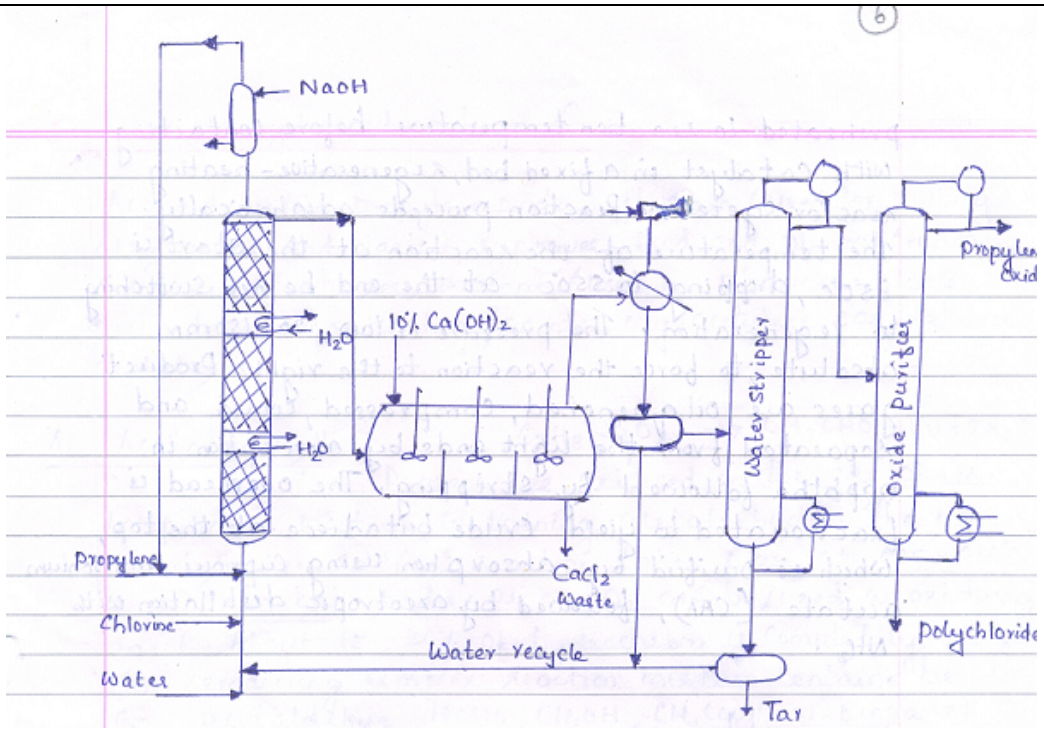
WINTER-15 EXAMINATION

Model Answer

Important Instructions to examiners:

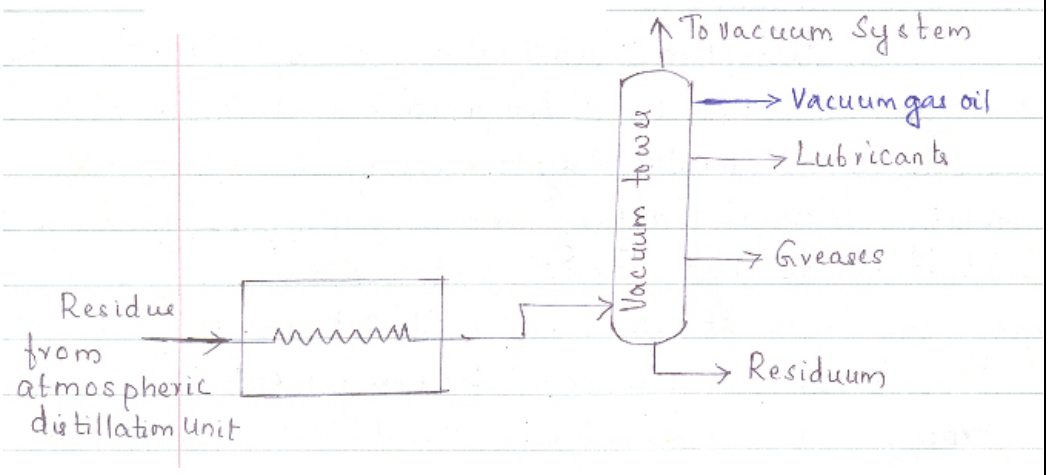
1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling errors should not be given more Importance (Not applicable for subject English and Communication Skills.
4) While assessing figures, examiner may give credit for principal components indicated in the figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.
5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.
6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.
7) For programming language papers, credit may be given to any other program based on equivalent concept.

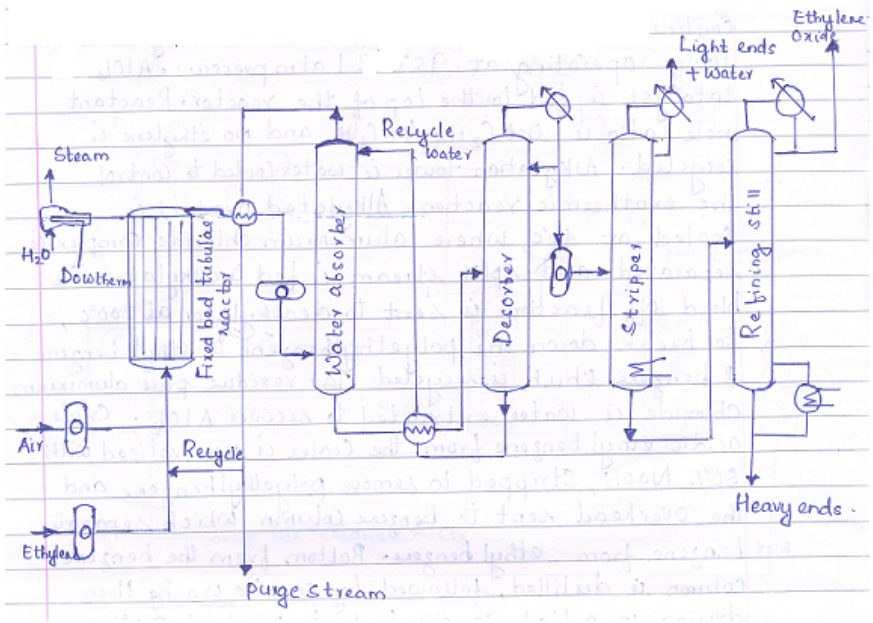
<table>
<tr><th>Q No.</th><th>Answer</th><th>marks</th><th>Total marks</th></tr>
<tr><td>1a-i</td><td>Four Indian refineries with their location and capacity.
<table>
<tr><th>Name</th><th>Location</th><th>Capacity (MMTPA)</th></tr>
<tr><td>Reliance petroleum Ltd</td><td>Jamnagar</td><td>33</td></tr>
<tr><td>Indian Oil Corporation Limited</td><td>Koyali in Gujarat</td><td>13.7</td></tr>
<tr><td>Manglore Refinery and Petrochemicals Ltd</td><td>Manglore in Karnataka</td><td>9.69</td></tr>
<tr><td>Chennai Petroleum Corporation Ltd</td><td>Manali</td><td>9.5</td></tr>
</table>
Note:
Any other Indian refineries should be given due consideration</td><td>1 mark each</td><td>4</td></tr>
<tr><td>1-a-ii</td><td>Definition:
1)OctaneNo:It is defined as the percentage volume of isooctane in a mixture of isooctane and – heptanes that gives the same knocking characteristics as the fuel under consideration.
2) Aniline point:It is defined as the minimum temperature at which equal volumes of anhydrous aniline and oil mix together.
3) Drop point.Drop point is the temperature at which the thickener is so soluble in the base oil that the grease becomes substantially fluid.
4)Flash point: It is the minimum temperature at which oil will give enough vapours for giving a momentary flash when a flame is brought near it.</td><td>1 mark each</td><td>4</td></tr>
<tr><td>1a-iii</td><td>Flow sheet for the manufacture of propylene oxide from propylene</td><td></td><td>4</td></tr>
</table>

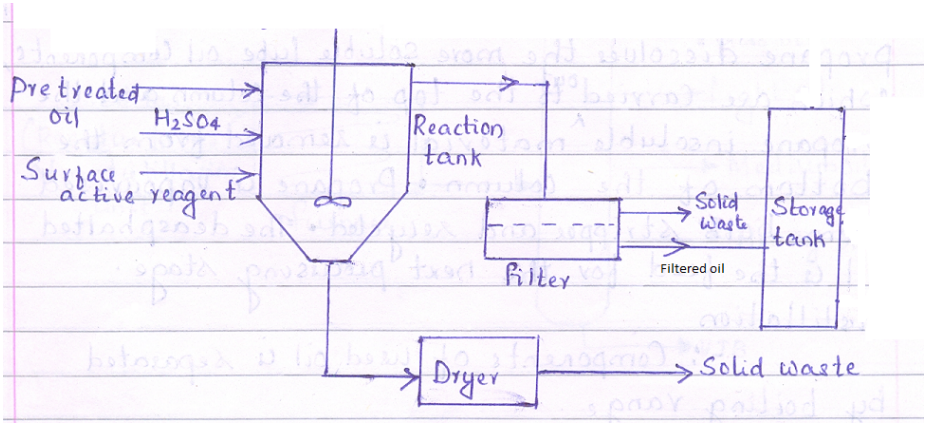
		4	
1a-iv	**Refinery:** Refinery is composed of a group of chemical engineering unit processes & unit operations used for refining certain material into products of value. **Explanation for types of refineries-** 1.Primary refinery: Simplest refinery consisting only of a distillation unit to produce residual asphalt and sell all of overhead to another refinery. 2. Intermediate refinery: Produces motor fuel, distillate fuels and residuals 3. Complex refinery: The products of distillation are send to other units for further processing and producing new products.	2 2	4
1b-i	**Fractions obtained from crude oil with their boiling point range and uses(Any six)**	1 mark each	6

Fractions	Boiling point range	Uses
1. Uncondensed gases	□ 30°C	Domestic fuel, synthesis of organic chemicals
2. Petroleum ether	30-70°C	Solvent for fats, essential oils, used in dry cleaning.
3.Gasoline or petrol or motor spirit	40-120°C	As a motor fuel for IC engines, solvent, in dry cleaning.
4. Naphtha	120-180°C	As a solvent and in dry cleaning, feed stock for petrochemicals.
5. Kerosene oil	180-250°C	Illuminant, fuel for stoves
6. Diesel oil	250-320°C	Diesel engine fuels, carbureting of water gas

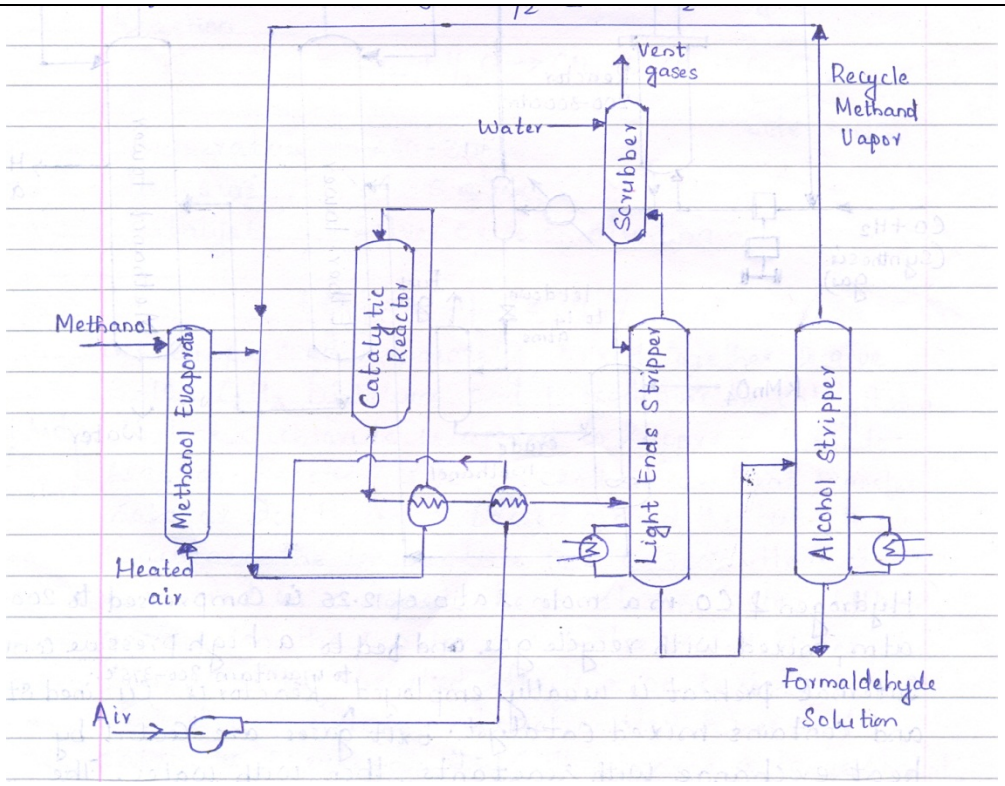
		7.Heavy oil On vacuum distillation of heavy oil gives lubricating oil, petroleum jelly, greases, paraffin wax etc.	320-400^{o}C	Fuel for ships, metallurgical furnaces, feed stock for cracking processes.		
		8.Residue	□ 400^{o}C	Used for making roads and water proofing roof, as a fuel, for moulding electrode rods.		
1b-ii	**Importance of vacuum distillation in crude oil refining.** In atmospheric distillation of crude oil, it is important not to subject the crude oil to temperature above 370 to 380^{o}C because the high molecular weight components will undergo thermal cracking and form petroleum coke at temperature above that. In vacuum distillation unit, distillation is carried out at an absolute pressure of 10 to 40 mm of Hg so as to limit the operating temperature to less than 370 to 380^{o}C. Vacuum distillation helps to maximize the recovery of valuable distillates. **Explanation with diagram.** The residue from the atmospheric distillation column is send to vacuum distillation unit where absolute pressure is maintained at 10 to 40mm of Hg using multiple stages of steam jet ejectors. Vacuum columns have large				2 2	6

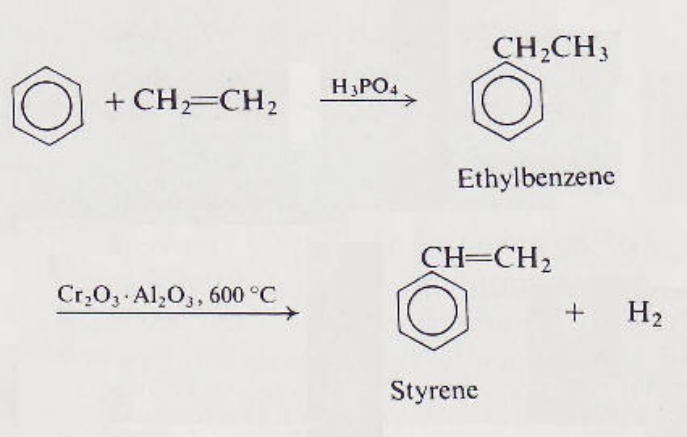
	diameters. They use distillation trays only when products have to be withdrawn from sides. Often packing materials like structured sheet metal or randomly packed Raschig rings are used because packings has low pressure drop than distillation trays. The bottoms of vacuum distillation column is known as Goudron or residuum.  	2	
2-a	**Factors affecting the prices of crude oil** (any four to be written) 1. Production of crude oil: OPEC nations are the major producers of worldscrude oil. Any decision by them to increase or decrease production affects the prices of crude oil. 2. Natural causes (weather) : Extreme weather conditions(hurricanes, thunderstorms) affects production and increases the prices of oil. 3. Supply and demand: Since OPEC has sufficient reserves, they can directly influence market pricing especially when supply of oil produced by non OPEC nation decreases. 4. Restrictive legislation: Energy policies and taxes of oil rich countries affectthe prices of oil. 5. Political unrest: If an oil rich area becomes politically unstable, supplier markets react by bidding up the prices of the oil so that supplies are available to	1 mark each	4

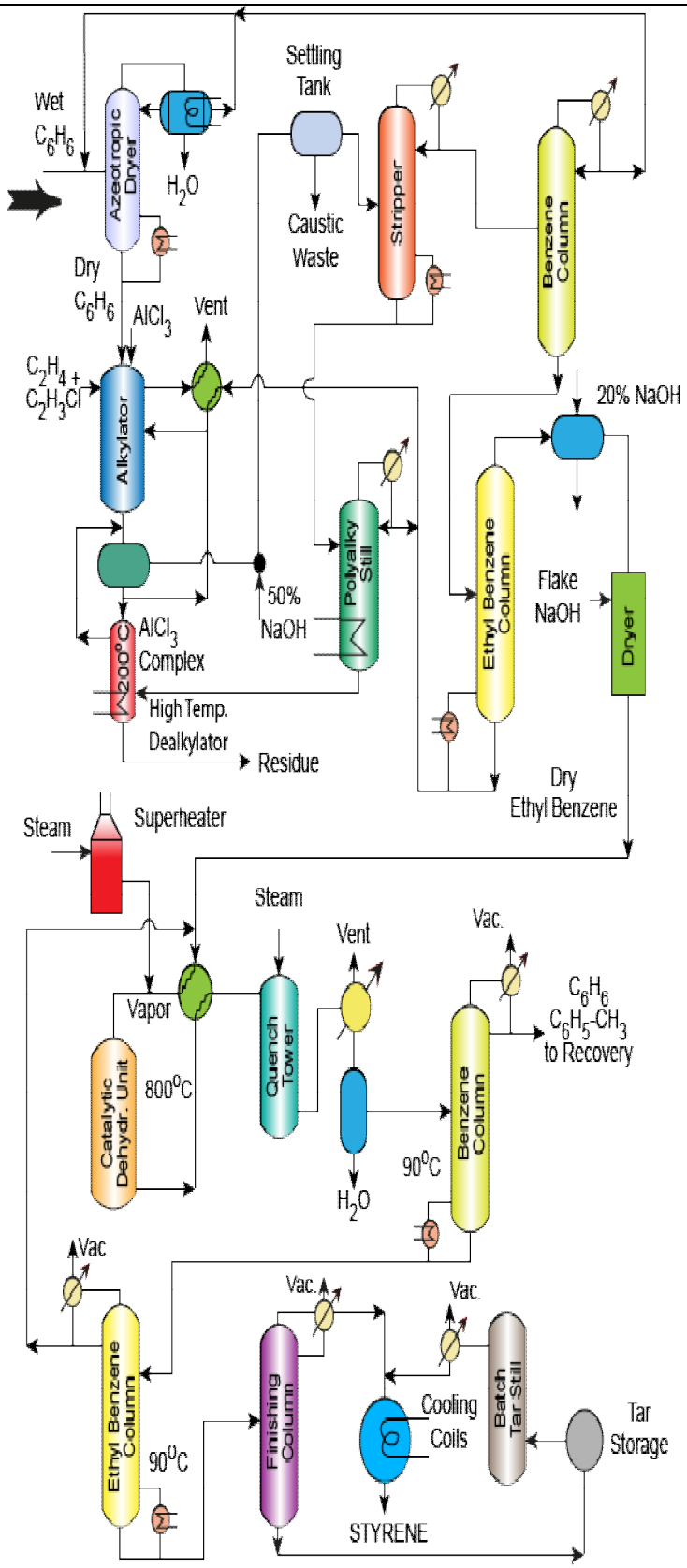
	the highest bidder. 6. Production: Location of reserves, amount and properties of oil found , geological formation in which oil is found, cost of extraction etc affects the cost of oil supplied from a particular reserve. 7. Exchange value of dollar: Dollar depreciation tends to increase oil demand and increases the prices of oil.		
2-b	**Flow sheet for the manufacture of ethylene oxide** 	4	4
2-c	**Reactions involved in the manufacture of methanol:** Methanol is produced by catalytic hydrogenation of CO Main reaction: $CO + 2H_2 \rightarrow CH_3OH$ Side reactions: $CO + 3H_2 \rightarrow CH_4 + H_2O$ $2CO + 2H_2 \rightarrow CH_4 + CO_2$ $xCO + y\ H_2 \rightarrow$ high molecular weight alcohols and hydro carbon **Reactions involved in the manufacture of propylene oxide:** It is produced via chlorohydrin route.	2	4

	Chlorohydrination: $CH_3CH=CH_2 + HOCl \rightarrow CH_3\text{-}CHCl\text{-}CH_2OH$ Dehydrochlorination: $2CH_3\text{-}CHCl\text{-}CH_2OH + Ca(OH)_2 \rightarrow 2C_3H_6O + CaCl_2 + 2H_2O$	2	
2-d	**Any one biological method for treatment of waste water** Biological treatment aims at the removal of all oxidizable and organic matter from the waste water. **Activated sludge process.**Itconsists of an aeration tank followed by a sedimentation tank. In this process high concentrations of newly grown and recycled microbial biomass are suspended uniformly throughout the holding tank to which raw waste water is added. Oxygen is introduced by mechanical aerators. Organic materials in the waste water are removed from the aqueous phase by the microbial biomass .The flocculent microbial growths removed in the sedimentation tank are recycled to the aeration tank to maintain a high concentration of active micro organisms.  ***(Due consideration should be given for any other biological method)***	4	4
2-e	**Composition of crude oil:** Crude oil is made up of the following elements 1. carbon-84% 2. hydrogen -14%	4	4

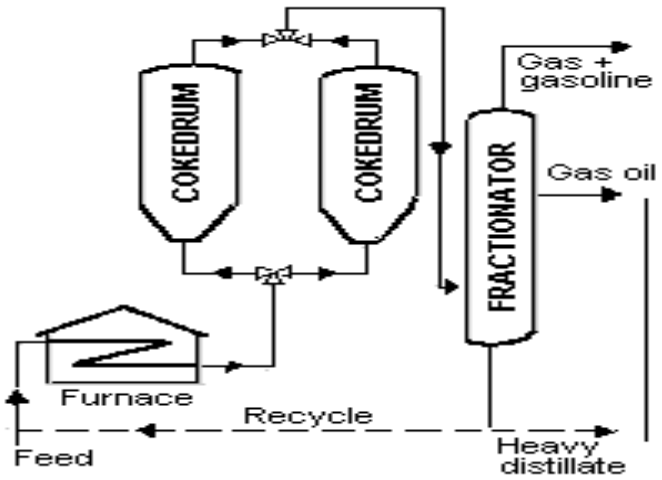
	3. sulphur-1-3% 4. nitrogen, oxygen, metals, salts- <1% The major compounds present in crude oil are: A. hydrcarbon i)Paraffins ii)Aromatics iii) Napthenes iv) dienes B. Non hydrocarbon i) S compounds ii)O_2 compounds iii)N_2 compounds C. Metallic compounds.		
2-f	**Flow sheet for the manufacture of formaldehyde from methanol:**	4	4

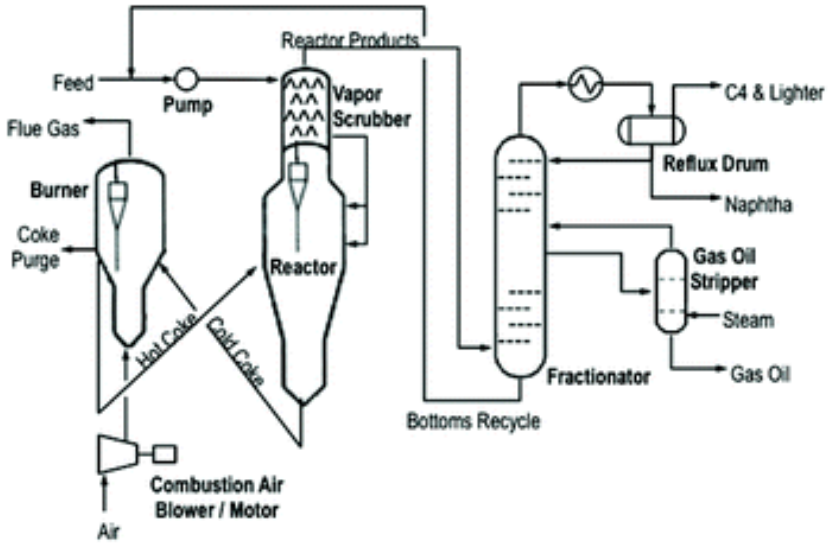
			
3-a	**Manufacturing of styrene from benzenewith flow sheet** Benzene is alkylated with ethylene using aluminum chloride or acid type catalyst. The resulting ethyl benzene is catalytically dehydrogenated in steam or excess benzene atmosphere to give styrene. All benzene feed must be dried by azeotropic distillation. Ethyl chloride is added to ethylene which is fed continuously with benzene to the alkylation tower operated at 950c & 1 atm.Crude acidic ethyl benzene from the cooler is neutralised with 50% NaOH,striped to remove polyethyl benzene & the overhead sent to benzene column which separates wet benzene from ethyl benzene. Dehydrogenation of ethyl benzene is the step which produces styrene The mixed feed passes through the preheated to achieve an input temp. Of 5000c.The dehydrogenation catalyst is promoted	2	8

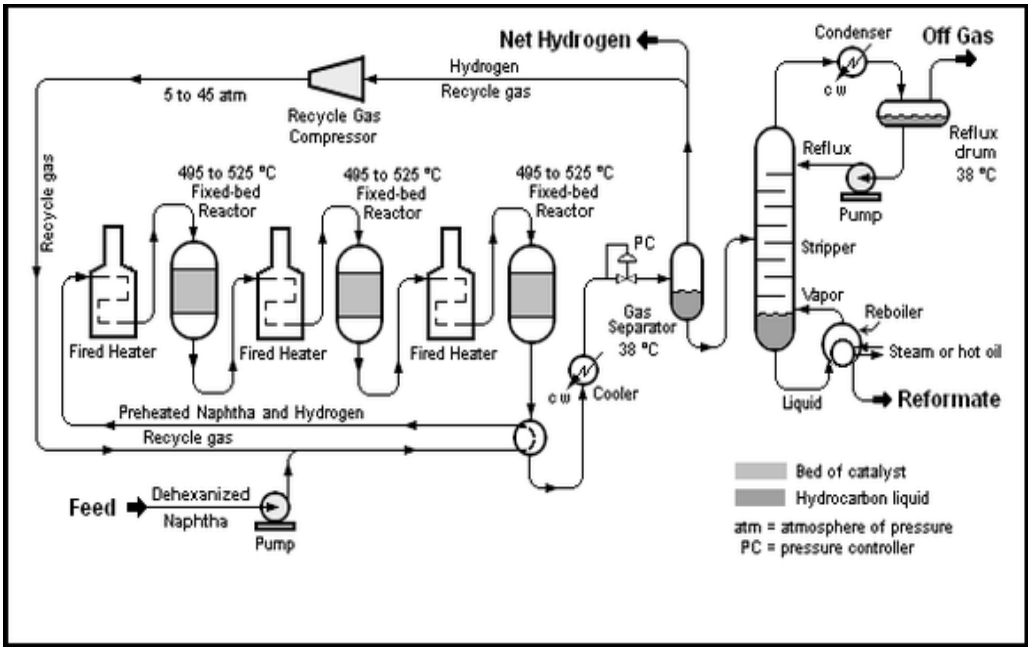
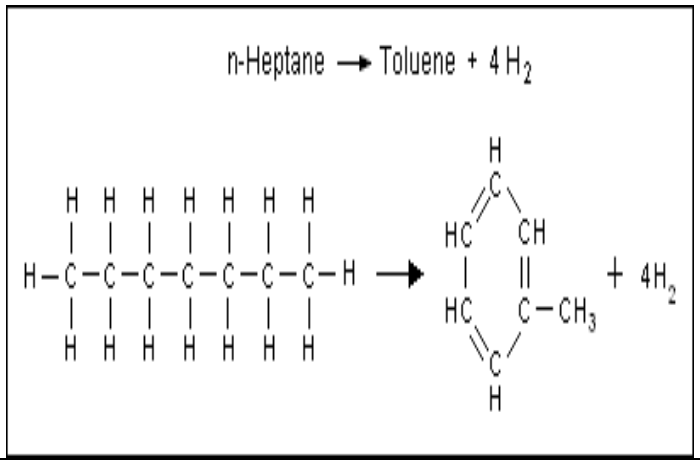
	zinc,chromium,iron.Reactionproduct is cooled in the feed preheated ,then by steam quenching. Hydrocarbon mixture is passed into a series of vacuum distillation column to allow the separation of impurities at low temp to avoid polymerization of styrene. The second column at 35mm & 900c reboiler temp separate styrene from ethyl benzene. **Reaction-**  	2	


Wet
C_6H_6
Azeotropic Dryer
H_2O
Settling Tank
Caustic Waste
Stripper
Benzene Column
Dry
C_6H_6
$AlCl_3$
Vent
C_2H_4 +
C_2H_3Cl
Alkylator
20% NaOH
Polyalky Still
50%
NaOH
Ethyl Benzene Column
Flake
NaOH
Dryer
200°C
$AlCl_3$
Complex
High Temp.
Dealkylator
Residue
Dry
Ethyl Benzene
Steam
Superheater
Steam
Vent
Vac.
Vapor
Quench Tower
C_6H_6
C_6H_5-CH_3
to Recovery
Catalytic Dehydr. Unit
800°C
90°C
Benzene Column
H_2O
Vac.
Vac.
Vac.
Ethyl Benzene Column
90°C
Finishing Column
Cooling
Coils
Batch Tar Still
Tar
Storage
STYRENE

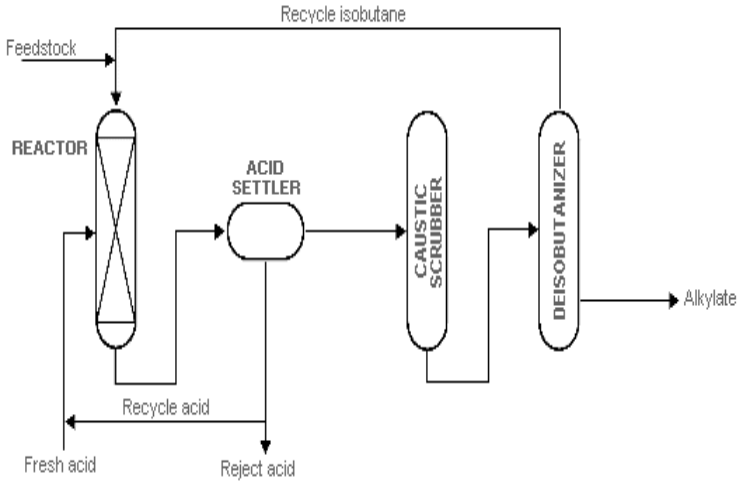
4

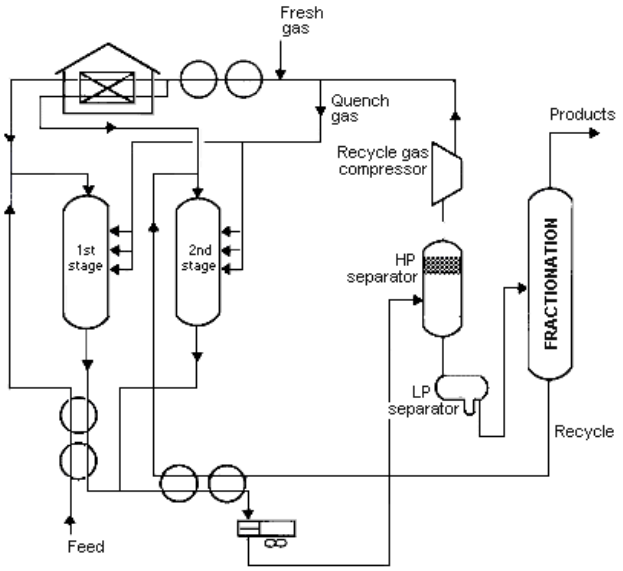
3-b	**Delayed coking**: Heated charge residue from atmospheric distillation is transferred to large coke drums which provides the long residence time needed to allow the cracking reaction. Initially heavy feed stock is fed to a furnace for heating the mixture is passed from the heater to one or more coke drums where the material is held approximately 24 hours until it cracks into lighter products. Vapours from the drums are return to fractionators where gas, naphtha and gas oils are separated out. After the coke reaches a pre determined level in one drum, the flow is diverted to another drum to maintain continuous operation and decoking is done.	2	
		2	
	Continuous coking: continuous coking is a moving bed process that operates at temp higher than delayed coking.In continuous coking thermal cracking occurs by using heat transferred from hot, recycle coke particles to feedstock in a radial mixer,called a reactor.Gases&vapours are taken from the reactor, quenched to stop any further reaction &fractionated.Coking occurs both in the reactor & the surge drum.The process is automatic in that there is a continuous flow of coke & feedstock.	2	

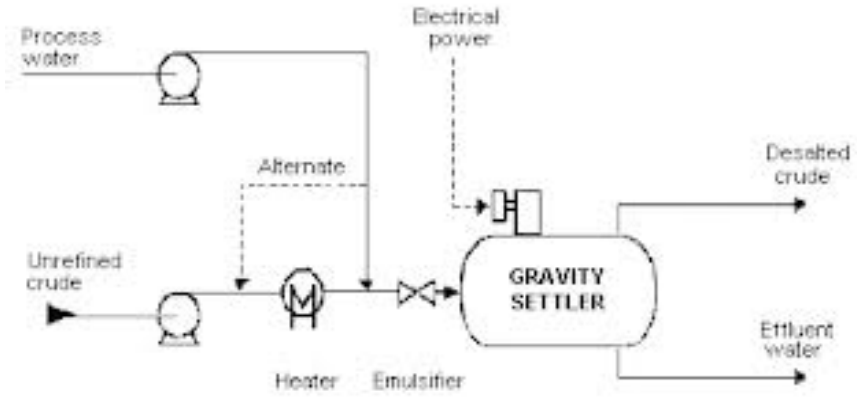
		2	
3-c	**Reforming** is an important process used to convert low octane naphtha into high octane gasoline blending components called reformates. Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, isomerization taking place simultaneously. **Catalytic reforming:** Naphtha feed is prepared in a prefractionator. It is pretreated by mild hydrogenation to remove S,N_2, and metals which lowers Pt catalyst activity . The treated feed is mixed with recycle H_2, preheated and charged to 3 or more cylindrical fluidized bed reactors in series. Reheat interstages are required since the overall reaction is endothermic. The catalyst can be regenerated every 2-3 months by burning off the C deposited by a mixture of steam, air and flue gases.	2 2	8

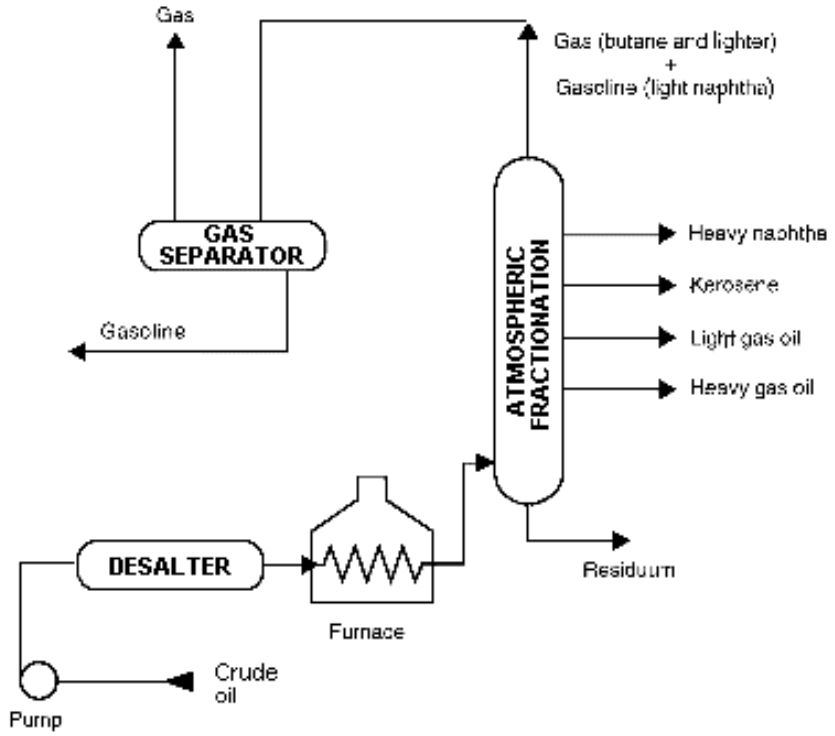
		3	
		1	
4a-i	**OPEC :**OPEC is Organization of Petroleum Exporting Countries. 43% of world crude produced is shared among the group members. **Objectives of OPEC are**	2	4

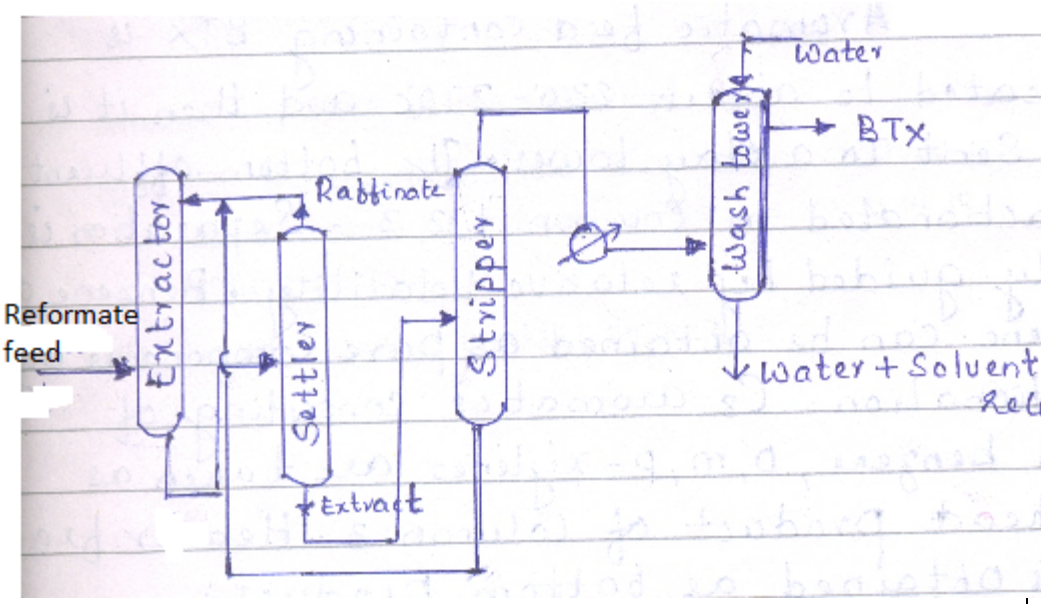
	1. To avoid useless fluctuation in prices in international market. 2. To provide an efficient economic and regular supply of petroleum to consuming and a fair return of capital to those investing in petroleum industries.	2	
4-a-ii	**Manufacture of acetaldehyde from ethylene:** **Reaction:**The process operates in the presence of an aq.liquid copper salt catalyst,promoted by a metal such as palladium.Thus,these are really two reactions ,a hydration reaction $C_2H_4 + 2CuCl_2 + H_2O \rightarrow CH_3CHO + 2CuCl + 2HCl$ & a catalyst regeneration reaction $2CuCl + 2HCl + 1/2\ O_2 \rightarrow 2CuCl_2 + H_2O$ Which add up to give the net overall reaction $C_2H_4 + 1/2O_2 \rightarrow CH_3CHO$ **Description**: The process is operated at pressure below 50 atm& temp of 50 to 100^0C.Typical reaction times range from 6 to 40 min. Air and ethylene is passed through a tower reactor along with catalyst solution. Catalyst solution containing acetaldehyde is separated in a stripper. The crude acetaldehyde is distilled twice. In the first stage, low boiling substances like chloromethane, chloromethaneetcare separated. In the second stage, water and high boiling biproducts like acetic acid are removed and acetaldehyde is obtained in pure form from overhead.	2 2	4
4a-iii	**Sulfuric acid alkylation process** In cascade type sulfuric acid alkylation units,the feedstock enters the reactor & contacts the conc.sulfuric acid catalyst.The reactor is divided into zones ,witholefins fed through distributors to each zone,& the sulfuric acid &isobutanes flowing over baffles from zone to zone.The reactor effluent is separated into hydrocarbon & acid phases in asettler,& the acid is return to the	2	4

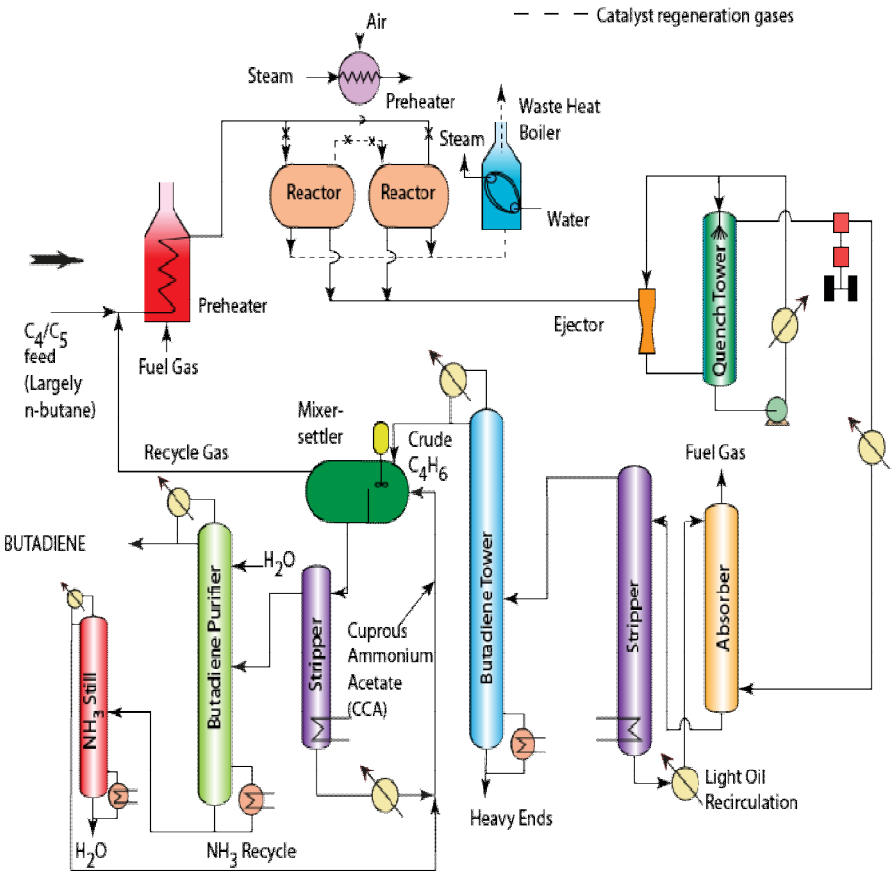
	reactor.The hydrocarbon phase is hot water washed with caustic for pH control before being successivelydepropanised ,deisobutanised&debutanised.The alkylate obtained from the deisobutanier can then go directly to motor fuel,blending or to produce aviation –grade blending stock.The isobutene is recycle to the feed.  	2	
4a-iv	**Flow sheet for two stage hydrocracking process.**	4	4

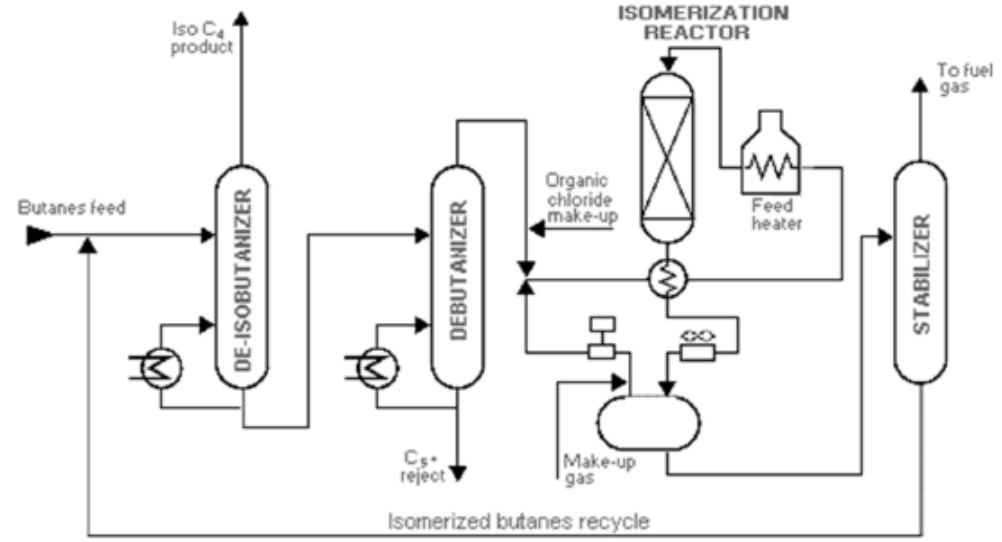
			
4b-i	**Desalting of crude with diagram:** To reduce corrosion, plugging & to prevent poisoning catalyst in processing units desalting is used. Electrical desalting applications of high voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids .Method is continuous. The feedstock crude is heated between 150^0& 350^0F to reduce viscosity & surface tension for easier mixing & separation of the water. The desalted crude is continuously drawn from the top of settling tanks & sent to the crude distillation tower	3	6

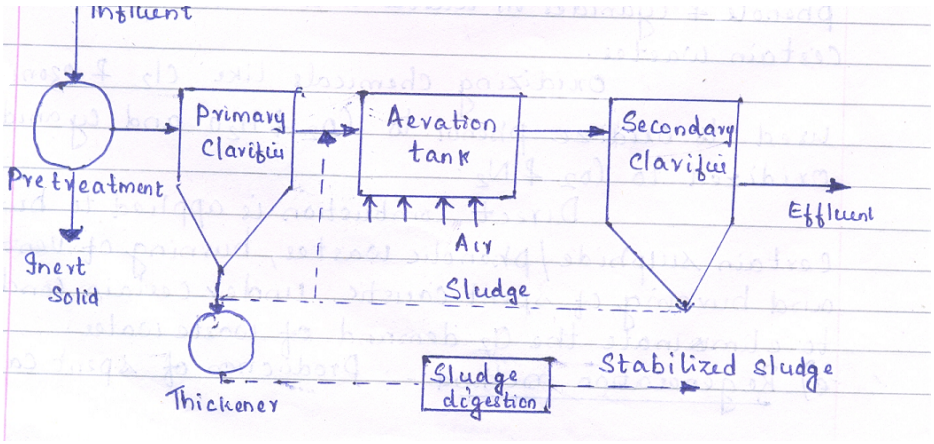
		3	
4b-ii	**Atmospheric distillation of crude oil with flow diagram** At the refinery ,the desalted crude feedstock is preheated using recovered process heat .The feedstock then flows to a direct fired crude charge heater where it is fed into the vertical distillation column just above the bottom ,at pressure above atmospheric pressure & at temp ranging from 650 to 700 0F.All but the heaviest fractions flash into vapour.As the hot vapour rises in the tower ,its temp is reduced.Heavy fuel oil residue is taken from the bottom.At successively higher points on the tower ,the various major products including lubricating oil,heatingoil,kerosene,gasoline& uncondensed gases are drawn off .	3	6

		3	
5-a	**Udex process for recovery of BTX from reformate gasoline.** Extractor consists of packed or plate column, where the feed is introduced at the bottom and the solvent is fed counter current to feed. The temperature is kept around 40-50^{o}C. Extract is the desirable product. Extract and raffinate are settled in a settling column. Most of the raffinate is send to the extractor as reflux. Rich extract from the bottom of the column goes to a stripper, where solvent and aromatics are separated. Aromatics still contain some solvent as impurity which is removed by washing with water in a wash column.BTX is obtained as top product from the washer. Non aromatics raffinate can be easily purified by washing with water alone.	4	8

		4	
5-b	**Manufacturing of butadiene**-A refinery gas of c4/c5 cut containing predominantly n-butane with some isopentaneis mixed with recycle gas & preheated to reaction temperature in a fixed bed regenerative-heating reactor system. Apair of reactor forms an adiabatic cycle with the heat of reaction required during the 5-15 minute make period equal to that supplied by the combustion of carbon deposit on the catalyst during the regenerative period. The product gases are oil quenched,compressed,cooled & separated from the light ends by absorption in naphtha followed by stripping. The overhead is fractionated to give crude butadiene at top which is purified by absorption using cuprous ammonium acetate, extractive distillation with furfural or azeotropic distillation with ammonia. **Reaction-** C_4H_{10}-→CH2=CH.CH=CH_2+2H_2 C_4H_{10} -→C_4H_8+H_2	3 1	8

		4	
5-c	**C_4Isomerization process with neat flow sheet** Butane (C4) isomerization process:		8

	 Butane isomerization produces feedstock for alkylation. Aluminum chloride catalyst plus hydrogen chloride are universally used for the low-temperature processes. Platinum or another metal catalyst is used for the higher-temperature processes. In a typical low-temperature process, the feed to the isomerization plant is n-butane or mixed butanes mixed with hydrogen (to inhibit olefin formation) and passed to the reactor at 230°-340° F and 200-300 psi. Hydrogen is flashed off in a high-pressure separator and the hydrogen chloride removed in a stripper column. The resultant butane mixture is sent to a fractionator (de-isobutanizer) to separate n-butane from the isobutene product.	4 4	
6-a	**C2 hydrocarbons derived from crude oil: (any two)** 1. Ethanol 2. Ethylene dichloride 3. Vinyl chloride 4. Ethylene oxide 5. Styrene **C3 hydrocarbons derived from crude oil(any two)**	2	4

	1.Propane 2. Isopropanol 3. Acetone 4. Cumene 5. Propylene oxide	2	
6-b	**Filtering and demineralization of waste water from oil refinery:** It is used to remove inorganic materials and certain additives from used oil (oil + water)) to produce a cleaner burner fuel or feed for re-refining.  Used oil feed stock is transferred to a reaction tank where it is mixed with sulphuric acid and a surfactive agent and heated to about 60^{o}c. The mixture is stirred well and allowed to stand which results in the separation of oil and aqueous phases. The surfactant causes the contaminants to accumulate in the aqueous phase, which is drained, dried and the solid waste is disposed off. The demineralized oil from the top of the reaction tank is filtered to remove the suspended fine particles.	4	4
6-c	**Reason for crude oil being called as black gold** Crude oil is yellowish black oil that is extracted from under the surface of the earth. It is one of the most necessitated worldwide required commodities. Any	4	4

	fluctuation in the crude oil prices can have direct and indirect influence on the economy of the counties.		
6-d	**Definition:** **(i) Ignition temperature:** The lowest temperature at which a material can catch fire and burn continuously without the aid of external firing agencies. **(ii) Fire point:** Fire point is the minimum temperature at which oil will produce enough vapourswhich will burn continuously for at least 5 seconds when a flame is brought near it. **(iii) Cloud point:** When oil is cooled slowly, the temperature at which it becomes cloudy is called cloud point. **(iv) Calorific value:** Calorific value is the quantity of heat released per quantity of fuel when it is burned completely with oxygen and the products of combustion returned to ambient temperature	1 mark each	4
6-e	**Reasons for considering distillation as a major unit operation in refining process:** Crude oil is a mixture of hydrocarbons with different boiling temperatures. By distillation it can be separated into different fractions with specified boiling range. Distillation of crude takes place in two stages- First stage(atmospheric distillation) and second stage (vacuum distillation)	4	4
6-f	**Reactions involved in hydrogenation:** It is the addition of hydrogen to unsaturated organic compounds. $RCH=CH_2 + H_2 \rightarrow RCH_2CH_3$ (Where R is alkyl or aryl group). **Reactions involved in hydration:** Hydration is addition of water. Synthetic ethyl alcohol is made by hydration of ethylene. $CH_2=CH_2+H_2O \rightarrow C_2H_5OH$	2 2	4