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DEPARTMENT OF CHEMICAL ENGINEERING

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TREATMENT TECHNIQUES

- 3.1 Treatment techniques for removal of objectionable gases and to improve performance
- 3.2 Treatment of gasoline,
- 3.3 Treatment of kerosene,
- 3.4 Treatment of lubes.
- 3.5 Extraction of aromatics and olefins

3.1 Treatment techniques for removal of objectionable gases and to improve performance

The essential purpose of the primary processes is to produce the required amounts of the various products from the available crude. The products obtained are, as a general rule, unsuitable as such for immediate use, for the following reasons :

- 1) Inadequate performance, 2) Instability in storage, and 3) Objectionable odor and appearance and contamination with water or particulate matter. Secondary refining processes (finishing or treating processes), are required to give the products acceptable with respect to the above criteria.

Main Finishing Processes

- a) The removal of the objectionable gases (Acid gas removal).

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UNIT III

SCH1308

b) The removal of the objectionable odors.

c) The improvement in storage stability.

d) The improvement in performance characteristics.

e) The removal of water and particulate matter.

a) The removal of the objectionable gases

Hydrogen sulphide : Has to be removed from products because :

a) toxic, b) foul smelling, c) corrosive, d) traces of it may seriously contaminate regenerative treating solvents such as a solventizer used for final sweetening of the products.

A) Scrubbing with caustic soda : It is still the most widely used process for the removal of H_2S , mainly because it simultaneously removes other constituents such as CO_2 , carbonyl sulphide, lower aliphatic mercaptans, phenols fatty acids and naphthenic acids.

The disadvantage of this processes is that there is no known cheap method of regenerating the spent soda, and if H_2S is present in gross amounts, as is frequently in crude gases, especially the C_2 - C_3 fractions , a regenerative method of extraction such as the girbotol method is more generally used. This method is more economical than caustic washing but caustic washing may still be required as a final cleaning-up operation for the removal of the last traces of H_2S . The combination of the two processes not only provides a very low H_2S content economically but

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UNIT III

SCH1308

also safe guards against high sulfur contents in the treated products should there be a temporary failure of the regenerative treating plant.

In the caustic washing of gases rather weak solutions of 2-10%wt NaOH have to be used to prevent the deposition of sodium sulphide crystals. The reaction proceeds almost to the complete conversion of NaOH to NaHS. Traces of H₂S often appear in fractions much heavier than C₂ -C₃ fraction because of a slight breakdown of sulfur compounds owing to pyrolysis during re-distillation or a similar operation. Caustic soda may be employed for its removal.

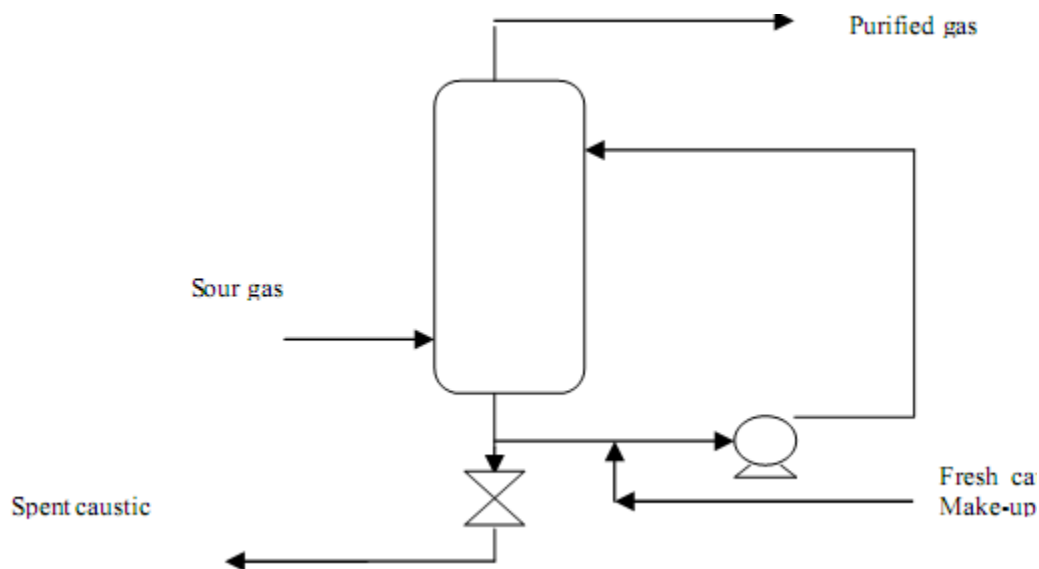


FIGURE.H₂S removal from gases by caustic washing

1) Copper Chloride Process

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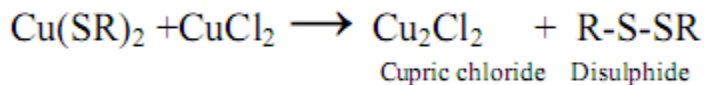
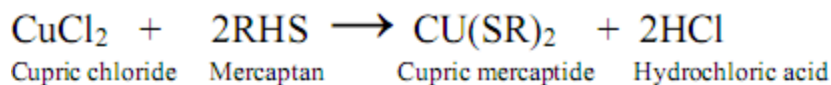
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UNIT III

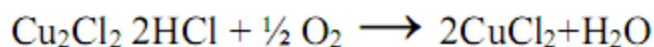
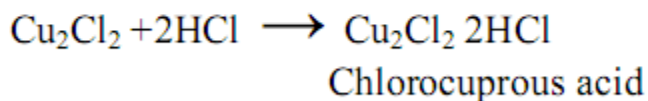
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The copper chloride process is used to sweeten gasolines and kerosenes by the directoxidation of mercaptans to disulphides, using cupric chloride as the oxidizing agent. The basic reactions of the process may be expressed as follows :

Sweetening



Regeneration



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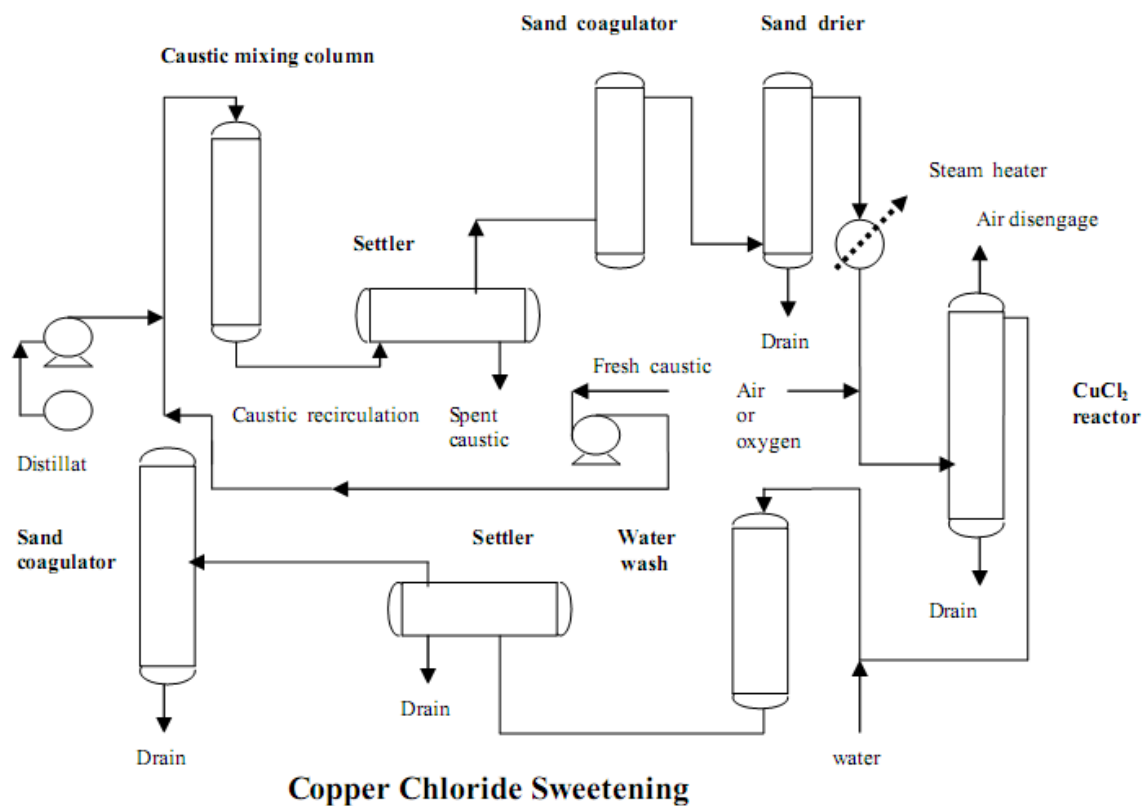
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UNIT III

SCH1308



1) The sour charge is caustic washed to remove traces of hydrogen sulphide which would otherwise deactivate the cupric chloride.

2) It then pass :

A) firstly through a sand coagulator to remove any caustic and / or water haze

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UNIT III

SCH1308

B) secondly through a rock salt drying lower to ensure complete removal of free water, which would adversely affect the water balance in the reactor.

3) After passing through a pre-heater to raise the temperature sufficiently to dissolve the water formed during the process, air or oxygen is injected into the line, and the dried and oxygenated feed flows upwards through the reactor which contains a bed of fullers earth impregnated with cupric chloride.

4) The sweetened product is water washed to remove traces of acidity, clarified from water haze in an up-flow sand coagulator and passed to storage.

2) Merox Process :

The Merox process, Developed by UOP (Universal Oil Products), is combination of mercaptan extraction and sweetening. The combined process is applicable to all gasoline and lighter boiling range fractions; the sweetening process is applicable to many jet fuel and kerosenes.

A) Merox Extraction:

1- The mercaptans are extracted by an aqueous solution of caustic soda according to

the reaction :

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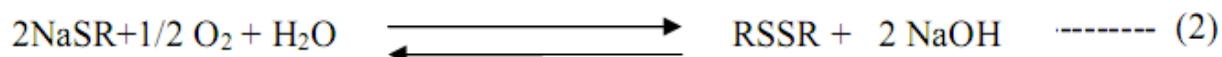
UNIT III

SCH1308



Since the reaction is reversible it is impossible to get complete removal of mercaptans by extraction without the use of an excessive amount of caustic soda solution. The forward reaction is favored by low temperature, low molecular weight of mercaptan and high caustic concentration. It is also promoted by the use of compounds that increase the solubility of the mercaptan in the aqueous phase, of these methanol, isobutyric acid and cresols.

2- The caustic is generated ,after separation from hydrocarbons by blowing with air in the presence of a catalyst at ambient temperature the reaction proceeding according to the reaction :



The disulphide so formed are insoluble in caustic soda and are removed in a gravity separator, the caustic is being re-circulated for further use. The catalyst which consists of an iron group metal chelate , may be in solution in the caustic, in which case the caustic and air are brought into contact in a reactor such as an orifice column, a mechanically stirred reactor or some other type of gas/liquid contactor. Alternatively the catalyst may be supported on a carrier, in which case the caustic and air are passed together over a packed bed.

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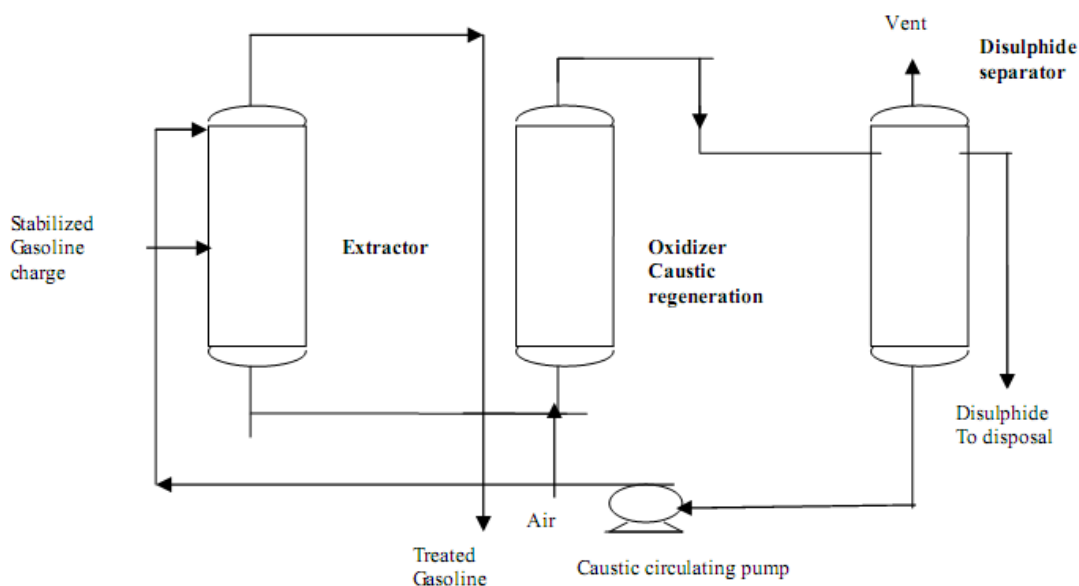
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UNIT III

SCH1308



Merox Extraction

B) Merox Sweetening

Sweetening is achieved by blowing a caustic hydrocarbon mixture with air in the presence of the catalyst where by disulphide are formed according to equation (2), and dissolve in the material being treated . As in the above mentioned regeneration process, the catalyst may be in solution in the caustic or held on carrier, and the process is carried out as described.

C) Combined Operation

The combined extraction/ Sweetening operation is carried out by a combination of the extraction and sweetening processes.

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UNIT III

SCH1308

c) Removal of Water and Particulate Matter In the Refinery

- 1) Water and particulate matter in the fuel can have disastrous effects on gas turbine blades.
- 2) Free water may cause corrosion through out a fuel distribution system.
- 3) Particulate matter may block filters or the fine orifices of fuel injection and burner.

Water may be removed by :

- 1) Physically 2) Chemically 3) Electro- statically

Particulate matter may be removed by:

- 1) Water washing 2) Filtration

Processes:

1) Salt Dryers: Used to remove water from water primary distillation products and to control the water content both before and after secondary processing. The product is passed through a vertical drum filled with suitably graded rock salt. Rock salts are not powerful desiccants; it will remove the free water but not dissolved water. If more dissolved water has to be removed it is usual to use calcium chloride in the dryer.

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COURSE MATERIAL

PETROLEUM AND PETRO CHEMICAL TECHNOLOGY

UNIT III

SCH1308

2) Electrostatic Coalescers : Uses electrical coalescing for the removal of free water and sodium chloride or calcium chloride for the removal of any residual traces of water. The process is used for the dehydration of heating oil, kerosene, jet fuel, diesel fuel and solvents. The dehydration product contains no free water but may contain some dissolved water.

3) Sand Coagulators and Filters : Vertical drums filled with fine sand are used for removal of particulate matter and water, this process have the advantage over salt dryers is not involving the use of chemicals. Down flow through the bed and up flow through a water separator will remove gross water but not haze. For this purpose the oil must pass upward through the bed with a bottom water drain so that it can emerge clear , and bright from the top of the drum, 5 micron peculator filter may be needed for turbo jet fuel.

4) Vacuum Flashing : Where difficulties might be met in the removal of water from high-boiling or viscous products by the previous methods, water may be removed by passing the product through a vessel at a sufficiently reduced pressure to cause the water to evaporates , it is used sometimes for the clarification of lubrication oil.

Improvement in Storage Stability

Owing to their complex composition and the presence of small amounts of N₂, S, organic acids, and oxygen, most petroleum products are subjected to deterioration in storage. This storage instability may be noticed by a darkening in color, the formation of gums, and in some cases a significant deterioration in those characteristics that control the performance of the products.

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COURSE MATERIAL

PETROLEUM AND PETRO CHEMICAL TECHNOLOGY

UNIT III

SCH1308

Instability may be accompanied by a marked degree of corrosiveness due to the presence of organic and/ or inorganic acids.

Caustic Extraction

In addition to the use of caustic soda for the removal of acidic gases and malodorous compounds as described earlier , it is widely used for the removal of substances which cause instability and corrosion.

e) Improvement in Performance

The performance characteristics of products from primary refining processes are seldom in keeping with the demands of modern machinery and engines. It is therefore often necessary to subject the products to secondary refining processes to remove those compounds that have an adverse effect on performance.

Performance improvement processes

1) SO₂ Extraction : Liquid SO₂ is very selective solvent for removal of aromatic hydrocarbons . SO₂ treatment removes aromatics and some polar compounds, including sulfur , gum and color constituents , as well as olefins. The process is used in the manufacture of premium kerosene the removal of aromatics leads to better burning properties.

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COURSE MATERIAL

PETROLEUM AND PETRO CHEMICAL TECHNOLOGY

UNIT III

SCH1308

2) H_2SO_4 Treatment : This process is used for the removal of sulfur and thiophene from aromatic streams . It is less applicable now a days as other treating methods are available . This process may be applicable for the pretreatment of straight run naphtha that are to be reformed.

3) Hydrodesulphurization : Hydrodesulphurization is the most modern and effective processes for the removal of sulfur from oil products and for general improvement in the quality of refinery streams, including the pretreatment of catalytic reformer feed. The process convert S to H_2S by reaction with hydrogen in the presence of catalyst. This process is used mainly for the processing of straight run and cracked medium and heavy distillates, while vapor phase hydrotreating is used for the processing of light distillates it operates at lower pressure.

Thiophen

Thiophen and mono-methyl thiophens have been isolates from gasoline: alkyl-thiophens and benzo-hiophens have been isolates from kerosience. In gas oil range substituted thiophens, benzo-hiophens and higher polycyclic thiophens are present

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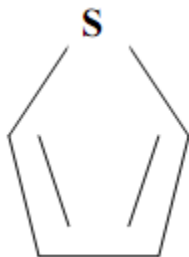
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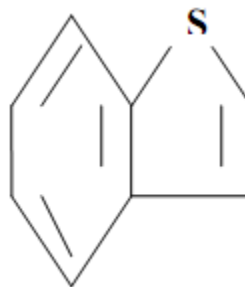
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UNIT III

SCH1308



Thiophen



Benzo thiophen

Two general methods of reducing the amount of sulfur have been developed, those which involve

- 1) solvent extraction of the sulfur compounds and
- 2) those by which most of the sulfur compounds are decomposed by the use of a catalyst into hydrogen sulfide and the remaining hydrocarbon part of the molecule.

The solvent extraction processes are not cheap or effective as the catalytic processes in the removal of sulfur because they remove the entire sulfur bearing molecule and at the same time certain hydrocarbons, particularly those with aromatic rings. This when the removal of aromatic hydrocarbons as well as sulfur is desirable, the solvent process may be superior. H_2SO_4 , HF are an effective solvent, but SO_2 and furfural are more frequently used. The solvent process tends to raise the pour point and moderately improve the Diesel Index, but the catalytic processes of desulphurization do not materially affect either of these properties. Yields by the catalytic processes may exceed 100% especially if outside hydrogen is used.

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UNIT III

SCH1308

By the addition of H_2 from outside sources more vigorous reaction (decomposition) and hydrogenation can be undertaken, and in the extreme, whole crude oils and residues can be desulphurization. Desulphurization is a mild selective hydrogenation, so mild that aromatic are not usually hydrogenation to naphthenes. Sulfur is removed as H_2S and the remaining part

of the molecule is hydrogenated. Mild decomposition result in an evolution of hydrogen which can be recycled for hydrogenation reactions but if higher boiling or refractory stocks are being treated, extra H_2 must be introduced from outside sources to maintain a higher concentration of hydrogen during the reaction. The decomposition leads to products of slightly lower boiling range than that of the parent material slightly API gravities.

Efficiency of desulphurization depends upon the charge stock and severity of treatment, ranging from as low as 50 to 60 % for mild operation to 80 to 99 % and 95 to 98% is not uncommon.

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UNIT III

SCH1308

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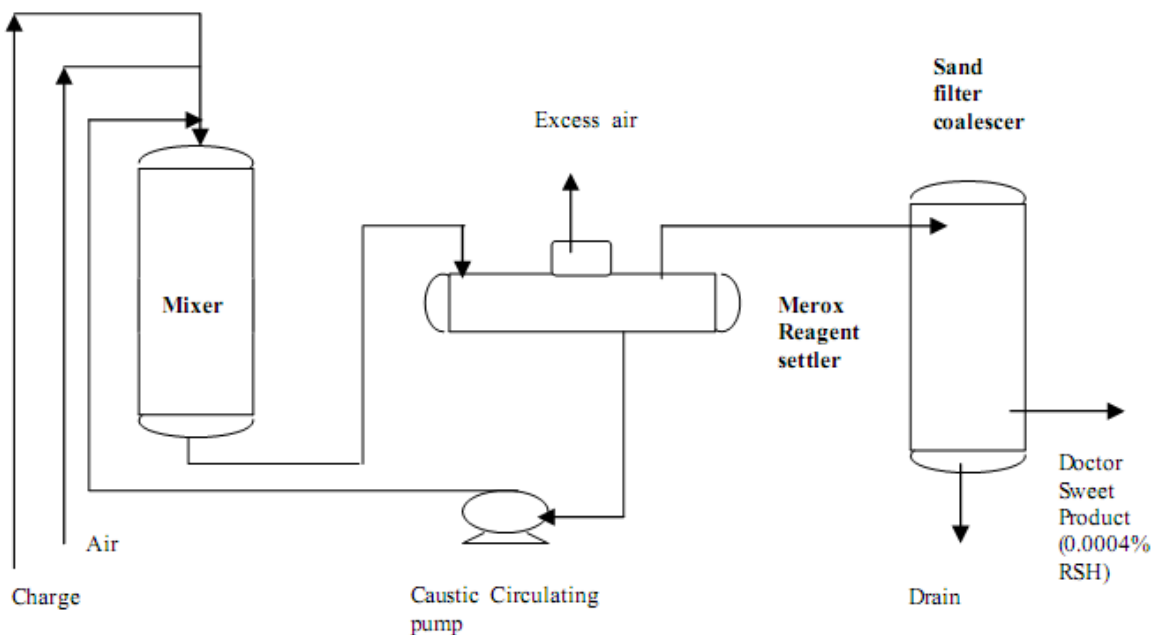
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UNIT III

SCH1308



Merox Sweetening

3.2 Treatment of gasoline,

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UNIT III

SCH1308

3.2 Treatment of Gasoline

Gasoline Treatment

Offending compounds in gasoline are doctored by contacting with different chemicals. In fact gasoline sweetening is done by all available techniques. Despite lead free gasolines command premium, it may not be possible to supply lead free gasoline always. When TEL is to be added, severe sweetening actually harms the product, so a meticulous balance should be maintained to give improved lead susceptibility. Odourous methyl and other mercaptans, and thiophenols are kept at less than 0.002 ppm in gasoline to give a negative doctor test, for jet fuels, the figure is kept at 20 ppm to give a satisfactory copper strip corrosion test (3 hrs at 50°C).

COPPER CHLORIDE PROCESS

Please refer the above pages

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UNIT III

SCH1308

3.3 Treatment of Kerosene

For kerosenes (illuminating oils) a single treatment technique like desulfurisation is not sufficient; as the illuminating quality of kerosene is not improved in this operation. Smoke point improvement is achieved by removing smoke causing ingredients, namely aromatics. Formulations of good kerosene touch a maximum limit of 20% aromatics. Aromatics in the kerosene range are preferably of single ring structures with side chains. Oldest process for the removal of aromatics is liquid sulfur dioxide extraction invented by Edeleanu (1905), since that time it continues to enjoy a commanding position.

Liquid sulfur dioxide extraction is carried out at a temperature of -14°C , the extract of which contains normally copious amounts of solvent. Aromatics from extract can be freed, just by self evaporation of solvent. The selectivity of anhydrous liquid sulfur dioxide is excellent for aromatic constituents. Although a good number of solvents are pressed into service, still the universal replacement of the old process has not been ventured.

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UNIT III

SCH1308

3.4 Treatment of lubes.

Manufacturing of Lubricating Oils

The large number of natural lubricating and specialty oils today are produced by blending a small number of lubricating oil base stocks and additives. The lube oil base stocks are prepared from selected crude oils by distillation and special processing to meet the desired qualifications. The additives are chemicals used to give the base stocks desirable characteristics which they lack or to enhance and improve existing properties.

The properties that are considered important : 1) Viscosity, 2) Viscosity index, 3) Pour point, 4) Oxidation resistance, 5) Flash point, 6) Boiling temperature, and 7) Acidity (Neutralization number)

Lubricating oil Processing

1) Separation of the individual fractions : according to viscosity and boiling range specifications in crude oil distillation units. The heavier lubricating oil row stocks are included in the vacuum fractionating tower bottoms with the asphaltenes resin, and other undesirable materials.

2) Removal of components which have undesirable characteristics

a) Reduce carbon- and sludge forming tendencies (Solvent deasphalting)

b) Improve viscosity index (Solvent extractions + Hydrocracking)

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c) Lower Cloud and pour points (Solvent De-waxing + Selective hydrocracking)

d) Improve color and oxygen stability (Hydrotreating)

e) Lower organic acidity (Hydrotreating)

Although the main effects of the processes are as discussed, there are also secondary effects which are not shown . For example, although the main result of solvent dewaxing is the lowering of the cloud and pour points of the oil, solvent dewaxing also slightly reduces the viscosity index of the oil. For economic reasons as well as process ones, the process sequence is usually in the order of :1) deasphalting, 2) solvent extraction, 3) dewaxing, and 4)finishing.

Propane Deasphalting

The lighter feed stocks for producing lubricating oil stocks can be sent directly to the solvent extraction units. The atmospheric and vacuum still residues require deasphalting to remove the asphaltenes and resins before undergoing solvent extraction. In come cases highest boiling distillates also contain sufficient asphaltenes and resins and need deasphalting. Propane : is usually used as the solvent in seasphalting but it may be used with ethane and butane in order to obtain the desired solvent properties. (40- 60 °C) paraffins are very soluble in propane, the solubility decreases with increasing temperature, until the critical temperature (96.8 °C) all HC becomes insoluble. (40 – 96.8 °C) the high molecular weight asphaltens and resins are largelyinsoluble in propane. The feed stock is contacted with 4-8 volumes of liquid propane in a cylindrical tower, usually RDC (rotating disc contactor). The asphalt recovered from the

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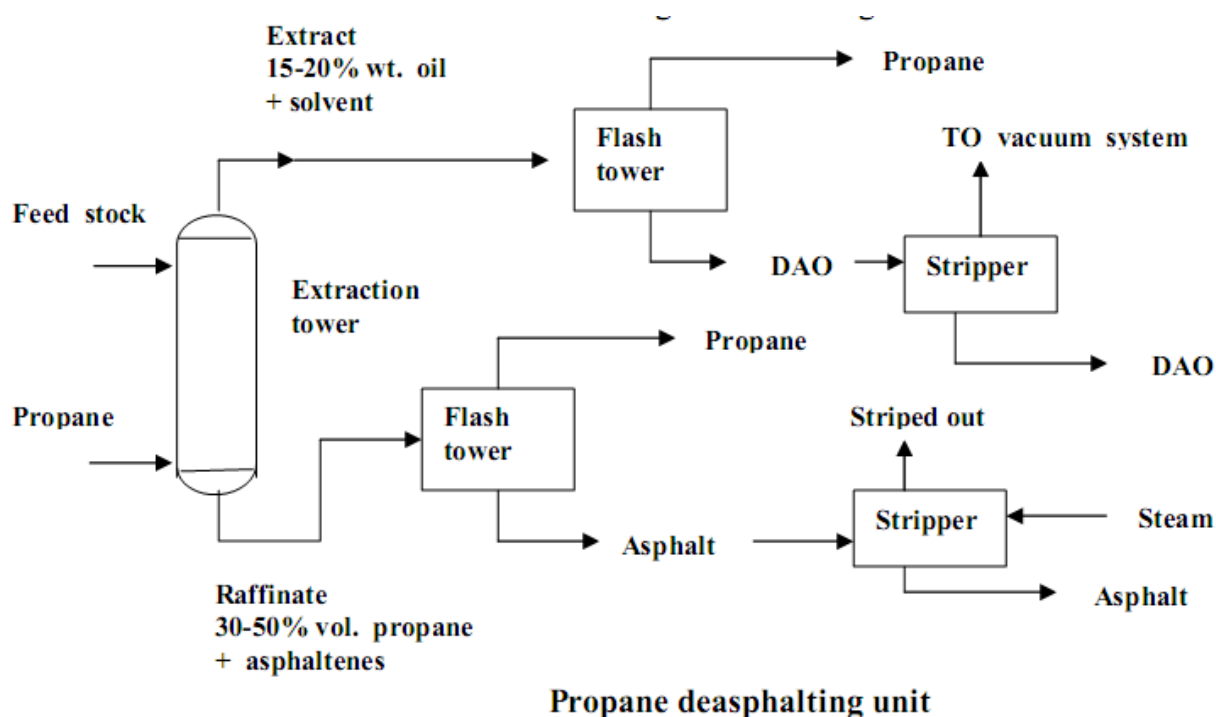
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UNIT III

SCH1308

raffinate can be blended with other asphalts, into heavy fuels, or used as a feed to the coking unit. The heavy oil product from vacuum residuum is called bright stock.



Solvent Extraction

There are three solvents used for the extraction of aromatics from lubricating oil feed stocks and the solvent recovery portions of the system are different for each.

The solvents are : 1) Furfural, 2) phenol, 3) N- methyl 2- pyrrolidone (NMP).

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UNIT III

SCH1308

The purpose of solvent extraction is :

- 1) Improve VI.
- 2) Improve oxidation resistance and color.
- 3) Reduce carbon and sludge forming tendencies of the lubricants by separating the aromatic portion from the naphthenic and paraffinic portion of the feed stock. Furfural Extraction The most important operating variables are :
 - 1) Furfural / oil ratio (F / O ratio) :It has the greatest effect on the quality and yield of the raffinate. Range 2:1 for light stocks to 4.5 : 1 for heavy stocks.
 - 2) Extraction temperature : Is selected as a function of the viscosity of the oil and the miscibility temperature.
 - 3) Extracted recycle ratio : Determines to some extent the rejection point for the oil and the sharpness of separation between the aromatics and naphthenes and paraffins.

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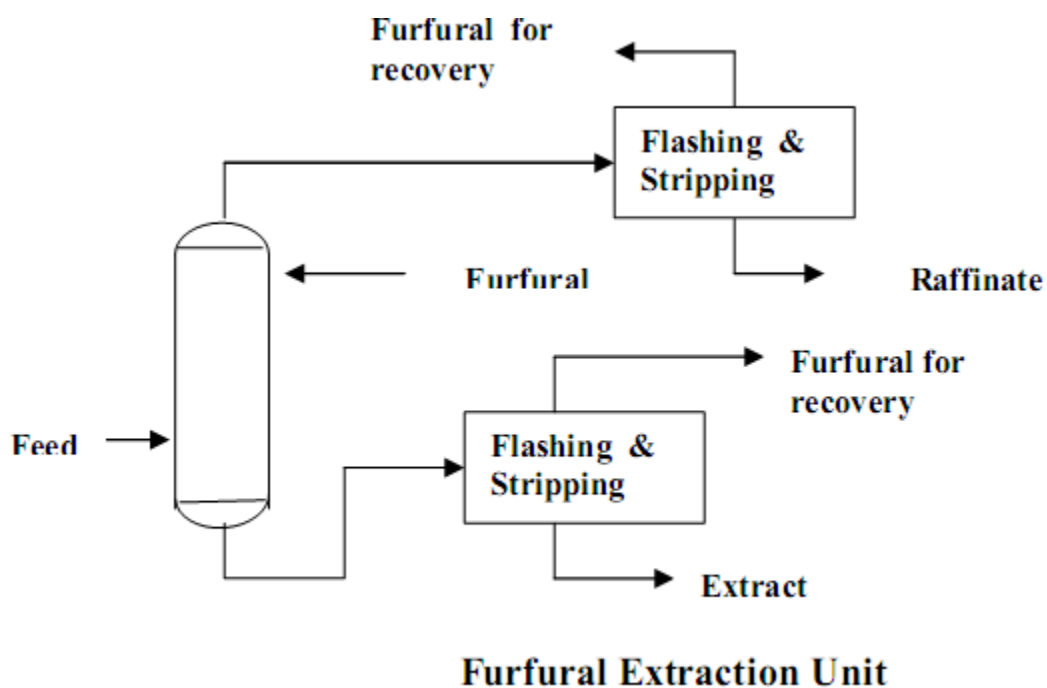
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UNIT III

SCH1308



Dewaxing

All the lubricating oil except those from a relatively naphthenic crude oils, must be dewaxed or they will not flow properly at ambient temperature. Dewaxing is one of the most important and most difficult processes in lubricating oil manufacturing.

There are two types of processes in use today :

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UNIT III

SCH1308

1) Uses refrigeration to crystallize the wax and solvent to dilute the oil portion sufficiently to permit rapid filtration to separate the wax from the oil.

2) Uses selective hydrocracking process to crack the wax molecules to light HC. Solvent dewaxing : The solvent used are

a) Propane

1) Readily available, less expensive and easier to recover

2) Direct chilling can be accomplished by vaporization of the solvent thus reducing the capital and maintenance costs of scraped- surface chiller.

3) High filtration rate can be obtained because of its low viscosity at very low temperature.

4) Requires use of a dewaxing aid.

5) Large difference between filtration temperature and pour point of finished oils (15 to 25 oC)

b) Ketone

1) Small differences between filtration temperature and pour point of dewaxing oil (5 to 10 oC).

2) Fast chilling rate.

3) Good filtration rate but lower than propane.

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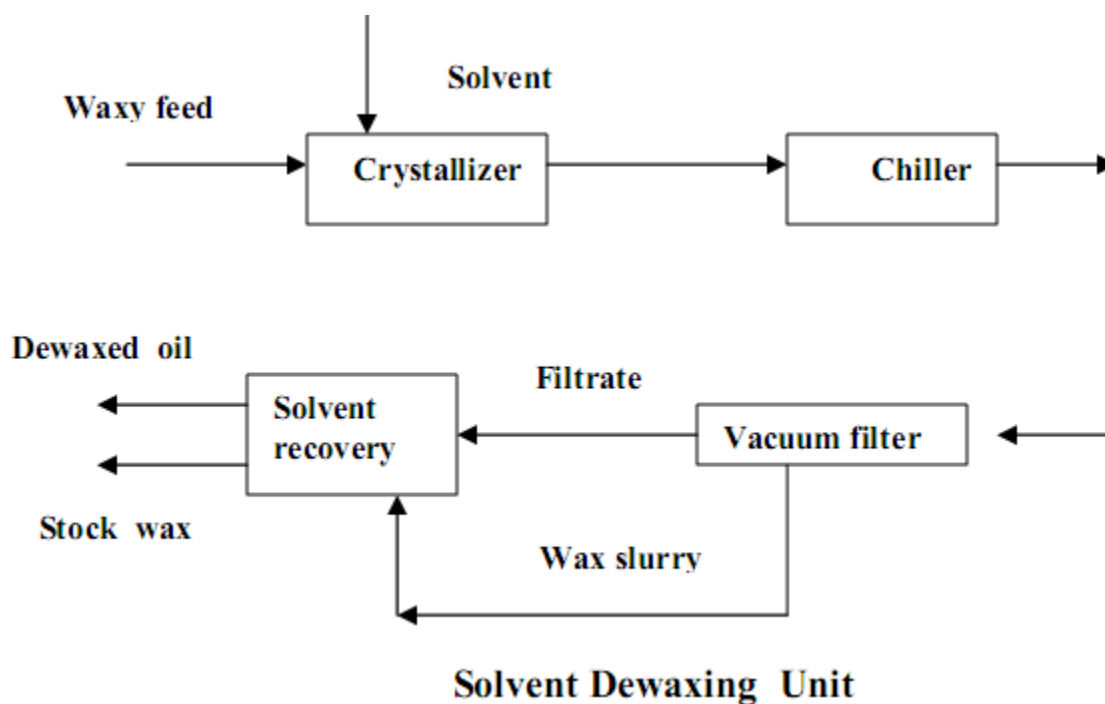
UNIT III

SCH1308

Lower pour point capability : Greater recovery of heat by heat exchanger lower refrigeration requirements.

The dewaxed oil next must go through a finishing step to improve its color and color stability.

The stock wax is used either for catalytic cracker feed or undergoes a de-oiling operation before sold as industrial wax.



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UNIT III

SCH1308

Selective hydrocracking :

The feed to selective hydrocracking unit is solvent extracted oil from aromatic extraction units.

The advantages over conventional solvent dewaxing unit

- 1) Production of very low pour and cloud oils from paraffinic stocks.
- 2) Lower capital investment.
- 3) Improved lubrication oils base stock yields.
- 4) A separate hydrofinishing operation is not necessary.

Hydrofinishing

This process is needed to remove chemically active compounds that affect the color stability of lubrication oils. Most hydrotreating operation use cobalt- molybdate catalysts. The removal of nitrogen compounds is a major requirement of the operation because it affect color, usually finished oil yields are approximately 98% of dewaxed oil feed.

Hydrotreating

Hydrotreating: It is a relatively mild operation whose primary purpose is to saturate olefins and/ or reduce the sulfur and/ or nitrogen content (and not to change the boiling range) of the feed.

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COURSE MATERIAL

PETROLEUM AND PETRO CHEMICAL TECHNOLOGY

UNIT III

SCH1308

Hydrocracking : Processes whose primary purpose is to reduce the boiling range in which 100% of the feed is converted to product with boiling ranges lower than that of the feed. Hydrotreating and hydrocracking set the two ends of the spectrum and those processes with a substantial amount of sulfur and/ or nitrogen removal and a significant change in boiling range of the products versus the feed are called hydro- processing.

Hydrotreating is a process to catalytically stabilize petroleum products and/ or to remove objectionable from products or feeds stocks by reacting them with hydrogen. Stabilization : Involves converting unsaturated hydrocarbons such as olefins and gum- forming unstable diolefines to paraffins, objectionable elements removed by hydrotreating include sulfur, nitrogen, oxygen , halides, and trace metals. Hydrotreating is applied to wide range of feeds stocks from naphtha to reduce crude . When the process is applied specifically for sulfur removal it is usually called hydrodesulfurization

- 1) The oil feed is mixed with hydrogen- rich gas either before or after it is preheated to the proper reactor inlet temperature, below 800 oF to minimize cracking in the presence of metal oxide catalyst.

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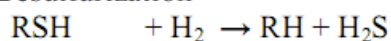
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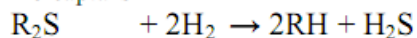
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Reaction

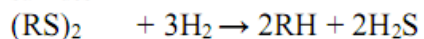
1) Desulfurization



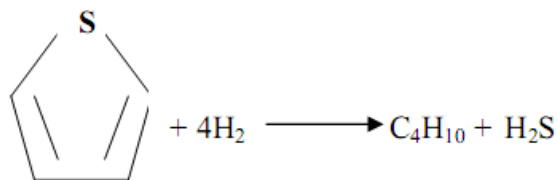
mercaptans



sulfides

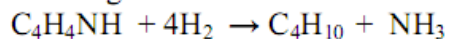


disulfides

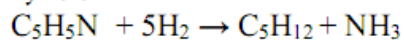


Thiophens

2) Denitrogenation

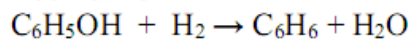


Pyrrole

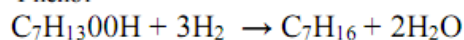


Pyridine

3) Deoxidation

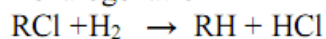


Phenol

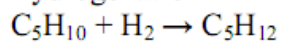


Peroxides

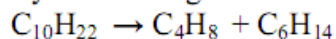
4) Dehalogenation



5) Hydrogenation



6) Hydrocracking



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Nitrogen removal requires more severe operating conditions than does desulfurization. The ease of desulfurization is dependent upon the type of compound. Lower boiling compounds are desulfurized more easily than higher boiling ones.

3.5 Extraction of Aromatics

EXTRACTION OF AROMATICS

- Benzene, toluene, xylenes (BTX), and ethylbenzene are obtained from the catalytic reforming of heavy naphtha.
- The product is rich in C6, C7, and C8 aromatics, which is extracted by sulfolane or ethylene glycol.
- These solvents are characterized by a high affinity for aromatics, good thermal stability, and rapid phase separation. The process is [Tetra extraction process](#) uses tetraethylene glycol as a solvent.
- The feed (reformate), contains a mixture of aromatics, paraffins, and naphthenes → heat exchange with hot raffinate, is countercurrently contacted with an aqueous tetraethylene glycol solution in the extraction column.
- The hot, rich solvent containing BTX aromatics is cooled and introduced into the top of a stripper column.
- The aromatics extract is then purified by extractive distillation and recovered from the solvent by steam stripping.

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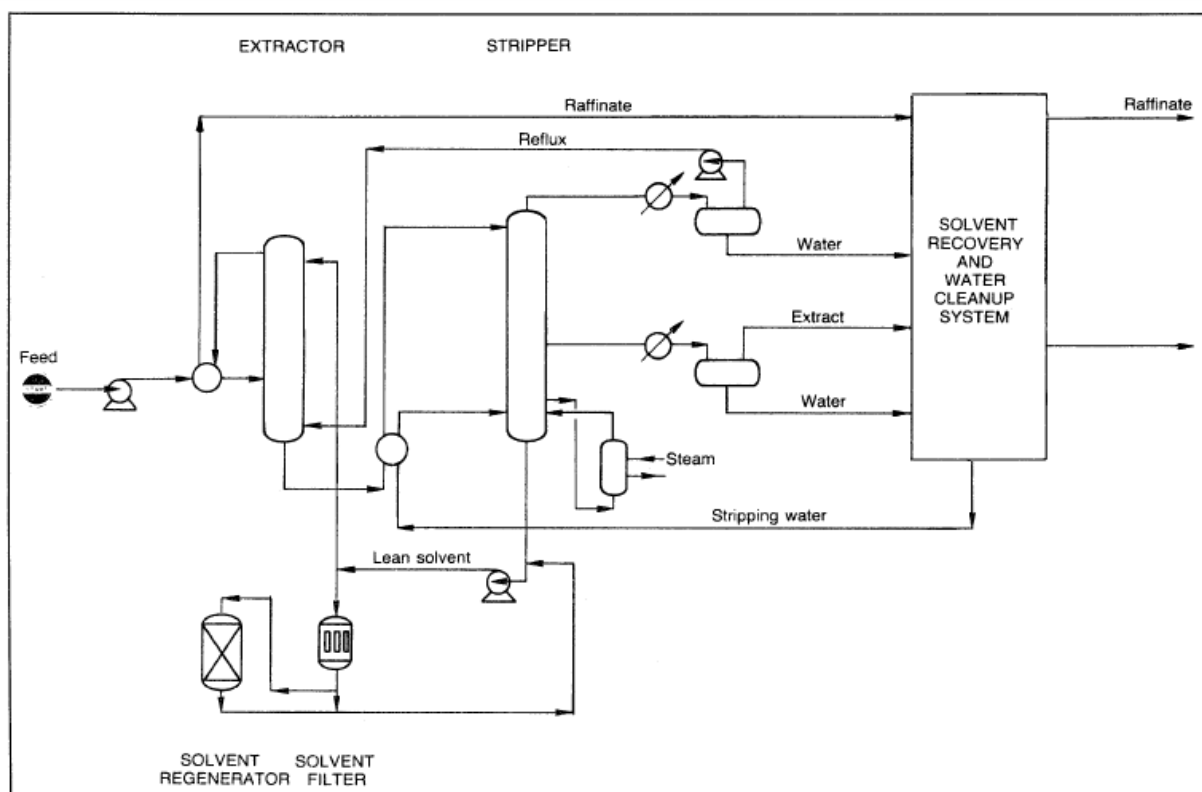
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The Union Carbide aromatics extraction process using tetraethylene glycol.

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- The raffinate (constituted mainly of paraffins, isoparaffins and cycloparaffins) is washed with water to recover traces of solvent and then sent to storage. The solvent is recycled to the extraction tower.
 - The extract, which is composed of BTX and ethylbenzene, is then fractionated. Benzene and toluene are recovered separately, and ethylbenzene and xylenes are obtained as a mixture (C8 aromatics).
 - Due to the narrow range of the boiling points: C8 aromatics are separation by fractional distillation is difficult. A super-fractionation technique is used to segregate ethylbenzene from the xylene mixture.
 - p-xylene is recovered from the xylene mixture by fractional crystallization.
-
- The overall yield of p-xylene is increased by incorporating an isomerization unit to isomerize o- and m-xylenes to p-xylene.
 - An overall yield of 90% p-xylene could be achieved.

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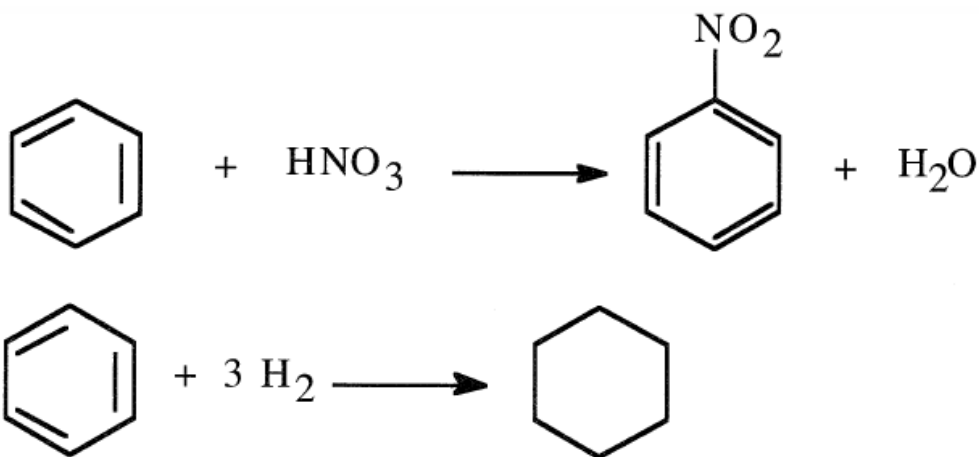
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- In this process, partial conversion of ethylbenzene to benzene also occurs. The catalyst used is shape selective and contains ZSM-5 zeolite.

Benzene

- Benzene (C_6H_6) is mainly obtained from catalytic reforming. Other sources are pyrolysis gasolines and coal liquids.
- Benzene is an important chemical intermediate and is the precursor for
- many commercial chemicals and polymers such as phenol, styrene for poly-styrenics, and caprolactom for nylon 6.



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Ethylbenzene

- Ethylbenzene ($C_6H_5CH_2CH_3$) is one of the C8 aromatic constituents in reformates and pyrolysis gasolines. It can be obtained by intensive fractionation of the aromatic extract.
- ethylbenzene is obtained by the alkylation of benzene with ethylene.

Methylbenzenes (Toluene and Xylenes)

- Methylbenzenes occur in small quantities in naphtha and higher boiling fractions of petroleum.
- The primary sources of toluene and xylenes are reformates from catalytic reforming units, gasoline from cat-cracking, and pyrolysis gasoline from steam reforming of naphtha and gas oils

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- Solvent extraction is used to separate these aromatics from the reformat mixture.
- Toluene and xylenes have chemical characteristics similar to benzene, but these characteristics are modified by the presence of the methyl substituents.
- Currently, the largest single use of toluene is to convert it to benzene. para-Xylene is mainly used to produce terephthalic acid for polyesters.
- o-Xylene is mainly used to produce phthalic anhydride for plasticizers.