) P-4, Q-1

Q.9 Pair the following reactors in Group I with their products in Group II.

| | Group I | | Group II |
|---|--------------|---|-----------------|
| P | Arc furnace | 1 | Citric acid |
| Q | Fermenter | 2 | Calcium carbide |
| R | Hydrogenator | 3 | Saturated fats |
| | | 4 | Alum |

[GATE-2006]

- (a) P-4, Q-1, R-3 (b) P-2, Q-1, R-3
(c) P-4, Q-3, R-1 (d) P-2, Q-3, R-1

Q. 10 Which one of the following process sequences is used in the production of synthesis gas?

[GATE-2008]

- (a) Desulphurization "steam reforming"
Hot K_2CO_3 cycle
(b) Steam reforming "Desulphurization"
Hot K_2CO_3 cycle
(c) Hot K_2CO_3 cycle "Steam reforming"
Desulphurization
(d) Hot K_2CO_3 cycle "Desulphurization"
Steam reforming

Q.11 The active component of catalysts used in steam reforming of methane to produce synthesis gas is

[GATE-2009]

- (a) nickel (b) iron
(c) platinum (d) palladium

Q.12 Match the products in Group I with the name of the processes in Group II.

| | Group I | | Group II |
|---|------------------|---|-----------------|
| P | Sodium carbonate | 1 | Haber |
| Q | Ammonia | 2 | Solvay |
| R | Sulphuric acid | 3 | Fischer-Tropsch |
| | | 4 | Contact |

[GATE-2009]

- P Q R
(a) 2 1 4
(b) 4 1 2
(c) 3 4 2
(d) 2 1 3

Q.13 Match the products in Group I with the material in Group II.

| | Group I | | Group II |
|---|-------------------|---|---------------|
| P | Ethylene | 1 | Natural gas |
| Q | Methanol | 2 | Synthesis gas |
| R | Pthalic anhydride | 3 | Naphtha |
| | | 4 | Naphthalene |

[GATE-2009]

- P Q R
(a) 1 2 3
(b) 2 1 4
(c) 3 1 4
(d) 3 2 4

Q.14 In the manufacturing of caustic soda from brine, which one of the following statements is true?

[GATE-2010]

- (a) The membrane cell cannot produce concentrated NaOH solution, and cannot tolerate calcium and magnesium ions in the feed brine
(b) The membrane cell cannot produce concentrated NaOH solution, and can

tolerate calcium and magnesium ions in the feed brine

(c) The membrane cell can produce concentrated NaOH solution, and cannot tolerate calcium and magnesium ions in the feed brine

(d) The membrane cell can produce concentrated NaOH solution, and can tolerate calcium and magnesium ions in the feed brine

Q.15 Match the processes in Group I with the products in Group II.

| | Group I | | Group II |
|---|---------------|----|----------|
| P | Claus process | 1. | Syngas |
| Q | Linde process | 2. | Oxygen |
| R | Lurgi process | 3. | sulphur |

[GATE-2010]

- | | P | Q | R |
|-----|---|---|---|
| (a) | 1 | 2 | 3 |
| (b) | 2 | 1 | 3 |
| (c) | 3 | 1 | 2 |
| (d) | 3 | 2 | 1 |

Q.16 The correct sequence of process equipment used in the production of sulphuric acid from sulphur by contact process is

[GATE-2011]

(a) burner, catalytic converter, 98% sulphuric acid absorption tower, oleum absorption column

(b) Catalytic converter, oleum absorption column, 98% sulphuric acid absorption tower, burner

(c) Burner, catalytic converter, oleum absorption column, 98% sulphuric acid absorption tower

(d) Burner, oleum absorption column, catalytic converter, 98% sulphuric acid absorption tower

Q.17 In the manufacturing of sulphuric acid by contact process the catalytic

oxidation of SO₂ is carried out in multiple stages mainly to

[GATE-2013]

(a) Increase the reaction rate by providing inter-stage heating

(b) Increase the overall conversion by providing inter-stage heating

(c) Increase the overall conversion by providing inter-stage cooling

(d) Decrease the overall conversion by removing Sulphur trioxide between stages

Q.18 Decomposition efficiency of an electrolytic cell used for producing NaOH is defined as

[GATE-2014]

(a) (Grams of NaOH produced/ grams of NaCl decomposed) x 100

(b) (Grams of NaOH produced/ grams of NaCl charged) x 100

(c) (Gram equivalent of NaOH produced/ gram equivalent of NaCl charged) x 100

(d) (theoretical current to produce one gram equivalent/actual current to produce one gram equivalent) x 100

Q.19 India has no elemental Sulphur deposits that can be economically exploited. In India, which one of the following industries produces elemental Sulphur as a byproduct?

[GATE-2016]

(a) Coal carbonization plants

(b) Petroleum refineries

(c) Paper and pulp industries

(d) Iron and steel making plants

Q. 20 Two pulp and paper plants P & Q use the same quality bamboo as a raw

material. The chemicals used in their digester are as follows:

| Chemicals | Plant P | Plant Q |
|---------------------------------|---------|---------|
| NaOH | Yes | No |
| Na ₂ S | Yes | No |
| Na ₂ CO ₃ | Yes | Yes |
| NaHCO ₃ | No | Yes |
| Na ₂ SO ₃ | No | Yes |

Which of the following is correct?

[GATE-2016]

- (a) Plant P and plant Q both use sulfite process
- (b) Plant P and plant Q both use kraft process
- (c) Plant P uses sulfite process
- (d) Plant P uses kraft process

Q.21 The DCDA process is used for the manufacture of

[GATE-2017]

- (a) Urea
- (b) Sulphuric acid
- (c) Nitric acid
- (d) Ammonia

Q. 22 Match the following

| | |
|---|------------------------------|
| 1. Fluidized bed | P. Paper making |
| 2. Multistage Reactor with interstage cooling | Q. Sodium hydroxide |
| 3. Fourdrinier Machine | R. SO ₂ oxidation |
| 4. Diaphragm cell | S. Catalytic cracking |

[GATE-2017]

- (a) 1-S, 2-R, 3-P, 4-Q
- (b) 1-S, 2-R, 3-Q, 4-P
- (c) 1-R, 2-S, 3-P, 4-Q
- (d) 1-R, 2-S, 3-Q, 4-P

ANSWER KEY

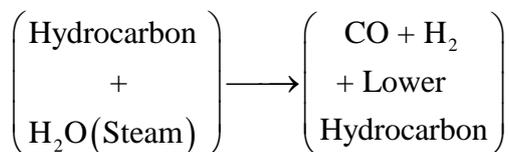
| | | | | | | | |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| b | a | b | a | d | c | d | a |
| 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| b | a | a | a | b | c | d | c |
| 17 | 18 | 19 | 20 | 21 | 22 | | |
| c | c | b | d | b | a | | |

2.1 Ammonia production

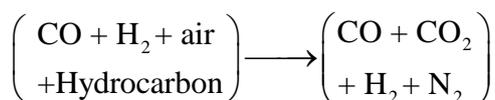
Firstly the natural gas containing sulphur in form of sulphide, disulphide, mercaptans etc. which are poisonous to catalyst enter desulphurisation unit to remove sulphur. It is two-step process. First hydrogenation of sulphur compounds in presence of catalyst Cobalt-molybdenum. Hydrogen reacts with organic sulphur and forms H_2S . H_2S is absorbed by Zinc Oxide in sulphur absorber where temperature is $350-390^\circ C$ and pressure is 40 bar. When heated to $350^\circ C$ everything becomes vapour and is passed through desulphurisation reactor. Here H_2S is separated at top sweetened hydrocarbon is obtained at bottom.

Reformer

Sweetened hydrocarbon mixed with steam and passes through tube having nickel as catalyst in it.



It then goes to secondary reformer in which reforming takes place in presence of air.

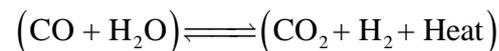


All these reformed gases are sent to main recovery boiler where large amount of heat is released and temperature reduces to $300^\circ C$.

Shift converter

It consists of 2 stage shift converter. High temperature shift converter followed by Low temperature shift converter.

In first converter Iron (Fe) is used as catalyst while in second converter Copper (Cu) is used as catalyst.

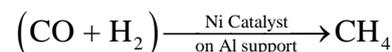


Stripper

The solution containing CO , CO_2 , H_2 , N_2 now enters stripping column to eliminate CO_2 . CO_2 is separated by benefit solution i.e. K_2CO_3 or ethanol amine solution.

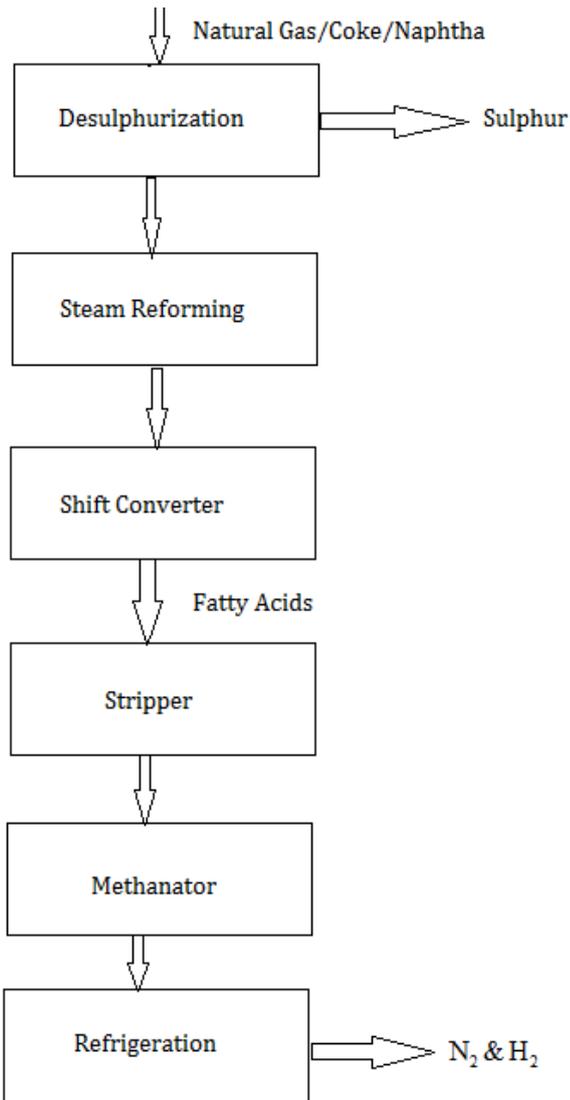
Methanation

Gas stream containing N_2 , H_2 , small amount of CO and unabsorbed CO_2 now enters methanation column. CO and CO_2 should be removed as they act as catalytic poison for ammonia synthesis. So their concentration should be reduced below 10 ppm. Hence CO and CO_2 are converted to CH_4 by hydrogenation over nickel catalyst.



Ammonia reactor

Here only 20% conversion into ammonia is achieved and remaining H_2 and N_2 are sent to refrigeration cycle where mixture is cooled down to $-35^\circ C$. It is a two-step process where pressure reduces and liquid NH_3 separates out and sent to urea plant and mixed with CO_2



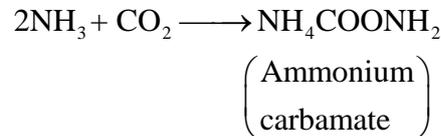
The reaction takes place in presence of Fe_2O_3 catalyst along with promoter like Silicon, Zirconium or Aluminium Oxide. It is used in manufacturing of nitro compound fertilizer such as ammonium nitrate, ammonium phosphate etc.

2.2 UREA

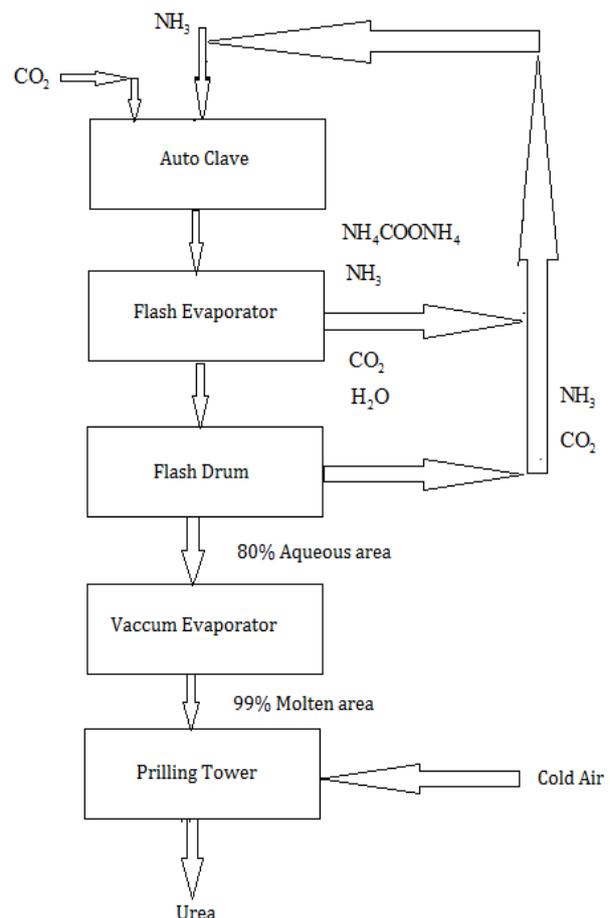
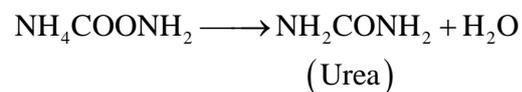
Urea is a nitrogen fertilizer which contains 40-42 % of nitrogen. It is also used to make urea formaldehyde resin. The main raw material required for urea production is CO_2 and NH_3 .

Process description

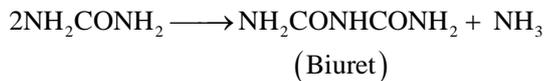
NH_3 and CO_2 are compressed separately under a pressure of 185 atm and 180°C temperature and enters the reactor.



From the reactor urea, ammonium carbamate, unreacted NH_3 , CO_2 and H_2O streams are heated and being pressurized and sent to Flash evaporator operating at 27 atm. The carbamate in urea are fed to Flash drum at 1 atm pressure followed by Vacuum Evaporator which produces 99% urea.

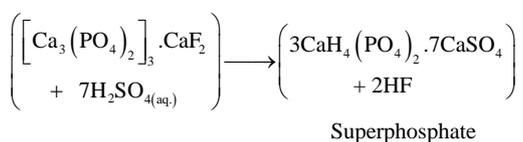


These molten urea is then sprayed to Prilling tower where the molten urea is sprayed from top and cooled air comes in contact with it in cross current flow. The temperature in the tower is maintained just above the melting point of urea. The residence time is kept very small i.e. 1-2 seconds to avoid biuret formation.

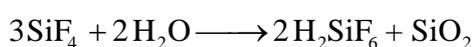


2.3 Single super phosphate & triple super phosphate

As seen in figure initially phosphate rocks are crushed in a Jaw crusher and ground to 100 mesh in a Hammer or Ring mill. A continuous feed of dilute sulphuric acid (65-70%) and powdered rock phosphate is monitored by automatic control into steel trough, lead-lined and brick-lined, covered with a hood to collect SiF_4 and HF fumes. The rotating mechanism is made of cast iron blades on a square shaft moves the product gradually forward at the rate of 0.2 to 0.5 meter per minute through the 12-15 meters reactor-conveyor unit. With proper grinding and acid control the reaction is effectively complete and can be sent directly to a granulator. The older method was to store for a nominal 24 hour period to ensure complete reaction.



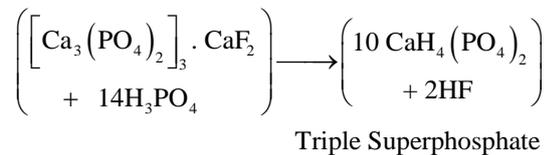
The SiF_4 and HF fumes along with CO_2 are scrubbed in water and the silica is removed by NaCl according to following reaction.



The porous crumbly material formed is mixed with rock dust from grinding sections of the plant and fed to the inside of

a sloping rotary drum. Water is sprayed on the tumbling solids to form free flowing granules and to enhance the acidulation reaction. Product is dried in a rotary dryer and packaged.

For triple super phosphate the process is similar but H_3PO_4 acid is used instead of H_2SO_4 .



2.4 Ammonium Phosphate

It acts as a fire retarding agent for wood, paper and clothes.

2.5 Nitric acid

Ammonia can be burned in air in presence of platinum and 10% rhodium and NO formed can be oxidised further and absorbed in water to form nitric acid. Extractive distillation is used to increase the concentration of nitric acid.

GATE QUESTIONS

Q.1 Consider the production of ammonia from methane and air as raw materials. The catalysts used are (A) for steam reforming of methane and (B) for ammonia synthesis.

[GATE-2002]

- | A | B |
|---------------------------------------|---------------------------------------|
| (a) Ni/Al ₂ O ₃ | Cu-ZnO/Al ₂ O ₃ |
| (b) Fe/Al ₂ O ₃ | Cu-ZnO/Al ₂ O ₃ |
| (c) Ni/Al ₂ O ₃ | Fe/Al ₂ O ₃ |
| (d) Fe/Al ₂ O ₃ | Ni/Al ₂ O ₃ |

Q.2 The composition of fresh feed to the high temperature high pressure urea autoclave is

[GATE-2003]

- (a) excess liquid ammonia and liquified CO₂
- (b) excess liquid ammonia and compressed CO₂ gas
- (c) excess liquid ammonia and excess compressed CO₂ gas
- (d) compressed NH₃ gas and excess compressed CO₂

Q.3 Prilling tower is found in the flow sheet for the manufacturing of

[GATE-2004]

- (a) ammonia
- (b) urea
- (c) superphosphate
- (d) triple superphosphate

Q.4 Match the products in Group I with the raw materials in Group II.

| | Group I | | Group II |
|---|-----------|---|--|
| P | Urea | 1 | Ammonia and carbon dioxide |
| Q | Polyester | 2 | Dimethyl terephthalate and ethylene glycol |
| | | 3 | Ammonia and carbon monoxide |
| | | 4 | Hexamethylene diamine and adipic acid |

[GATE-2004]

- | | |
|--------------|--------------|
| (a) P-1, Q-4 | (b) P-3, Q-2 |
| (c) P-3, Q-2 | (d) P-1, Q-2 |

Q.5 For making superphosphate by acidulation of phosphate rock, use of nitric acid is desirable because

[GATE-2010]

- (a) nitric acid is less expensive than sulphuric acid
- (b) the availability of nitrogen enhances the value of the superphosphate as a fertilizer
- (c) the process produces non-hygroscopic superphosphate
- (d) the process produces superphosphate having higher phosphorus content than the sulphuric acid

Q.6 The main unit processes used for the production of hydrogen from natural gas are steam reforming (SR), pressure swing adsorption (PSA), low temperature water gas shift reaction (LT WGS), high temperature water gas shift reaction (HT WGS). The correct sequence of these in the plant is

[GATE-2012]

- (a) SR;LT WGS;HT WGS;PSA
- (b) PSA;SR;LT WGS;HT WGS

- (c) SR;HT WGS;LT WGS;PSA
(d) PSA;HT WGS;LT WGS;SR

Q.7 Match the following raw materials with their final product

| | |
|--------------------------|---|
| 1.Single super phosphate | P.Phosphate rock + sulphuric acid + NH_3 |
| 2.Triple super phosphate | Q.Brine |
| 3.Diammonium phosphate | R.Phosphate rock + sulphuric acid |
| 4.Caustic Soda | S.Phosphate rock + phosphoric acid |

[GATE-2015]

- (a) 1-Q, 2-R, 3-S, 4-P
(b) 1-S, 2-P, 3-Q, 4-R
(c) 1-R, 2-S, 3-P, 4-Q
(d) 1-S, 2-R, 3-P, 4-Q

Q.8 Select the wrong statement regarding water gas shift converters from the list below.

[GATE-2015]

- (a) Inter stage cooling is provided between the two stages of shift converters
(b) Usually high temperature shift reactor has an iron based catalyst and low temperature shift reactor has a copper based catalyst
(c) HTS reactor followed by LTS
(d) LTS reactor followed by HTS

Q.9 The purpose of methanation reaction used in ammonia plants is to

[GATE-2017]

- (a) Remove CO as it is a catalyst poison
(b) Increase the amount of hydrogen
(c) Remove sulphur as it is catalytic poison
(d) Utilize methane as a catalyst for ammonia synthesis
-

ANSWER KEY

| | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| C | B | B | D | D | C | C | D | A |

3.1 Paper & Pulp industry

Pulp is obtained from bamboo, wood, bagasse etc. pulping means disintegration of bulky fibrous material into small fibers. These is done by 3 modes

- I.Mechanical
- II.Chemical
- III.Semi-Chemical

Chemical method is most widely practised as the energy needed for mechanical method is very high. Chemical pulping can be done by 2 processes.

- I.Sulfate Kraft Process
- II.Sulfite Process

SULFATE KRAFT PROCESS

It is most widely used process. It is an alkaline process. The presence of sodium sulphide makes bleaching of pulp easy and paper produced has better strength.

Manufacturing process:

Chipper Bin:

Logs are conveyed to the chipper where the wood is reduced to a size of 2-5 cm of flat chips. Size reduction is done to maximize penetration of process chemicals by increasing surface area.

Digester Tower:

Here digestion is done to free lignin and other non-cellulosic component by adding NaOH and Na₂S (white liquor). The temperature in digester tower is maintained at 170 °C and residence time is 90 minutes.

Blowdown Valve & Blow Tank:

First the blowdown valve reduces pressure and then the mixture enters into blow tank. Here heat is recovered in the form of steam. The blow tank has high concentration of pulp and low concentration of water.

Screens & Filters:

Pulp is screened to remove wood knots and undigested residue. Pulp is filtered to separate black liquor.

Bleaching:

Bleaching is done to produce white paper. Earlier bleaching was done using chlorine but it used to release dioxins and other harmful products which are carcinogenic. Now-a-days bleaching is done with ozone, hydrogen peroxide, oxygen, chlorine dioxide etc. They produce white paper by removing small amounts of lignin which remains after digestion.

Recovery of black liquor:

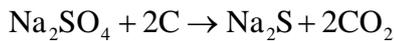
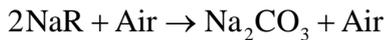
Black liquor which contains 95-98% of digested chemicals is recovered to reduce pollution & making the process more economical by recovering the chemicals which are added in digester tank.

Multi effect evaporator:

It concentrates the black liquor from 15-18% to 60-65%.

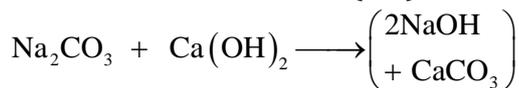
Mixing Tank & Boiler:

In mixing tank make up chemicals i.e. Na₂SO₄ and S are added. It then enters boiler which produces molten slag. Here the organic carbon present in black liquor is burned.



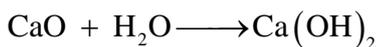
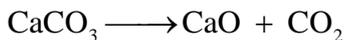
Dissolving Tank:

The molten chemical is smelt dissolved with cold water and yield green liquor. After that it reacts with Ca(OH)_2



Green Liquor

The above reaction takes place during castisizing operation where we get CaCO_3 as by product. CaCO_3 is converted to Ca(OH)_2 by following reaction



Beater:

Pulp fibres are mechanically disintegrated with help of metal blades.

Web Formation:

Here water is added to mixture such that there is 99% water and 0.9% pulp fibres.

Pressing & Drying:

In this section rolls are used to reduce water content to 65% followed by drying where water content is reduced to 5-6%

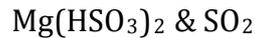
Finishing:

Calendering rolls are used and finally paper is produced.

Filers are added like AKD (alkyl ketine dimer), ASA (alkyl saxsanic anhydride), AKA etc.

Chemicals used in sulphite process

I.Magnifite process:



II.Natural sulphite:



III.Acid Sulfitte:



3.2 OILS & FAT INDUSTRY

Oils are mainly of two types:

- 1) Vegetable oil
- 2) Essential oil

Oils and fats are mixture of glycerides of fatty acid. They are reactive with oxygen when double bond increases. Melting point decreases and reactivity towards oxygen increases as no. of double bond increases.

To decrease the double bond character hydrogenation takes place in presence of raney nickel catalyst i.e. Ni-Al alloy

Vegetable oil Extraction:

Cleaning & Dehulling:

Cleaning of seeds of oil seed plant is done to remove impurities and other unwanted substances.

Digester:

Here the seeds are softened by means of steam. Because of steam the seeds gets swollen. Generally for 100 parts of seeds 5-10 parts of water is mixed.

Expeller:

The shell of the seeds gets rupture due to pressure applied by expeller and oil is released. Oil is further sent for purification.

Mixed Tank:

Alkaline chemicals like NaOH or Na₂CO₃ is added in oil to remove fatty acids.

Centrifuge:

Fatty acids are separated from oil. These fatty acids are sent for soap manufacturing.

Rotary Filter:

The oil here is dark and has very bad colour so it is treated with some bleaching chemical like fuller earth carbon. The clear oil then enters rotary filter drum to remove left seed shells. The finished oil is obtained.

3.3 SOAP INDUSTRY

Soaps are generally sodium and potassium salts of fatty acid. The soap contains two parts a hydrophobic tail and a hydrophilic head. During cleaning the hydrophobic part of the soap gets attached to the dirt present and the hydrophilic part gets attached to water and hence dirt gets removed. They are called surface active agent or surfactants. TiO₂ is an additive which is used for whiteness.

MANUFACTURING PROCESS

Hydrolyser:

The fats along with catalyst enters the hydrolyser where hot water is added with intimate mixing. The fatty acid & glycerine is produced as top and bottom stream respectively.

Flash Tank:

The mixture then enters flash tank where water is removed and fatty acids are concentrated.

Vacuum Still:

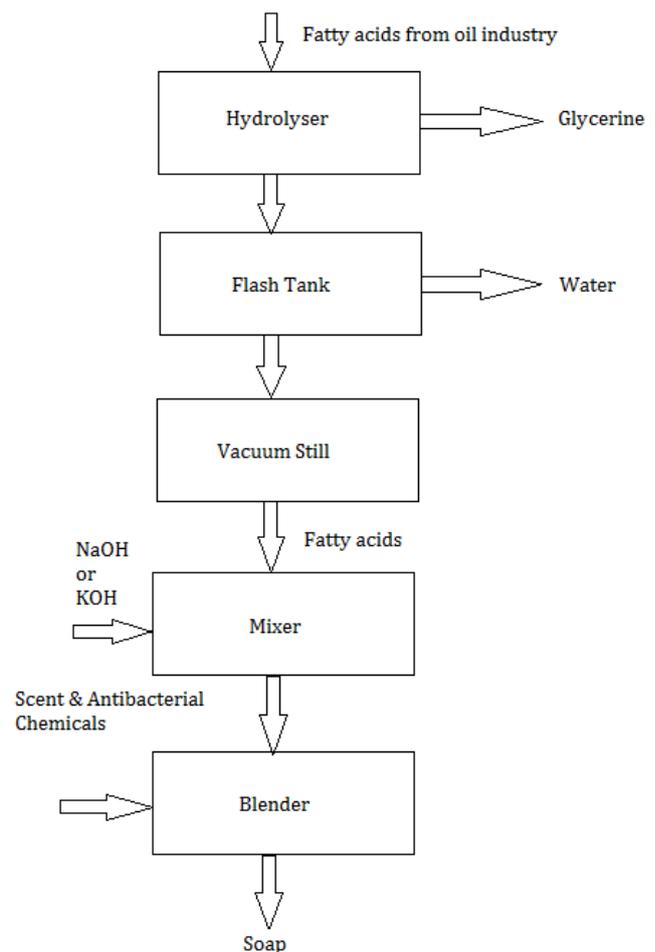
The concentrated fatty acids enters vacuum still where jet ejectors are used to create vacuum.

Mixer

Fatty acid produced from vacuum still is now pumped to mixer where base such as NaOH & KOH are added.

Blender:

Ingredients like antifungal agents, anti-caking agent, scents etc. are added here and the solids which comes out of blender is known as soaps.



3.4 GLYCERIN:

Ion Exchange:

15-20% glycerine along with impurities from hydrolyser goes to ion exchange for removing impurities.

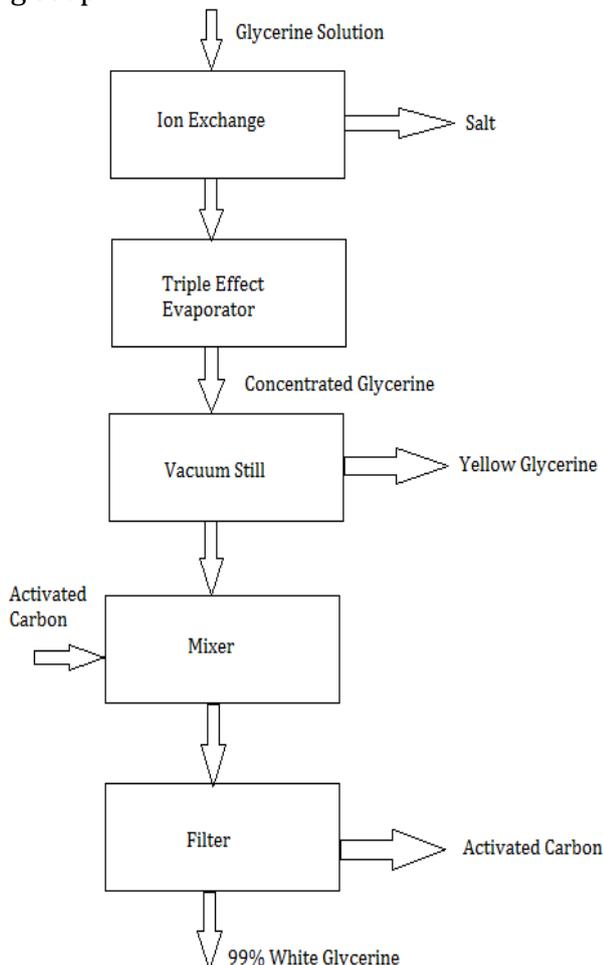
Triple Effect Evaporator & Vacuum Still:

The glycerine solution is concentrated in triple effect evaporator. It then enters vacuum still where yellow glycerine is obtained.

Mixer:

The solution is then passed through activated carbon to remove colour and white glycerine is obtained.

The yield of glycerine is 30-35 kg for 1000 kg soap



3.5 DETERGENTS:

Detergents are of two types:

- 1) Anionic
- 2) Cationic

Anionic:

These are those which releases R^- ions in water. They are most widely used. Some examples of it are sulfates, sulfonates, alkyl benzene sulfonate (ABS).

Cationic:

These are those which releases R^+ ions in water. They have excellent germicidal properties. Some examples of it are ammonium compounds.

3.6 SUGAR INDUSTRY:

Sugar is obtained from fruits and vegetables and is obtained in maximum quantity from sugarcane. Sugar is disaccharides ($C_{12}H_{22}O_{11}$).

Manufacturing:

Cutter & Rolls:

The cutter cuts sugarcane into small pieces. It then goes to crushing rolls where it is crushed and its juice is obtained.

Clarifier:

Here $CaHPO_4$ along with milk of lime is added for flocculation to separate impurities. Because of this the solution becomes alkaline and to maintain its pH (=7) SO_2 is added. SO_2 not only maintains its pH but also acts as bleaching agent. SO_2 can be replaced by phosphoric acid and CO_2 . The impurities are settled at bottom.

Rotary Filter:

The solution from the clarifier enters rotary filter where the impurities are removed from sugar solution.

Multi effect evaporator:

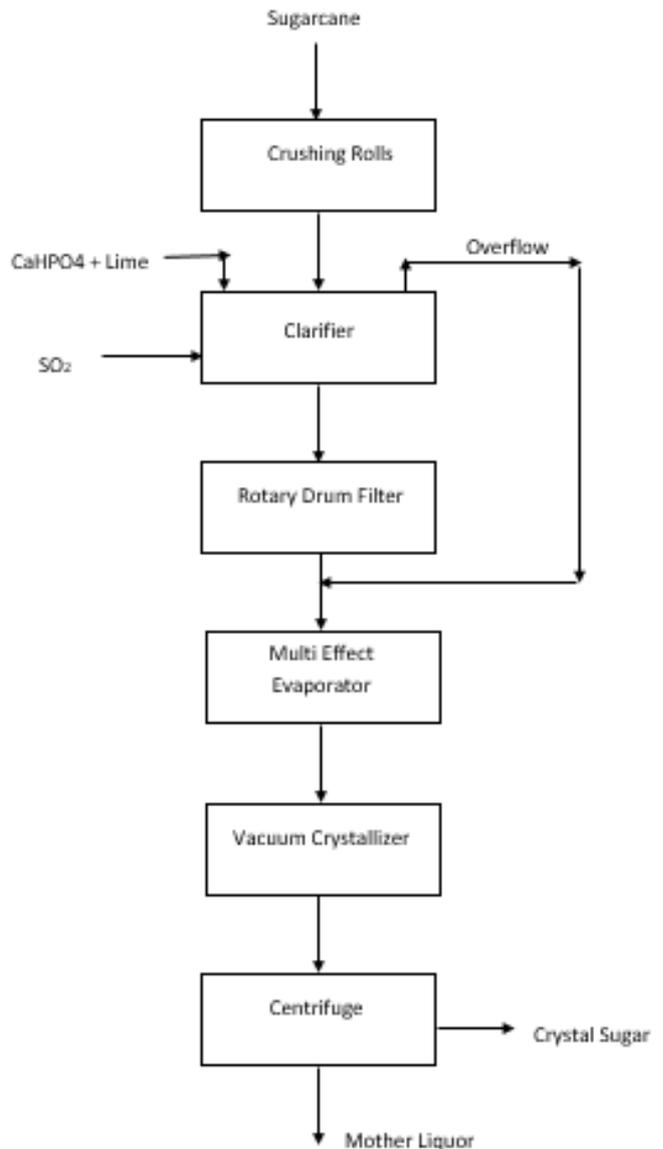
The Clarified overflow solution goes to multi effect evaporator where it is concentrated from 80% water to 40% water.

Crystallizer:

The concentrated sugar solution goes to crystallizer where it is further boiled in vacuum pans at its vapor temperature until crystals are seen.

Centrifuge:

The mixture of crystal and syrup which is called masscuite enters centrifuge where the mother liquor (molasses) is separated from crystals. Hence sugar crystals are obtained.



GATE QUESTIONS

Q.1 One of the steps during refining of cane sugar consists of addition of hydrated lime to the sugar syrup followed by carbonation of the resulting solution. The purpose of this step is to

[GATE-2001]

- (a) adjust the pH of the syrup
- (b) remove the colouring matter from the syrup
- (c) reduce the viscosity of the syrup
- (d) improve the rate of crystallization of sugar

Q.2 For the hydrogenation of oils,(A).... is commonly used as catalyst, and(B).... is a catalyst poison.

[GATE-2002]

- | A | B |
|---------------|---------|
| (a) platinum | sulphur |
| (b) palladium | oxygen |
| (c) nickel | sulphur |
| (d) nickel | oxygen |

Q.3 Match the items in Group I with the items in Group II.

| | Group I | | Group II |
|---|--------------------------|---|--------------------|
| P | Black liquor | 1 | Petroleum refining |
| Q | Activated silica alumina | 2 | Sugar industry |
| R | Press mud | | |

[GATE-2003]

- | | |
|--------------|--------------|
| (a) P-1,R-2 | (b) P-2, Q-1 |
| (c) Q-1, R-2 | (d) Q-2, R-1 |

Q.4 Which of the following is a detergent?

[GATE-2005]

- (a) Benzene hexachloride

- (b) Cellulose nitrate
- (c) Polyvinyl chloride
- (d) Alkyl benzene sulphonate

Q.5 Choose the most appropriate pairs from Group I and Group II.

| | Group I | | Group II |
|---|--------------|---|----------------|
| P | Nitration | 1 | Detergent |
| Q | Sulphonation | 2 | Pulp and paper |
| R | Carbonation | 3 | Explosives |
| | | 4 | Sugar |

[GATE-2006]

- | | |
|-------------------|-------------------|
| (a) P-1, Q-2R-4 | (b) P-3, Q-1, R-2 |
| (c) P-3, Q-1, R-4 | (d) P-3, Q-2, R-4 |

Q.6 Multiple effect evaporators are commonly used in the manufacturing of

- P) Paper
- Q) superphosphate
- R) sugar
- S) fats

[GATE-2007]

- | | |
|-------------|-------------|
| (a) P and Q | (b) P and R |
| (c) P and S | (d) R and S |

Q.7 In the sulphite process for paper manufacturing, the 'cooking liquor' is

[GATE-2007]

- (a) magnesium bisulphite and sulphur dioxide in acid medium
- (b) magnesium sulphite and magnesium dicarbonate
- (c) sodium sulphite and magnesium sulphite
- (d) sodium sulphite and sodium bisulphite and sulphur dioxide

Q.8 Which one of the following process sequences is used in the sugar industry?

[GATE-2008]

- (a) Ca_2HPO_4 /Lime treatment "Crystallization" Crushing
- (b) Ca_2HPO_4 /Lime treatment "Multiple stage evaporation" Crystallization
- (c) Crushing "Crystallization" Ca_2HPO_4 /Lime treatment
- (d) Multiple stage evaporation "Crystallization" Ca_2HPO_4 /Lime treatment

Q.9 Identify which of the statements are wrong

(P) oils with an oleic radical (1 double bond) are more suitable than oils with a linolenic radical (3 double bonds) as film forming vehicles for paints.

(Q) production of synthesis gas from coal and steam is an endothermic process.

(R) Use of chlorine for bleaching of wood pulp results in the release of dioxins

(S) In the manufacturing of urea from ammonia, the main intermediate product formed is ammonium bicarbonate

[GATE-2013]

- (a) P & Q
- (b) R & S
- (c) Q & R
- (d) P & S

Q.10 The molecular formula of the predominant chemical compound in commercial sugar is

[GATE-2018]

- (a) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
 - (b) $\text{C}_{12}\text{H}_{24}\text{O}_{12}$
 - (c) $\text{C}_6\text{H}_{10}\text{O}_5$
 - (d) $\text{C}_6\text{H}_{12}\text{O}_6$
-

ANSWER KEY

| | | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| A | C | B | D | C | B | A | B | D | A |

4

POLYMER INDUSTRY

Polymer is derived from the “poly” which means many and “mer” means units i.e. polymer means having many repeating units. This repeating structural unit is derived from some simple and reactive molecules called monomers and the process of formation of polymers from these monomers is called polymerisation.

4.1 Polymers

Types of polymers:

1) Based on sources:

- i. Natural
- ii. Semi synthetic
- iii. Synthetic

2) Based on structure:

- i. Linear
- ii. Branched
- iii. Cross linked

3) Based on bonds:

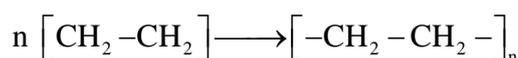
- i. Additional polymer
- ii. Condensation polymer

• Additional polymer

They are also called chain growth polymer. Addition of monomer having double or triple bond is called addition polymerisation. They are further divided into homo polymerisation and co polymerisation.

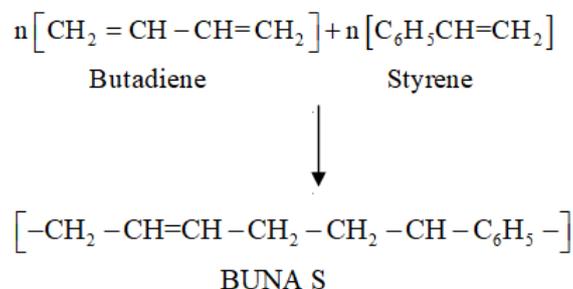
○ Homo polymerisation

In homo polymerisation the monomer is of single species i.e. addition of same type of monomer occurs.



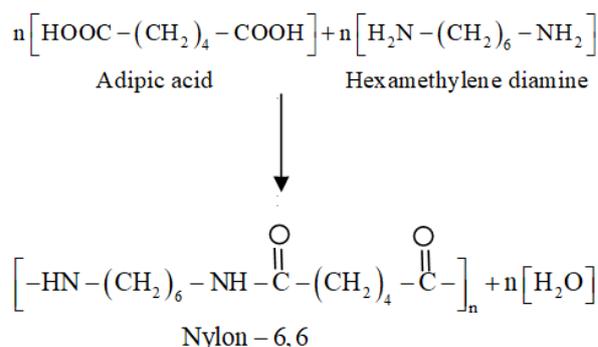
○ Co polymerisation

Polymerisation takes place by two different types of monomer is called co polymerisation.



• Condensation Polymerisation

Condensation polymerisation small molecules such as water, alcohol, HCl etc are eliminated during reaction between bi functional or tri functional monomers.



Silicone rubber

These are elastomers composed of silicone together with carbon, hydrogen & oxygen monomer. They have exceptional mechanical & electrical properties.

Chlorobutyl rubber:

It is produced by reacting isobutylene with isoprene (1-3%). It is used in tubeless tires.

4.2 Fibres

Thread forming solid possessing high tensile strength and high modulus. These characteristic is due to strong intermolecular force like hydrogen bond. These strong forces also lead to close packing of chain and thus impart crystalline structure.

Fibres are classified into:

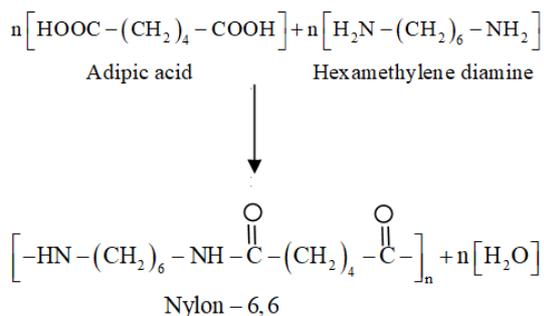
- 1) Polyamide
- 2) Polyester
- 3) Acrylic
- 4) Cellulosic

4.3 Polyamides

These are polyamides because it possess amide linkage and are example of synthetic fibres and are termed as nylon. Examples of polyamides are nylon 6,6 & nylon 6.

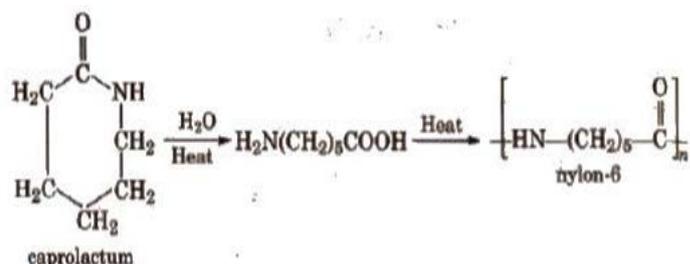
Nylon 6,6

Nylon 6,6 is prepared by reacting diamines with dicarboxylic acid i.e. by reacting adipic acid with hexamethylene diamine. It is used in textile Industries. It is example of condensation polymer as H₂O molecule is eliminated.



Nylon 6

It is obtained by heating caprolactum in presence of water at high temperature. The temperature is 533 – 543 K. It is used in manufacturing of ropes, tires, fabrics etc.

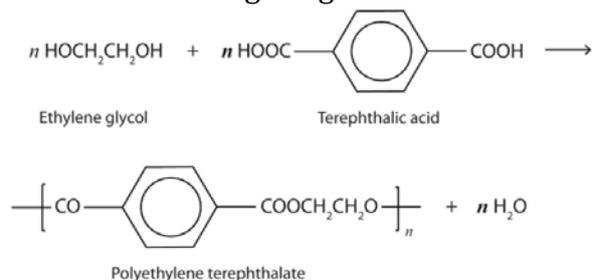


4.4 Polyester

This is example of condensation polymer as H₂O is eliminated in final product. It is product of diols and dicarboxylic acid. Example of polyester is dacron or terylene.

Dacron/Terylene

Dacron is product of two different monomers i.e. ethylene glycol and terephthalic acid at 420-460 K in presence of zinc acetate antimony trioxide. It is used in blending with cotton and wool. It is also used in reinforcing the glass.



4.5 Acrylic fibers

The commercial acrylic fibers are orlon and dynel. For orlon the monomer is acrylonitrile while dynel is modified acrylonitrile. Dynel is co polymer of acrylonitrile and vinyl chloride.

4.6 Cellulosic fibers

Viscous Rayon, acetate rayon and cupra ammonium rayon are examples of cellulosic fibers. The raw materials/monomers required for these are as follows.

Viscous rayon

Raw materials: Cellulose
Carbon disulphide
Sodium hydroxide

Acetate rayon

Raw materials: Wood pulp
Acetic anhydride
Sulphuric Acid

Cupra ammonium rayon

Raw materials: Copper salt
Ammonia
Cellulose

4.7 THERMOPLASTIC POLYMER

This polymers have intermediate intermolecular force of attraction between fibres and elastomers. They are long chain molecules capable of softening on heating and hardening on cooling. Polyethylene, polypropylene, polystyrene, poly vinyl chloride (PVC), polycarbonates etc are all examples of thermoplastic polymer.

Polyethylene

LDPE (low Density Poly Ethylene):

For LDPE the pressure is high generally around 1000-2000 atm pressure and 350-370 K temperature. These takes place in presence of catalyst like dioxygen or peroxide.

LLDPE (linear low density poly ethylene)

It takes place at lower pressure than LDPE and with significant short branches. These process takes place in presence of zeigler nata catalyst (Triethyl Aluminium Titanium Tetrachloride). T has high tensile strength and flexible under elongated stress.

HDPE (High Density Poly Ethylene)

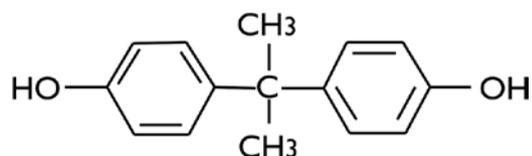
These reaction takes place in Presence of 6-7 atm and catalyst used here is zeigler nata catalyst.

Poly Vinyl Chloride (PVC):

Major portion of chlorine manufactured is used in PVC. The catalyst used here is butyllithium. It contains 56.8% Cl and balance hydrogen and carbon. Its monomer is vinyl chloride.

Polycarbonate:

They are prepared by reaction between bis-phenol and Phosgene gas (CoCl₂).



Bis-Phenol

4.8 THERMOSETTING

This polymer are cross linked or heavily branched when on heating undergoes extensive cross link and becomes unusable.

They can't be reused. Phenol formaldehyde resin, urea formaldehyde resin, melamine formaldehyde resin, epoxy resin etc are examples of thermosetting polymers

Phenol formaldehyde resin

There are two types of phenol formaldehyde resin:

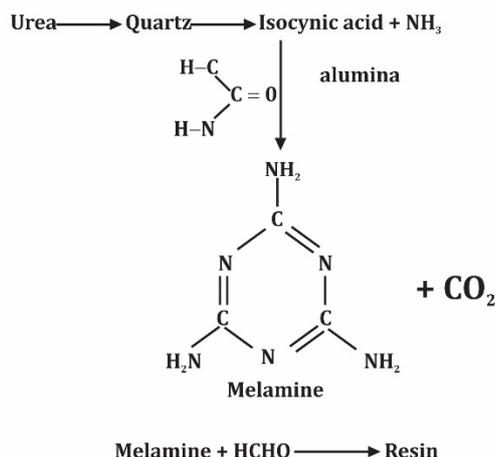
- I. Novalac phenol formaldehyde
- II. Resole phenol formaldehyde

Novalac - It is catalysed by acid and is used in paints. Novalac on heating with formaldehyde undergoes cross linking to form infusible solid called Bakelite.

Resole - It is catalysed by base. It is used in making combs.

Melamine formaldehyde resin

Melamine is produced from urea. Urea is heated in presence of quartz at 360-700 °C and the molten urea gets decomposed to isocyanic acid. Isocyanic acid then gets converted to melamine in presence of alumina catalyst. Melamine then reacts with formaldehyde to form melamine formaldehyde resin. It is used in non-breakable crockery having better chemical and heat resistant properties.



Epoxy resin

Epoxyresin is prepared by reacting two monomers i.e. epichlorohydrine and bis phenol. It is used in coating surfaces.

Types of additional polymer

- I. Bulk polymerisation
- II. Solution polymerisation
- III. Suspension polymerisation
- IV. Emulsion polymerisation

Bulk polymerisation

Bulk polymerisation is very simple process as the starting product is just pure monomer and reaction take place without any solvent or initiator. As there is only pure monomer the rate of reaction is high and yield is also very high. As the starting material is pure monomer the product is relatively pure. The major disadvantage is the reaction is exothermic i.e. it releases heat so heat removal becomes very important operation but as there is only pure monomer and no solvent it's thermal conductivity is low and is very viscous. Due to this there might be local hotspots and material may degrade. Polyethylene, Polypropylene, PET (polyethyl triethylene) are examples of bulk polymerisation.

Solution polymerisation

Unlike in bulk polymerisation in this the starting material is monomer dissolved in solvents like aliphatic, alcohol, aromatic, water etc. Because of the presence of solvent heat removal becomes easier and there are no local hot spots as in case of bulk polymerisation. The disadvantage is that the final product is not pure and solvent is also present with it. Vinyl acetate and acrylonitrile are examples of solution polymerisation.

Suspension polymerisation

It involves fine droplets of insoluble monomer suspended in water. These droplets are dispersed in water which also acts as heat transfer medium. Examples of suspension polymers are Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Epsom ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), bleaching powder (CaOCl_2), glaubers salt, PVC etc.

Emulsion polymerisation

It is carried out by suspending large droplets of insoluble monomer along with catalyst in water. The water to monomer ratio is 1:1 to 4:1 in most cases. It is used for production of polymer requiring high molecular weight like SBR and Teflon.

GATE QUESTIONS

Q.1 Identify the group in which all the polymers mentioned can be used to make fibres.

[GATE-2003]

- (A) Butadiene copolymers, Polyimides, Urea aldehydes
- (B) Cellulose derivatives, Polyisoprene, Polyethylene
- (C) Cellulose derivatives, Polyamides, Polyethanes
- (D) Polypropylenes, Polyvinylchloride, Silicones

Q.2 Pair the following polymers in Group I with their chain characteristics in Group II.

| | Group I | | Group II |
|---|---------|---|--|
| P | HDPE | 1 | Very few branches |
| Q | LDPE | 2 | Short and regular branches |
| R | LLDPE | 3 | High branching with both short and long chain branches |

[GATE-2006]

- (A) P-1, Q-2, R-3
- (B) P-2, Q-1, R-3
- (C) P-1, Q-3, R-2
- (D) P-2, Q-3, R-1

Q.3 Match the appropriate pairs from Group I and Group II.

| | Group I | | Group II |
|---|-------------------|---|-----------------|
| P | Carbon disulphide | 1 | Nylon 6 |
| Q | Caprolactum | 2 | Nylon-6,6 |
| R | Gypsum | 3 | Phosphoric acid |
| | | 4 | Viscose rayon |

[GATE-2006]

- (A) P-4, Q-2, R-3
- (B) P-2, Q-1, R-3
- (C) P-3, Q-1, R-4
- (D) P-4, Q-1, R-3

Q.4 Match the polymerisation mechanism in Group I with the corresponding polymers in Group II.

| | Group I | | Group II |
|---|---|-----|---------------------------|
| P | Chain growth/addition polymerisation | I | Polyethylene |
| Q | Step growth/condensation polymerisation | II | Polyvinyl chloride |
| | | III | Polythylene terephthalate |

[GATE-2011]

- (A) P-III; Q-I, II
- (B) P-I, II; Q-III
- (C) P-II, III; Q-I
- (D) P-I; Q-II, III

Q.5 Match each of the following techniques of polymerization in Group I, with the corresponding process characteristics in Group II.

| | Group I | | Group II |
|---|------------|---|--|
| P | Bulk | 1 | Polymer with very high molecular weight can be obtained |
| Q | Solution | 2 | Heat removal is crucial but very difficult |
| R | Suspension | 3 | Small amount of undesired low molecular weight polymer is formed |

| | | | |
|---|----------|---|--|
| S | Emulsion | 4 | Polymer concentration in the product stream is low |
|---|----------|---|--|

[GATE-2010]

| | | | | |
|-----|---|---|---|---|
| | P | Q | R | S |
| (A) | 1 | 2 | 3 | 4 |
| (B) | 2 | 4 | 3 | 1 |
| (C) | 2 | 3 | 4 | 1 |
| (D) | 2 | 3 | 1 | 4 |

Q.6 Match each of the polymers in Group I with the raw material in Group II, from which they are made.

| | Group I | | Group II |
|---|---------------|---|-----------------|
| P | Polyester | 1 | Ethylene glycol |
| Q | Polyamide | 2 | Adipic acid |
| R | Viscose rayon | 3 | Cellulose |
| S | Epoxy resin | 4 | Bisphenol |

[GATE-2010]

| | | | | |
|-----|---|---|---|---|
| | P | Q | R | S |
| (A) | 1 | 2 | 3 | 4 |
| (B) | 2 | 1 | 3 | 4 |
| (C) | 1 | 2 | 4 | 3 |
| (D) | 3 | 2 | 4 | 1 |

Q.7 Which of the following is not employed in the commercial production of linear polyvinyl chloride?

[GATE-2005]

- (A) Emulsion polymerization
- (B) Suspension polymerization
- (C) Addition polymerization
- (D) Condensation polymerization

Q.8 Match the products in Group I, with the raw materials in Group II.

| | Group I | | Group II |
|---|-----------|---|------------------------|
| P | Nylon 6,6 | 1 | Chlorodifluoro methane |

| | | | |
|---|----------|---|--|
| Q | Terylene | 2 | Dimethyl terephthalate and ethylene glycol |
| | | 3 | Acetylene and hydrogen cyanide |
| | | 4 | Hexamethylene diamine and adipic acid |

[GATE-2005]

- (A) P-3, Q-4
- (B) P-4, Q-3
- (C) P-4, Q-2
- (D) P-1, Q-2

ANS: (C)

Q.9 Match the products in Group I with the nature of reactions in Group II.

| | Group I | | Group II |
|---|--------------|---|-----------------------------|
| P | Polyethylene | 1 | Condensation polymerization |
| Q | Nylon | 2 | Additional polymerization |
| R | Polystyrene | | |

[GATE-2004]

- (A) P-1, Q-1, R-2
- (B) P-2, Q-2, R-1
- (C) P-1, Q-2, R-1
- (D) P-2, Q-1, R-2

Q.10 Pair the following industrial processes in Group I with the catalysts used in Group II.

| | Group I | | Group II |
|---|---------------------|-----|---------------|
| P | Polyethylene | I | Elastomeric |
| Q | Phenol Formaldehyde | II | Fiber |
| R | Polyisoprene | III | Thermoplastic |
| S | Polyester | IV | thermosetting |

[GATE-2012]

- (a) P-III, Q-IV, R-I, S-II
- (b) P-IV, Q-II, R-III, S-I

(c) P-III, Q-II, R-I, S-IV

(d) P-IV, Q-III, R-I, S-II

Q.11 Match the following polymers with their respective catalyst

| | |
|-------------------------------|---------------------|
| 1. Low density polymer | P. Ziegler- nata |
| 2. High density polymer | Q. Traces of oxygen |
| 3. Polyethylene terephthalate | R. Butly lithium |
| 4. PVC | S. Antimony |

[GATE-2015]

(a) 1-Q, 2-R, 3-S, 4-P

(b) 1-S, 2-P, 3-Q, 4-R

(c) 1-Q, 2-P, 3-S, 4-R

(d) 1-S, 2-R, 3-P, 4-Q

Q.12 "Nylon 66" is so named because

[GATE-2003]

(A) the average degree of polymerization of the polymer is 1966

(B) the number of carbon atoms between two nitrogen atoms are 6

(C) the number of nitrogen atoms between two carbon atoms are 6

(D) the polymer was first synthesized in 1966

Q.13 Match the raw materials with their respective products

| Group 1 | Group 2 | Group 3 |
|-----------------|--------------------------|--------------------|
| P1 Ethylene | Q1 Ammonia | R1 Synthetic fibre |
| P2 Propylene | Q2 Butene | R2 Nylon 6,6 |
| P3 Adipic | Q3 Ethylene glycol | R3 LLDPE |
| P4 Terephthalic | Q4 Hexamethylene diamine | R4 Acrylonitrile |

(A) $P1 + Q2 \rightarrow R3; P2 + Q1 \rightarrow R4;$
 $P3 + Q4 \rightarrow R2; P4 + Q3 \rightarrow R1$

(B) $P1 + Q1 \rightarrow R3; P2 + Q3 \rightarrow R1$
 $P3 + Q4 \rightarrow R4; P4 + Q2 \rightarrow R2$

(C) $P1 + Q2 \rightarrow R4; P2 + Q3 \rightarrow R1;$
 $P3 + Q4 \rightarrow R3; P4 + Q1 \rightarrow R2$

(D) $P1 + Q1 \rightarrow R4; P2 + Q2 \rightarrow R3;$
 $P3 + Q4 \rightarrow R2; P4 + Q3 \rightarrow R1$

Q.14 Match the following

| | Group I | | Group II |
|---|-----------------------------|---|---------------------|
| P | Free radical polymerisation | 1 | Nylon 6,6 |
| Q | Ziegler nata | 2 | Polypropylene |
| R | Condensation | 3 | Poly vinyl chloride |
| | | | |

[GATE-2017]

(A) P-1, Q-2, R-3

(B) P-3, Q-2, R-1

(C) P-1, Q-3, R-2

(D) P-2, Q-1, R-3

Q.15 Polyvinyl chloride is produced by

[GATE-2018]

(A) co polymerization

(B) addition polymerization

(C) reacting chlorine with polyethylene

(D) reacting hydrochloric acid with polyethylene

Q.16 Choose the correct statement in viscose rayon manufacturing process

[GATE-2018]

(A) Carbon disulphide used as a reactant for xanthate formation is regenerated in a later step

(B) Caustic soda used as reactant for steeping of cellulose is regenerated in a later step

- (C) Sulphuric acid is used in steeping process of cellulose
- (D) The spun viscose rayon is hardened in an alkali bath

ANSWER KEY

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| B | A | D | B | B | A | C | C |
| 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| D | A | C | B | A | B | B | A |

5

PETROLEUM REFINING

Crude oil is a multicomponent mixture containing more than 10^8 compounds. This crude contains carbon 84-87%, Hydrogen 11-14%, Sulphur 0.2%, Oxygen 0-0.6%, nitrogen 100 ppm etc. Petroleum refining means removal of this impurities from crude by various reactions and processes.

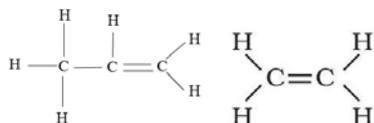
5.1 Classification of crude:

Paraffin

They do not have any unsaturation and they are generally alkanes like methane, ethane, propane, butane, pentane, iso pentane etc.

Olefin

They possess unsaturation i.e. they possess alkenes like ethylene, propylene, butylene etc. They are not found in measureable quantity in crude.

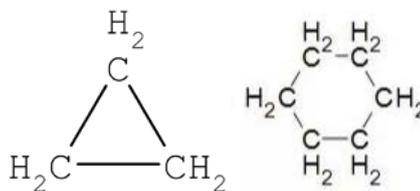


Butene

Ethene

Napthene

They are cycloalkanes like cyclopropane, cyclohexane etc. which are present in crude. These compounds are not aromatic and hence do not contribute much to octane number. They are generally target in reforming process for converting them to aromatics.

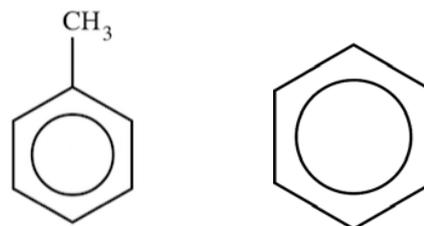


Cyclopropane

Cyclohexane

Aromatic

These compounds contribute most to the octane number. Benzene, xylene, toluene etc. are examples of aromatic compounds. The target in reforming process is to maximize their quantity.



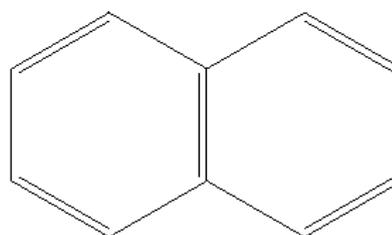
Toluene

Benzene

Naphthalene

Polynuclear aromatics such as naphthalene have at least or more than 2 aromatic rings.

Not all compounds in crude are hydrocarbons comprising of carbon and hydrogen. It consists of many other impurities.



Naphthalene

Sulphur

Organic sulphur is present in crude as thiophenes, pyridine etc. sulphur needs to be removed as it acts as catalytic poison and is generally removed by hydro treating. Crude possessing sulphur is called sour crude while crude free from sulphur is called sweet crude. Also presence of sulphur decreases octane number of the crude.

Oxygen

Generally oxygen is present in 0-0.6% in crude. Compounds which contains oxygen are acetic acid, benzoic acid etc. They have to be removed from crude as it causes corrosion.

Moisture

Water in fuel is undesirable as it causes flame failure and corrosion. It is present in crude up to about 1 %.

Resins

Resins are polynuclear aromatic structure with side chain of small paraffins. They contain elements like sulphur, oxygen, nitrogen, nickel etc.

Asphalts

Petroleum with high content of naphthanic compounds is known as asphalt. They are polynuclear aromatic structure consisting of at least 20 rings. Crude having high asphalt content is generally target for coke production.

5.2 PROPERTIES OF PETROLEUM PRODUCTS

Flash point

It is the minimum temperature at which the crude gives sufficient vapours to produce

instantaneous flash is called flash point. If the flash is sustained for more than 5 seconds it is called fire point. Generally the fire point is 4-5°C greater than flash point. This both points indicates suitability of temperature for crude. They indicate temperature upto which the fuel can be used safely.

Cloud point

The minimum temperature at which the oil becomes cloudy or hazy on cooling is called cloud point.

Pore point

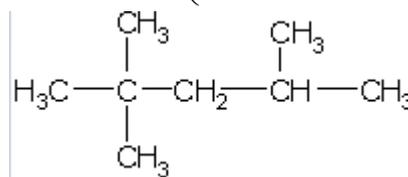
When the oil is cooled it first becomes hazy and on further cooling it just stops to flow. The minimum temperature below which the oil stops to flow is called pore point. Pore point is 4-5°C lower than cloud point.

Octane number

It is a characteristic of petrol engine. It is expressed in spark ignition and knocking characteristic.

High octane number is preferred for petrol. Octane number is defined as % volume of iso octane upon % volume of isooctane + % volume of n heptane. Octane number of iso octane is 100 while octane number of n heptane is 0. Iso octane is 2,2,4 trimethyl pentane.

$$\text{Octane No.} = \frac{(\% \text{ Vol of iso-Octane})}{\left(\begin{array}{l} \% \text{ Vol of iso-Octane} + \\ \% \text{ Vol of n-Heptane} \end{array} \right)}$$



Iso octane

5.3 Petroknock

Knocking is characteristic of petrol engine. When we use low grade/quality fuel it might adhere to the wall of engine. During the starting of engine the piston is in its return stroke. This compression is done to produce heat and ignite the spark plug. Due to this spark is produced in the spark plug and centre flame propagates. Because of the fuel adhered to the wall it gets heated and another flame is produced when this flame collides with central flame an audible sound is produced which is knocking.

In India gasoline of octane number 87 is sold while in US gasoline of 95 is sold. Octane number can be increased by TEL (Tetra Ethyl Lead) but nowadays because of economic considerations TEL is not used. Higher the octane number better is the performance of engine and lower the knocking.

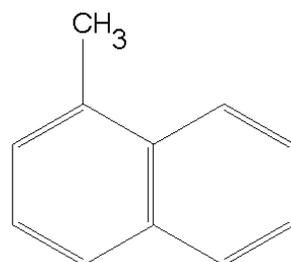
Octane number decreases in following order:

Aromatics > Iso paraffins > Olefins > Naphthenes > Paraffins

Cetane number

It is the characteristic property of diesel engine. It facilitates the easy starting of diesel engine. Cetane number is defined as % volume of cetane upon % volume of cetane + % volume of methyl naphthalene. Aromatics are undesired for higher cetane number.

$$\text{Cetane No.} = \frac{(\% \text{ Vol of } n\text{-cetane})}{\left(\begin{array}{l} \% \text{ Vol of } n\text{-cetane} + \\ \% \text{ Vol of methyl Naphthalene} \end{array} \right)}$$



Methyl Naphthalene

Smoke point

It is characteristic property of kerosene and it determines suitability of kerosene as fuel. Higher the smoke point higher is the quality of kerosene. Smoke point is defined as sample of kerosene burned in standard flame for 5 min without leaving any smoking tail. The height of this flame is called smoke point. Generally good quality kerosene the smoke point should be around 25 mm.

Higher the aromatic content lower will be the smoke point. So aromatic is undesirable for smoke point as they are the major component for producing smoke. Paraffin are most desirable in this.

Carbon residue

It is the percentage of carbon residue left after distillation of crude oil for its product in absence of air. Carbon deposits foul the surface and effects regeneration of catalyst. It gives an indication of relative coke formation for evaporation and pyrolysis of oil. For a good fuel it should be less than 0.1%.

Aniline point

It is the lowest temperature at which equal volume of oil is completely miscible with equal volume of aniline. It is measure of aromatic content of an oil. More is the aniline point lesser will be aromatic content. The aromatic content in oil have a

tendency to deteriorate rubber sealing and packing.

Acid number

Acid number is defined as milligrams of KOH required to neutralize the free acid present in 1 gram of an oil. It determines the acidity of oil. Higher acid number indicates sludge formation and corrosion problems. Acid number should be less than 0.1%.

5.4 Calorific Value

Total heat produced per unit mass of fuel completely burned with pure oxygen. There are two types of calorific value:

Gross calorific value

Net calorific value

Gross calorific value

It is the amount of heat released by complete combustion of unit mass of gas. It is also called higher heating value.

Net calorific value

It is obtained by subtracting heat of vaporization of water vapour from gross calorific value. It is also called lower heating value

ADU Unit

| Fraction | T (°C) | Carbon chain | Used in |
|-----------------------|---------|----------------------------------|----------------------------|
| Fuel gas | >40 | C ₁ -C ₂ | Fuel |
| LPG | >40 | C ₃ -C ₄ | Domestic fuel |
| Straight run gasoline | 20 - 90 | C ₆ -C ₁₀ | Gasoline |
| Naphtha | 120-180 | C ₆ -C ₁₀ | Feed stock, steam cracking |
| Kerosene | 150-270 | C ₁₁ -C ₁₂ | Aviation turbine fuel |
| Light gas oil | 230-270 | C ₁₃ -C ₁₇ | High speed diesel |
| Heavy gas oil | 340-380 | C ₁₈ -C ₂₅ | High speed diesel |

VDU Unit

| Fraction | T (°C) | Carbon chain | Used in |
|----------------------|-----------|-----------------------------------|-------------|
| Light vacuum gas oil | 320 - 425 | C ₁₈ - C ₂₅ | Feed to FCC |
| Heavy gas oil | 425 - 550 | C ₂₈ - C ₃₈ | Feed to FCC |
| Vacuum residue | >560 | >C ₃₈ | Visbreaking |

5.5 Cracking

Cracking means heating of high boiling petroleum fraction at high temperature and pressure to produce lower boiling petroleum fraction i.e. breaking of a long molecule into smaller ones by heating. It is used to produce smaller molecules from larger ones like gasoline, olefins etc. They are also used to lower the viscosity of oil. Thermal cracking is carried out at high temperature 450-700 °C and high pressure 1-70 atm while for catalytic cracking the temperature required is 350-700 °C and pressure is 1-15 atm. The catalyst used in cracking are in form of pellets or bed. The catalyst is generally silica, zeolite, aluminium, natural clay etc.

Fluid catalytic cracking

The fluidised catalytic cracking requires two units working simultaneously which are fluid catalytic cracking reactor (FCCR) and catalytic regenerator. The basic principle of FCCR is fluidisation of catalyst. Catalyst regenerator is required to regenerate catalyst by burning coke in air

Fluid catalytic cracking reactor

FCCR consists of two main components: Riser and cyclones. In riser the feed comes in contact with hot catalyst. The catalyst is risen upwards through lift media which is generally steam. Riser contact time is generally 250 millisecond. From riser it goes to cyclone separator. Catalyst along with finished product goes to cyclone separator. Here the catalyst is fully coked and needs to be regenerated the finished product comes out from the top of the cyclone separator while the catalyst goes to regenerator.

The spent liquor which is relatively cold enter regenerator unit. The catalyst is burned in air. Due to the burning of catalyst the coke gets removed and from the catalyst and gets released as flue gases and it also helps in increasing the temperature of catalyst. This hot catalyst whose activity is regained is sent to riser through a pipe. The temperature of the catalyst is 650-750 °C. These burning of catalyst helps in raising the temperature of catalyst which is required to carry out endothermic reaction in FCCR. The FCCR unit is endothermic while the catalyst regenerator is exothermic.

Hydrocracking:

Cracking in presence of hydrogen is called hydrocracking. Catalyst used is tungsten sulphide for vapour phase while iron catalyst is used in liquid phase. The temperature and pressure are 400-500 °C and 70-700 atm. It produces lower

molecular weight product from higher ones. It completely removes sulphur, nitrogen, oxygen and olefins. It is possible because of surplus amount of hydrogen available.

Hydro treating

It is used to remove impurities like sulphur, oxygen, nitrogen etc. It is possible because of surplus amount of hydrogen. It is also used to stabilize the petroleum products by saturating the olefins. The temperature and pressure are 300-350 °C and 15-17 atm. The catalyst for this process is cobalt molybdenum. Generally H₂S is recovered from this process and is sent to contact process for production of H₂SO₄.

5.6 Reforming

Reforming means changing the arrangements of molecule without much changing the molecular weight of it i.e. rearrangement of molecules. Generally naphthenes are converted to aromatics. There are three types of reforming:

- Fixed bed
- Moving bed
- Fluidised bed

Polymerisation

Gases produced in cracking are rich in olefins this gases undergoes polymerization in presence of phosphoric acid to give a branched chain polymer. E.g. 2-iso butane undergoes polymerisation to form di-iso butane which is a branched chain polymer. Its main aim is to increase the branching.

Alkylation

Alkylation means reaction of olefins with paraffin or with aromatics. The reaction takes place in presence of sulphuric acid or

hydrofluoric acid which acts as catalyst. Its main aim is to produce larger isoparaffins having higher octane number e.g. isobutane + n-butane gives iso-octane

Isomerisation

It aims to convert normal paraffins to isoparaffins. This reaction takes place in the presence of Aluminium chloride (AlCl_3) which acts as catalyst. Example is isomerisation of n-butane to iso-butane.

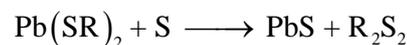
5.7 Sweetening process

Removal of sulphur and its related compounds like H_2S , mercaptans etc. from petroleum products is called sweetening process. Five different sweetening processes are:

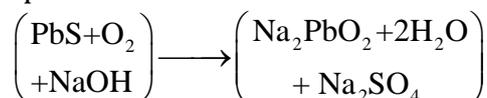
- I. Doctors test
- II. Copper chloride sweetening process
- III. Solutizer process
- IV. Catalytic desulphurisation
- V. Hydrofinning process

Lead doctoring of gasoline

In this method treating stock i.e. sour gasoline is thoroughly agitated with caustic plumbite solution. Lead becomes lead sulphide during reaction:



This lead sulphide is reacted with fresh sulphur to free lead sulphide from disulphide. Lead sulphide is converted back to sodium plumbite by blowing air into spent solution which.

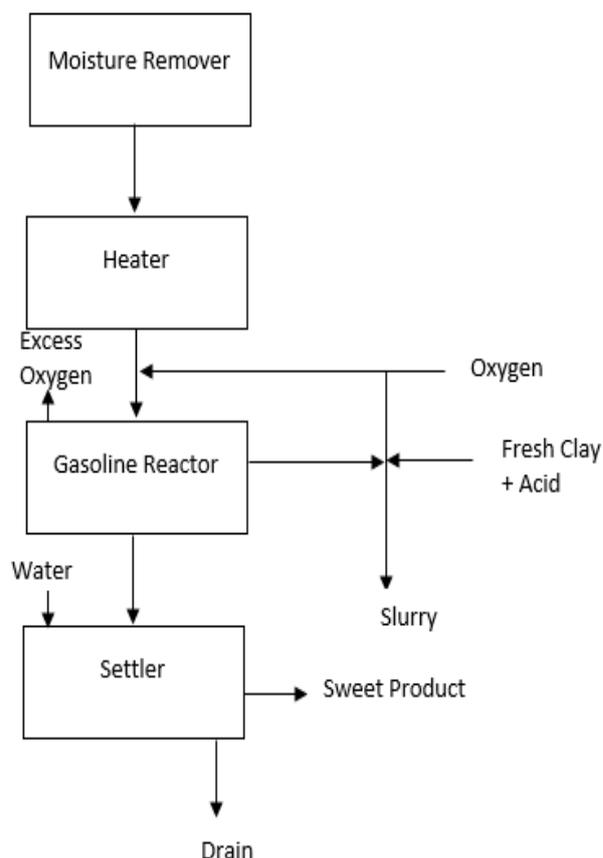


The regenerated solution is reused again for treatment. As can be seen consumption of lead is negligible as it is again

regenerated back but alkali consumption is high.

Copper chloride process

Gasoline free of sulphur and hydrogen sulphide is first passed through a moisture remover. Moisture is removed by passing through dehydrating agents like NaCl or CaCl_2 . The feed is heated by exhaust steam to a temperature of $40\text{--}60^\circ\text{C}$ and then sent to a mixer. Part of the circulating slurry consisting of copper chloride and clay in water is mixed up thoroughly with the feed. Oxygen is admitted into the mixer containing slurry and gasoline. This mixer acts as a reactor when air is sent in it. The floating layer consists of gasoline and is taken to a water washing system. Water removes the trapped particles of catalyst and acid. After settling the gasoline phase is routed through another dehydrator to a storage tank.



Solutizer process

This process requires solute for removing of sulphur from sour gasoline and converts into sweet gasoline. When methanol is the agent for promoting solutes as solutizer this process is called unisol process. While if naphthanic acid is used instead of methanol it is called mercapsol process.

Catalytic desulphurisation

In such processes whole molecule containing sulphur is not removed as in extraction or acid treatment but only sulphur atom is picked and thrown out. Thus material loss is negligible with possible recovery of sulphur. Generally the catalyst used in this processes are oxides of transitional metals.

Hydrofinning process

It is similar to catalytic desulfirisation but it takes place in presence of hydrogen

Dewaxing

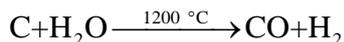
Removal of wax from petroleum product is important because at low temperature waxes crystallizes out and gets precipitated. Solvent used in dewaxing are methyl ethyl ketone, propane etc.

Bergius process

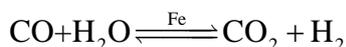
Finely powdered coal is made into paste with heavy oil and then heated to 400-800 °C under 200-250 atm pressure in presence of organic compound tin which acts as catalyst. It is then sent to converter followed by cracking and hydrogenation to yield gasoline, middle oil and heavy oil.

Fisher tropsh process

This method involves conversion of coal into water gas with the help of water at 1200 °C.



This mixture is not called synthesis gas as synthesis gas means presence of CO and H₂ in ratio of 1:2. It is called water gas. Hence a part of CO is removed and converted to CO₂ by following reaction.



Hydrogen so obtained is mixed with the water gas in ratio of synthesis gas i.e. H₂:CO is 2:1. The synthesis gas is passed at atmospheric pressure over cobalt catalyst at 180-200 °C to yield straight run gasoline, paraffins and olefins.

5.8 Composition of various gaseous fuels

Natural Gas

CH₄ = 96%
N₂ = 3%
CO₂ = 1%

Coke oven gas

H₂ = 53%
CH₄ = 32%
CO = 6%
N₂ = 3%
CO₂ = 2%

Water gas (blue gas)

H₂ = 50%
CO = 43%
CO₂ = 3%
N₂ = 3%

Producer gas

N₂ = 51%
CO = 27%
H₂ = 17%
CO₂ = 5%

The heating value of producer gas is 15 % of natural gas.

The value decreases in the following order

Natural gas > Coke oven gas > Carbureted gas > Water gas > Producer gas

Carbureted gas is obtained by atomized oil spraying in water gas

GATE QUESTIONS

Q.1 In the Fluid Catalytic Cracker (FCC), the cracking reaction is (A) and the regeneration is (B)

[GATE-2001]

- | A | B |
|-----------------|-------------|
| (A) exothermic | endothermic |
| (B) exothermic | exothermic |
| (C) endothermic | endothermic |
| (D) endothermic | exothermic |

Q.2 Among the following, choose one that is not an exothermic process.

[GATE-2002]

- (A) Methanol synthesis
- (B) Catalytic cracking
- (C) Ammonia synthesis
- (D) Oxidation of Sulphur

Q.3 The average boiling point of aviation turbine fuel is closest to that of

[GATE-2002]

- | | |
|----------------------|--------------|
| (A) lubricating oils | (B) LPG |
| (C) diesel | (D) Kerosene |

Q.4 The order of preference for feedstock to a catalytic reformer is

[GATE-2003]

- (A) catalytic naphtha - coking naphtha - virgin naphtha
- (B) coking naphtha - virgin naphtha - catalytic naphtha
- (C) virgin naphtha - catalytic naphtha - coking naphtha
- (D) virgin naphtha - coking naphtha - catalytic naphtha

Q.5 The proper arrangement of the petroleum fractions in the order of their boiling points is

[GATE-2004]

- (A) lubricating oil > diesel > petrol > LPG
- (B) lubricating oil > petrol > diesel > LPG
- (C) petrol > lubricating oil > diesel > LPG
- (D) petrol > diesel > LPG > lubricating oil

Q.6 Match the feeds in Group I with the processes in Group II.

| | Group I | | Group II |
|---|---------------|---|----------------------|
| P | Gas oil | 1 | Acetylene production |
| Q | Residue crude | 2 | Ethylene production |
| | | 3 | Coking |
| | | 4 | Cracking |

[GATE-2005]

- | | |
|--------------|--------------|
| (A) P-3, Q-4 | (B) P-4, Q-3 |
| (C) P-2, Q-3 | (D) P-1, Q-4 |

Q.7 In a fluid catalytic cracking unit, the nature of the reactions occurring in the reactor and the regenerator is

[GATE-2006]

- (A) Reactor - Exothermic, Regenerator - Exothermic
- (B) Reactor - Exothermic, Regenerator - Endothermic
- (C) Reactor - Endothermic, regenerator - Exothermic
- (D) Reactor - Endothermic, Regenerator - Endothermic

Q.8 Which of the following is desirable in gasoline but undesirable in kerosene?

[GATE-2007]

- (A) Aromatics
- (B) Mercaptans
- (C) Naphthenic acid
- (D) Paraffins

Q.9 Which one of the following is not a major constituent of crude oil?

[GATE-2008]

- (A) Paraffins (B) Olefins
(C) Naphthenes (D) Aromatics

Q.10 Match the unit processes in Group I with industries in Group II.

| | Group I | | Group II |
|---|----------------|---|----------------------|
| P | Saponification | 1 | Petroleum refining |
| Q | Calcination | 2 | Synthetic fibres |
| R | Alkylation | 3 | Cement |
| | | 4 | Soaps and detergents |

[GATE-2008]

- | | P | Q | R |
|-----|---|---|---|
| (A) | 1 | 3 | 4 |
| (B) | 2 | 3 | 4 |
| (C) | 4 | 2 | 1 |
| (D) | 4 | 3 | 1 |

Q.11 In petroleum refining operations, the process used for converting paraffins and naphthalenes to aromatics is

[GATE-2009]

- (A) catalytic reforming
(B) catalytic cracking
(C) hydrocracking
(D) alkylation

Q.12 Match the unit processes in Group I with the industries in Group II.

| | Group I | | Group II |
|---|----------------|---|----------------------|
| P | Steam cracking | 1 | Petroleum refining |
| Q | Hydrocracking | 2 | Petrochemicals |
| R | Condensation | 3 | Polymers |
| | | 4 | Soaps and detergents |

[GATE-2009]

- | | P | Q | R |
|-----|---|---|---|
| (A) | 1 | 2 | 3 |
| (B) | 2 | 3 | 3 |

- (C) 1 2 4
(D) 2 1 3

Q.13 Which one of the following sequences is arranged according to increasing calorific value?

[GATE-2011]

- (A) Producer gas, Natural gas, Water gas
(B) Natural gas, Producer gas, Water
(C) Producer gas, Water gas, Natural gas
(D) Water gas, Natural gas, Producer gas

Q.14 Hydrotreating is used for

[GATE-2011]

- (A) removal of water from crude oil
(B) treatment of crude oil with water
(C) improving octane number of gasoline
(D) removal of sulphur and nitrogen from petroleum fractions

Q.15 Zeolite ZSM-5 is added to commercial FCC catalyst for

[GATE-2011]

- (A) promoting SO₂ reduction
(B) promoting CO oxidation
(C) improving tolerance to metal content in feed
(D) enhancing octane number

Q.16 In petroleum refining catalytic reforming is used to convert

[GATE-2012]

- (A) Paraffin's and naphthenic to aromatics
(B) Paraffin's to hydrogen and CO
(C) Gas oil to diesel and gasoline
(D) Light olefins to gasoline

Q.17 The final boiling points of gasoline, diesel, atmospheric gas oil (AGO) and lubricating oil vary as

[GATE-2012]

- (A) Gasoline>diesel>AGO>lubricating oil
(B) Lubricating oil>AGO>diesel> gasoline

- (C) AGO>lubricating oil>diesel> gasoline
(D) Lubricating oil>diesel>AGO> gasoline

Q.18 Catalytic cracking is

[GATE-2014]

- (A) A hydrogen addition process
(B) A carbon rejection process
(C) An exothermic process
(D) A coking process

Q.19 Which one of the following statements is correct?

[GATE-2014]

- (A) The major components of biodiesel are triglycerides
(B) Biodiesel is essentially a mixture of ethyl esters
(C) Biodiesel is highly aromatic
(D) Biodiesel has a very low aniline point

Q.20 Match the following processes with their respective catalyst

| Group I | Group II |
|---|--------------------|
| Ethylene polymerization | Nickel |
| Petroleum feedstock cracking | Vanadium pentoxide |
| Oxidation of SO_2 to SO_3 | Zeolite |
| Hydrogenation of oil | Zeigler Nata |

[GATE-2014]

- (A) P-IV, Q-III, R-II, S-I
(B) P-I, Q-IV, R-III, S-II
(C) P-I, Q-II, R-III, S-IV
(D) P-II, Q-III, R-IV, S-I

Q.21 In connection with petroleum refining, identify the incorrect statement among the following options

[GATE-2018]

(A) Desalting of crude oil is done before processing it in atmospheric distillation unit

(B) A stream of hydrogen is produced in catalytic reforming of naphtha

(C) Asphalt used for paving is a petroleum product

(D) Cetane no. indicates the quality of petrol

| ANSWER KEY | | | | | | |
|-------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| D | B | D | B | A | B | C |
| 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| D | B | D | A | D | C | D |
| 15 | 16 | 17 | 18 | 19 | 20 | 21 |
| D | A | B | B | B | A | D |

| | | | | | | |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| D | B | D | B | A | B | C |
| 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| D | B | D | A | D | C | D |
| 15 | 16 | 17 | 18 | 19 | 20 | 21 |
| D | A | B | B | B | A | D |

6.1 Introduction

Petroleum is a fossil fuel. It is called a fossil fuel because it was formed from the remains of tiny sea plants and animals that died millions of years ago. When the plants and animals died, they sank to the bottom of the oceans. They were buried by thousands of feet of sediment and sand that turned into rock. Petroleum is a complex, naturally occurring liquid mixture containing mostly hydrocarbons, but containing also some compounds of oxygen, nitrogen and Sulphur. It is often referred to as the 'black gold'.

Over time this organic mixture was subjected to enormous pressure and heat as the layers increased. The mixture changed chemically, breaking down into compounds made of hydrogen and carbon atoms. Finally, an oil saturated rock much like a wet household sponge was formed. All organic material buried underground does not turn into oil. A typical petroleum reservoir is mostly sandstone/limestone in which oil is trapped.

It has wide application in manufacturing of polymer; ethylene and propylene are main products. Steam cracking is the heart of petrochemical industry.

Steam cracking has 3 sections:

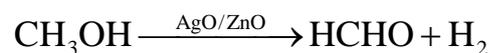
- 1) Hot section
- 2) Quench section
- 3) Cold section

In 1st hydrocarbon feed stock is preheated and mixed with steam heated to a temperature of 800°C and thermal cracking takes place. In quench section products are quenched with water to

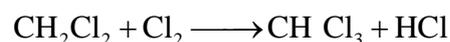
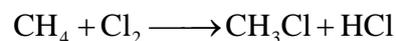
recover heat and to generate steam which is used in plant in cold section. Now firstly H₂ separation takes place then ethylene separation takes place then propylene separation takes place and so on.

6.2 Formation of HCHO in two step

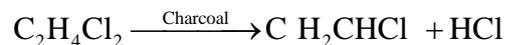
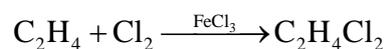
Catalytic conversion of CH₃OH to CH₃OH in presence of copper zeolite. CH₃OH is cracked to form HCHO in presence of silver or zinc oxide.



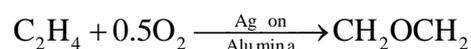
Chloromethanes:



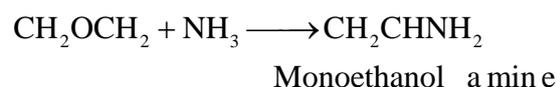
Vinyl Chloride:



Ethylene Oxide:

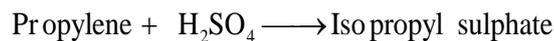


Ethanol amine:

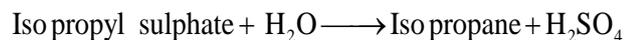


Isopropanol:

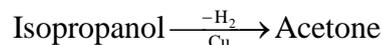
Sulphonation



Hydration



Acetone:



Cumene (isopropyl benzene):

Alkylation

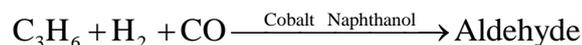


Acrylo Nitrile:

By ammoxidation of propylene



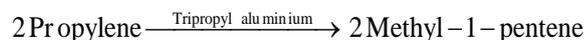
Oxo processing:



The reaction for aldehyde is known as hydroformylation reaction. For making of alcohols aldehyde undergoes hydrogenation in presence of Ni catalyst.

Isoprene:

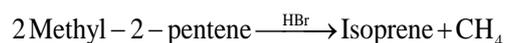
Dimerization



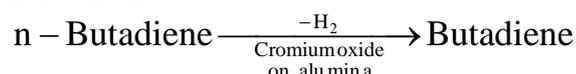
Isomerization



Pyrolysis

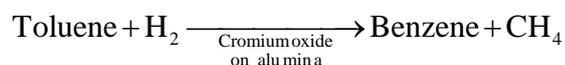


Butadiene:



Benzene:

Hydroalkylation of toluene to produce benzene

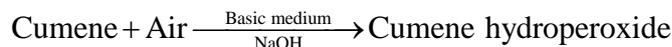


Phenol:

Phenol is produced by three methods:

1. From Cumene
2. From Toluene
3. From Benzene

1. From Cumene

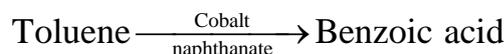


Sulphation



2. From Toluene

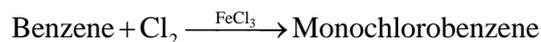
Oxidation of toluene to produce benzoic acid



Benzoic acid is reduced to give phenol



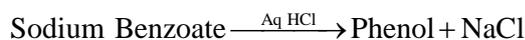
3. From Benzene



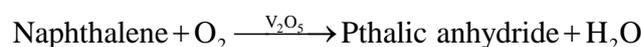
Causticizing



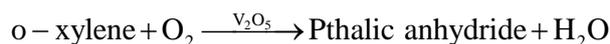
Hydrolysis in acidic medium



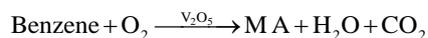
Phthalic Anhydride:



OR

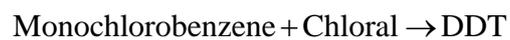
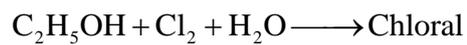


Maleic Anhydride (MA):



Dichloro Diphenyl Trichloro Ethane (DDT):

Chlorination of ethanol



Styrene:

1. Alkylation of benzene from ethyl benzene in presence of AlCl_3
2. Dehydrogenation of ethyl benzene in presence of FeO

GATE QUESTIONS

Q. 1 Styrene is produced from ethylbenzene by the process of

[GATE-2001]

- (A) dehydrogenation
- (B) oxidation
- (C) alkylation
- (D) dehydration

Q. 2 The commonly used solvent in supercritical extraction is

[GATE-2002]

- (A) methyl - ethyl - ketone
- (B) water
- (C) carbon tetrachloride
- (D) carbon dioxide

Q. 3 In a refinery, petroleum crude is fractionated into gas fraction, light ends, intermediate distillates, heavy distillates, residues and by products. The group of products including gas oil, diesel oil and heavy fuel oil belongs to the fraction

[GATE-2003]

- (A) heavy distillates
- (B) intermediate distillates
- (C) light ends
- (D) residues

Q. 4 The chief raw material for the commercial production for methanol is

[GATE-2005]

- (A) Synthesis gas
- (B) Formaldehyde
- (C) Acetic acid
- (D) Ethanol

Q. 4 Pair the following industrial processes in Group I with the catalysts used in Group II.

| | Group I | | Group II |
|---|---|-----|-------------------------------|
| P | Oxidation of o-xylene to phthalic anhydride | I | V ₂ O ₅ |
| Q | Oxidation of ethanol to acetaldehyde | II | Pd |
| R | Oxidation of ammonia to oxides of nitrogen | III | Ag |
| | | IV | Pt |

[GATE-2006]

- (A) P-1, Q-3, R-4
- (B) P-2, Q-1, R-4
- (C) P-4, Q-3, R-1
- (D) P-1, Q-3, R-2

Q. 5 The oxo-reaction is used for converting

[GATE-2006]

- (A) alcohol to aldehyde
- (B) paraffins to olefin
- (C) olefin to aldehyde
- (D) aldehyde to alcohol

Q. 6 Match the chemicals in Group I with their functions in Group II.

| | Group I | | Group II |
|---|-------------------------|-----|----------|
| P | Styrene | I | Buffer |
| Q | Tert-dodecyl mercaptan | II | Catalyst |
| R | Potassium pyrophosphate | III | Modifier |
| | | IV | Monomer |

[GATE-2007]

| | | | |
|-----|---|---|---|
| | P | Q | R |
| (A) | 1 | 4 | 4 |
| (B) | 4 | 1 | 2 |
| (C) | 4 | 1 | 3 |
| (D) | 4 | 3 | 1 |

Q. 7 Match the products in Group I with its applications in the industries of Group II.

| | Group I | | Group II |
|---|--------------------|-----|--------------|
| P | Lithium stearate | I | Cosmetics |
| Q | Magnesium stearate | II | Paper |
| R | Aluminium sulphate | III | Dry cleaning |
| | | IV | Greases |

[GATE-2007]

| | | | |
|-----|---|---|---|
| | P | Q | R |
| (A) | 2 | 3 | 1 |
| (B) | 3 | 4 | 2 |
| (C) | 4 | 2 | 3 |
| (D) | 4 | 1 | 2 |

Q. 8 Match the petrochemical derivatives in Group I with the raw materials in Group II.

| | Group I | | Group II |
|---|---------------|-----|-----------|
| P | Acrylonitrile | I | Methane |
| Q | Ammonia | II | Ethane |
| R | Dodecene | III | Ethylene |
| | | IV | Propylene |

[GATE-2007]

| | | | |
|-----|---|---|---|
| | P | Q | R |
| (A) | 1 | 2 | 1 |
| (B) | 2 | 1 | 2 |
| (C) | 3 | 4 | 3 |
| (D) | 4 | 1 | 4 |

Q. 9 Match the reactions in Group I with the products in Group II.

| | Group I | | Group II |
|---|-----------------|-----|------------------------------|
| P | Amoxidation | I | Aniline from benzene |
| Q | Nitration | II | Benzoic acid from toluene |
| R | Dehydrogenation | III | Acrylonitrile from propylene |
| S | Oxidation | IV | Styrene from ethylbenzene |

[GATE-2011]

- (A) P-III, Q-I, R-IV, S-II
 (B) P-IV, Q-I, R-III, S-II
 (C) P-I, Q-III, R-IV, S-II
 (D) P-I, Q-II, R-III, S-IV

Q.10 Pair the following industrial processes in Group I with the catalysts used in Group II.

| | Group I | | Group II |
|---|----------------------------------|-----|--------------------------------|
| P | Fischer tropesch | I | Nickel |
| Q | Formaldehyde from methanol | II | Fe ₂ O ₃ |
| R | Hydrogenation of vegetable oil | III | Ag |
| S | Dehydrogenation of methylbenzene | IV | Cobalt |

[GATE-2012]

- (A) P-III, Q-IV, R-I, S-II
 (B) P-IV, Q-II, R-I, S-III
 (C) P-IV, Q-III, R-I, S-II
 (D) P-III, Q-IV, R-II, S-I

Q.11 Pair the following industrial processes in Group I with the catalysts used in Group II.

| | Group I | | Group II |
|---|------------------------------------|-----|------------------|
| P | Propylene-butanol | I | Pyrolysis |
| Q | Cumene-phenol | II | Dehydrogenation |
| R | Butane-butadiene | III | Hydroformylation |
| S | Ethylene dichloride-vinyl chloride | IV | Peroxiation |

[GATE-2013]

(A) P-3, Q-2, R-4, S-1

(B) P-2, Q-4, R-3, S-1

(C) P-1, Q-3, R-2, S-4

(D) P-3, Q-4, R-2, S-1

| ANSWER KEY | | | | | | | | | | |
|-------------------|--|--|--|--|--|--|--|--|--|--|
|-------------------|--|--|--|--|--|--|--|--|--|--|

| | | | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| A | D | A | A | C | D | D | D | A | C | C |