SUMMER-16 EXAMINATION

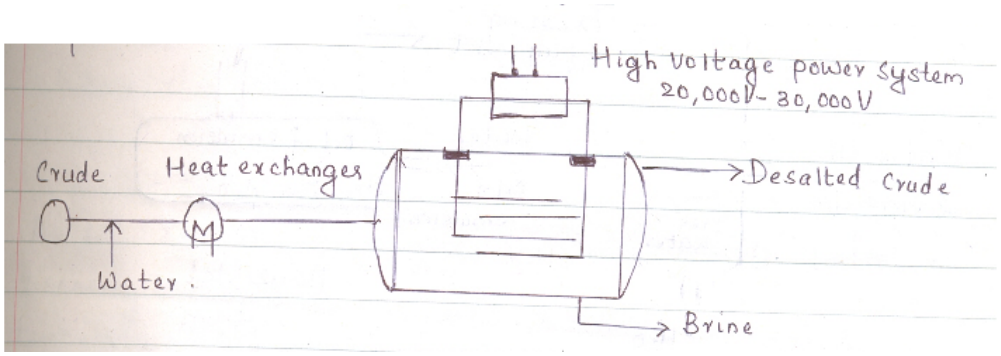
Model Answer

Subject code :(17651)

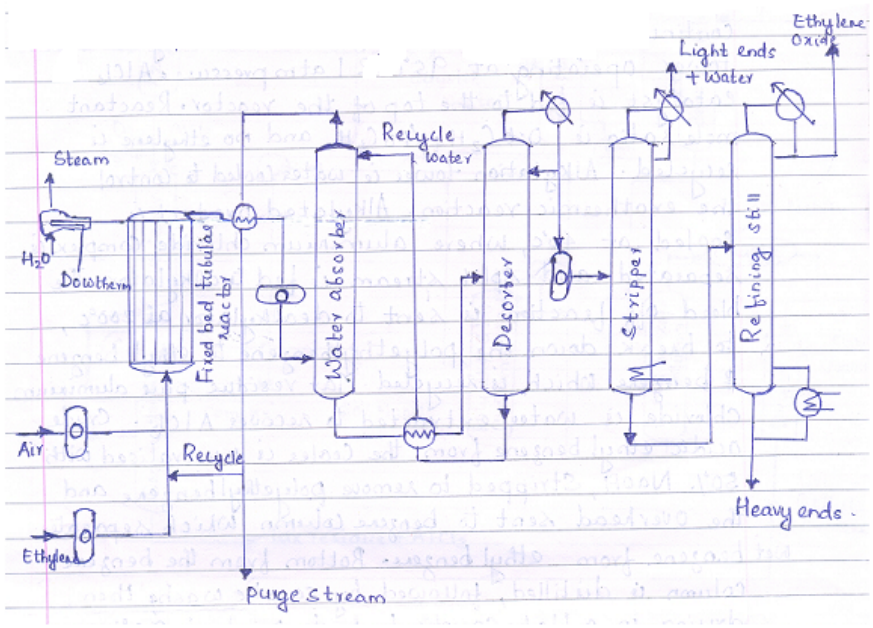
Important Instructions to examiners:

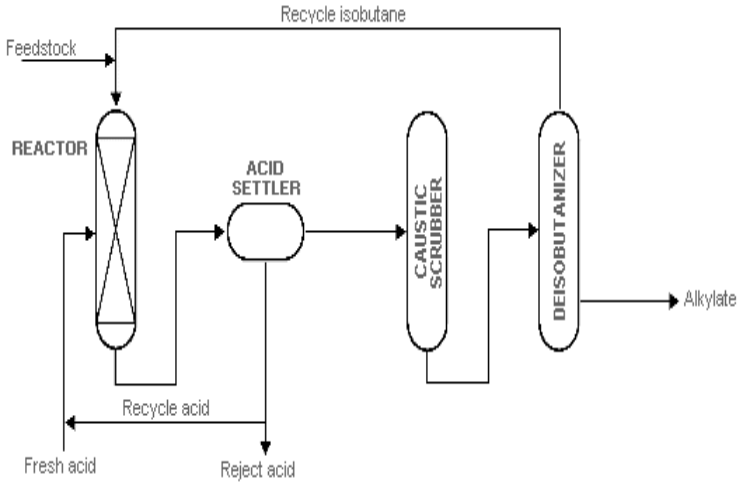
1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling 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.

Q No.	Answer	marks	Total marks
1	**Attempt any FIVE of the following**		**20**
1a	**Six major refineries in India.** 1. Reliance petroleum Ltd, Jamnagar. 2. Indian Oil Corporation Limited, Koyali in Gujarat. 3. Manglore Refinery and Petrochemicals Ltd, Manglore in Karnataka. 4. Chennai Petroleum Corporation Ltd, Manali 5. Cochin Refineries Ltd, Cochin , Kerala. 6. Hindustan Petroleum Corporation Ltd, Visakhapattanam in Andhra Pradesh. 7. Indian Oil Corporation Limited, Panipat in Haryana. 8. Hindustan Petroleum Corporation Ltd, Mumbai 9. Bharat Petroleum Corporation Ltd, Mumbai. 10. Indian Oil Corporation Limited, Mathura in Uttar Pradesh. **Largest refinery:** Reliance petroleum Ltd, Jamnagar.	1/2 mark for any six 1	4
1-b	**OPEC** OPEC is Organization of Petroleum Exporting Countries. . 43% of world crude produced is shared among the group members. OPEC is a 13 member body consisting of Algeria, Iran, Iraq, Saudi Arabia, Gabon, Kuwait, Ecquador, Libya, Indonesia, Nigeria, Qatar, UAE and Venezuela. **Names of four oil producing countries in the world.** Russia - 14% Saudi Arabia - 13% United States - 9% China - 5%	2 1/2 mark for any four	4

	Iran - 4.14% Canada – 4%		
1-c	**Desalting of crude:** Desalting of crude is the removal of corrosive salts and water from the crude which will otherwise cause corrosion, plugging &catalyst poisoning. Desalting of crude is done in two ways – 1. By chemical treatment 2. Electric desalting **Electric desalting:** The feedstock crude is heated between 150^0& 350^0F to reduce viscosity & surface tension for easier mixing & separation of the water. The principle of operation is that under a charged electric field, the polar molecules orient. A potential of 20,000-30,000 volts is applied between electrodes through which crude is passed. Water present in the form of emulsion also coalesces and agglomerates into a stream entrapping all the salts in the process. Brine collects at the bottom of the desalter, while crude floats above and forms a separate stream.  ***(Description of chemical treatment should also be given due consideration)***	4	4
1-d	**Fractions obtained from crude oil with their boiling point range** **Fractions** | **Boiling point range** 1. Uncondensed gases | <30°C	4	4

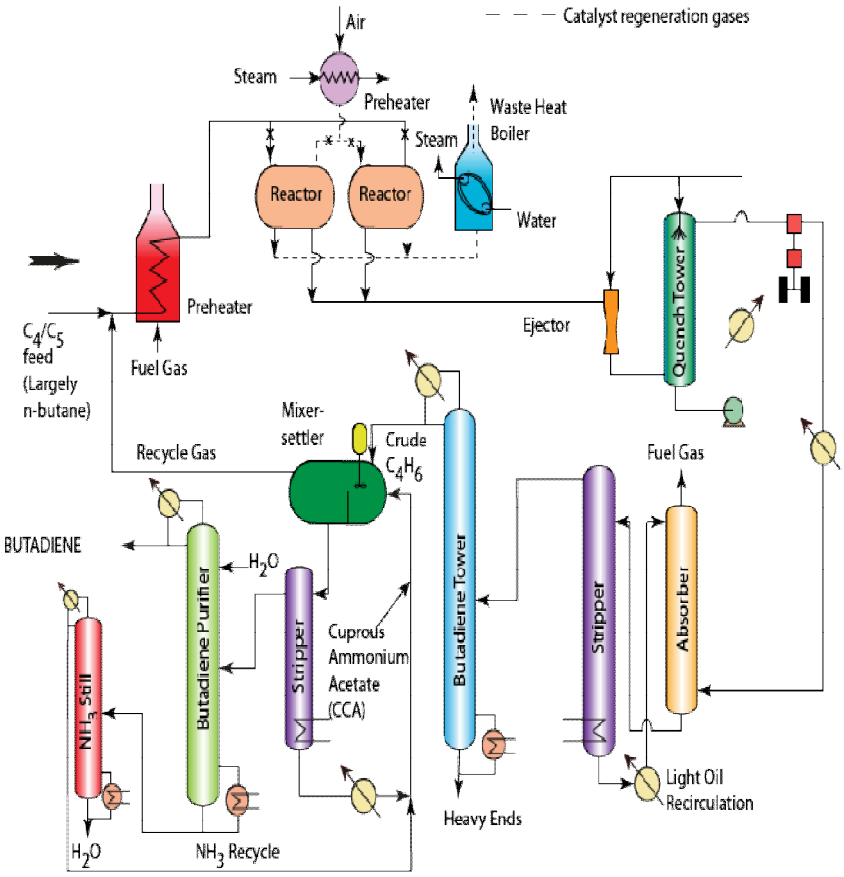
<table>
<tr><td></td><td><table>
<tr><td>2. Petroleum ether</td><td>30-70^{o}C</td></tr>
<tr><td>3.Gasoline or petrol or motor spirit</td><td>40-120^{o}C</td></tr>
<tr><td>4. Naphtha</td><td>120-180^{o}C</td></tr>
<tr><td>5. Kerosene oil</td><td>180-250^{o}C</td></tr>
<tr><td>6. Diesel oil</td><td>250-320^{o}C</td></tr>
<tr><td>7.Heavy oil
On vacuum distillation of heavy oil gives lubricating oil, petroleum jelly, greases, paraffin wax etc.</td><td>320-400^{o}C</td></tr>
<tr><td>8.Residue</td><td>> 400^{o}C</td></tr>
</table></td><td></td><td></td></tr>
<tr><td>1-e</td><td>Flow sheet for the manufacture of ethylene oxide</td><td></td><td>4</td></tr>
</table>

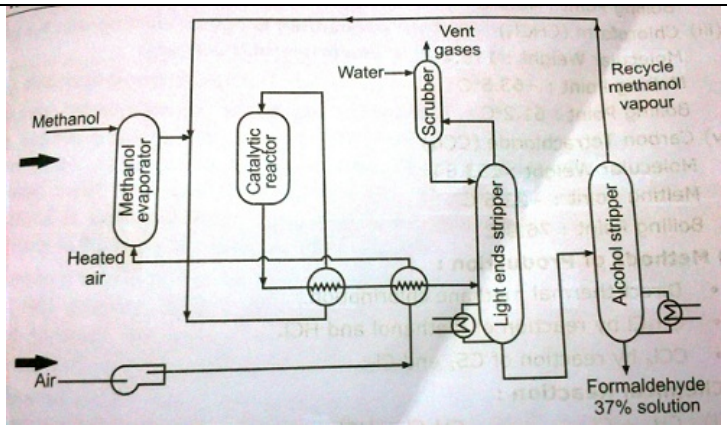
		4	
1-f	**Denatured alcohol:**It is ethanol that has additives in it to make it poisonous to discourage recreational consumption and at the same time can be used for diversified industrial applications. **Denaturants :(Any two)** Methanol,isopropyl alcohol, methyl ethyl ketone, methyl isobutyl ketone.	2 1 mark each	4
1-g	**Reason for crude oil being called black gold:** Crude oil is yellowish black oil that is extracted from under the surface of the earth. Itis one of the most necessitated worldwide required commodities. Any fluctuation in thecrude oil prices can have direct and indirect influence on the economy of the counties.	4	4
2	**Attempt any FOUR of the following**		**16**
2-a	**Alkylation process:** **Sulphuric acid alkylation process:** **Reaction:** $C_4H_8 + C_4H_{10} \rightarrow C_8H_{18}$(2,2,4 Trimethyl Pentane)	1	4

	CH_2=CH-CH_2-CH_3 + CH_3-$CHCH_3$-CH_3→ $(CH_3)_3$-C- CH_2-CH-$(CH_3)_2$ Feed stock (propene, butene, isobutane) enters a multistage cascade reactor. Iso butane and acid passes from one stage to another cascading serially. Olefin is split and introduced in to each cascade. To avoid polymerization, large excess of iso butane is used. Sulphuric acid catalyst is introduced at 4-10^{0}C. alkylate formed is taken out from the reactor, cooled and fractionated. Isobutane from the fractionator is recycled.  ***(Hydrofluoric acid alkylation should also be given due consideration)***	3	
2-b	**Characteristics of waste water produced in petrochemical plant:** Free oil: 2000-3000 mg/ l H_2S and sulphides: 10-220 mg / l Phenol : 12-30 mg / l Suspended solids: 200-400 mg / l 5 day BOD at 20^{0}c : 100-300 mg / l Alkalinity: 10-250 mg / l	4	4
2-c	**Names of two types of cracking process** Two different types of cracking are thermal cracking and catalytic cracking.	2	4

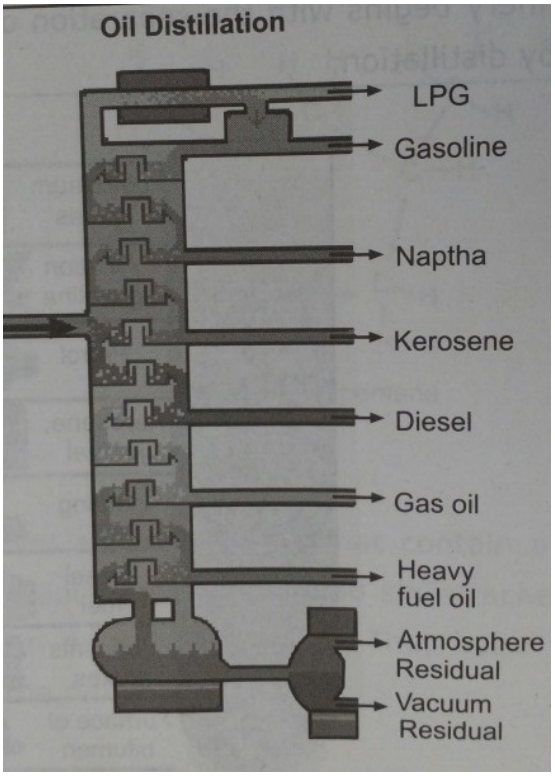
	Basic difference between thermal cracking and catalytic cracking: Thermal cracking is a refining process in which heat (> 800^{o}C) and pressure 700KPa) are used to break down, rearrange hydrocarbon molecules. Catalytic cracking breaks complex hydrocarbon molecules in to simpler molecules under less severe operating conditions with the help of a catalyst.	2	
2-d	**LEL:**Lower Explosive Limit (LEL) is the minimum concentration of a particular combustible gas or vapor necessary to support its combustion in air. Below this level, the mixture is too lean to burn. **HEL:** The maximum concentration of a gas or vapor that will burn in air is defined as Higher explosive Limit(HEL). Above this, the mixture is too rich to burn. **Ignition temperature:** The lowest temperature at which a material can catch fire and burn continuously withoutthe aid of external firing agencies.	1.5 1.5 1	4
2-e	**Chemicals derived from C1 hydrocarbon (any two)** Methanol, formaldehyde, chloromethane, methylene dichloride. **Chemicals derived from C2 hydrocarbon (any two)** Ethanol, ethylene oxide, styrene, acetaldehyde.	2 2	4
2-f	**Polymerization:** Poymerisation is defined in petroleum industry as the combining of two or more olefin molecules to yield larger molecules. **Different methods of polymerization :** The different methods of polymerization are condensation or step growth polymerization and addition or chain growth polymerization. Addition polymerization can be further classified into homogeneous and heterogeneous polymerization. Homogeneous polymerizations are of two types- bulk polymerization and	2 2	4

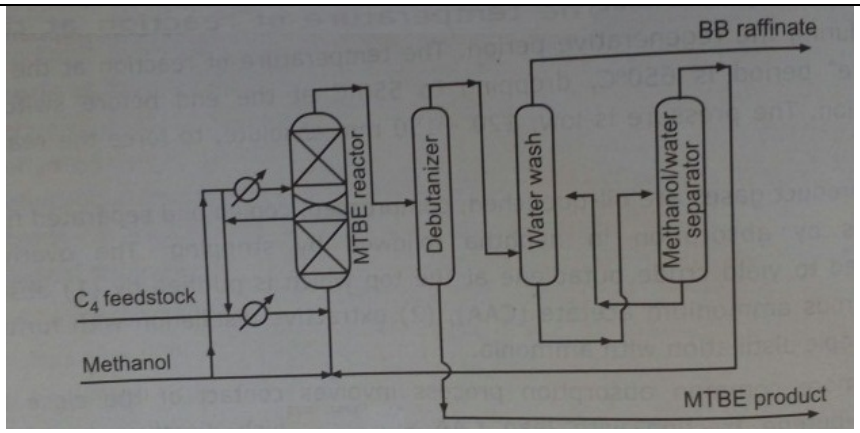
	solution polymerization. Heterogeneous polymerization are of two types – emulsion and suspension polymerization.		
3	**Attempt any FOUR of the following**		**16**
3-a	**i) Flash point**-It is the lowest temperature at which the oil gives off enough vapors which ignite for moment, when small flame is brought to near it. **(ii) Drop point**-It is the temperature at which the grease passes from a semisolid to a liquid state under the conditions of test. **(iii) Pour point**-The temperature at which oil stops flowing or getting poured is called pour point of oil. **(iv) Cloud point**-When oil is cooled slowly, the temperature at which it becomes cloudy is called as cloud point.	1 mark each	4
3-b	**Manufacture of butadiene:** **Description:** A refinery gas of C4/C5 containing n-butane with some isopentane is mixed with recycle gas & preheated to reaction temp.prior to contact with catalyst in a fixed bed, regenerative heating reactor system. The temp. of reaction at start of make period is 650^0C,dropping to 550^0C at the end before switching to regeneration. The pressure is low 120-150mm absolute ,to force reaction to right. 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 yield crude butadiene at the top which is purified by absorption using cuprous ammonium acetate,extractive distillation with furfural or azeotropic distillation with ammonia. Main reaction-$C_4H_{10} \rightarrow CH_2=CH.CH=CH_2+2H_2$ Side reaction-$C_4H_{10} \rightarrow C_4H_8+H_2$	2	4

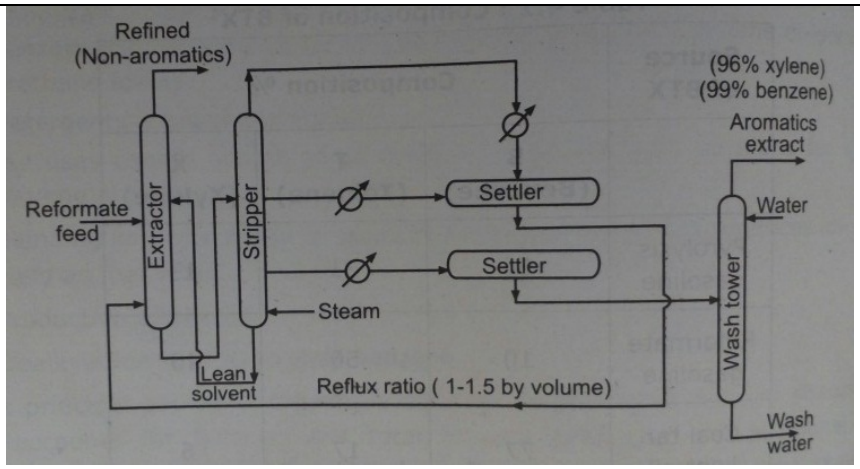
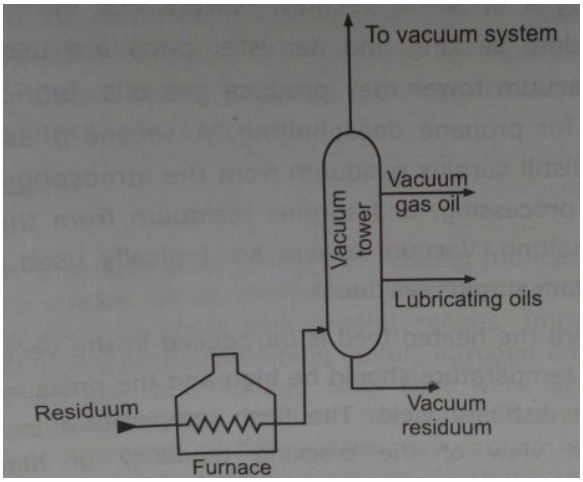
	Flow sheet  	2	
3-c	**Flow sheet for the manufacture of formaldehyde:**	4	4

			
3-d	**Factors affecting the prices of crude oil** 1. Production of crude oil: OPEC nations are the major producers of worlds crude 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 affecttheprices 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 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.	1 mark each for any 4 points	4

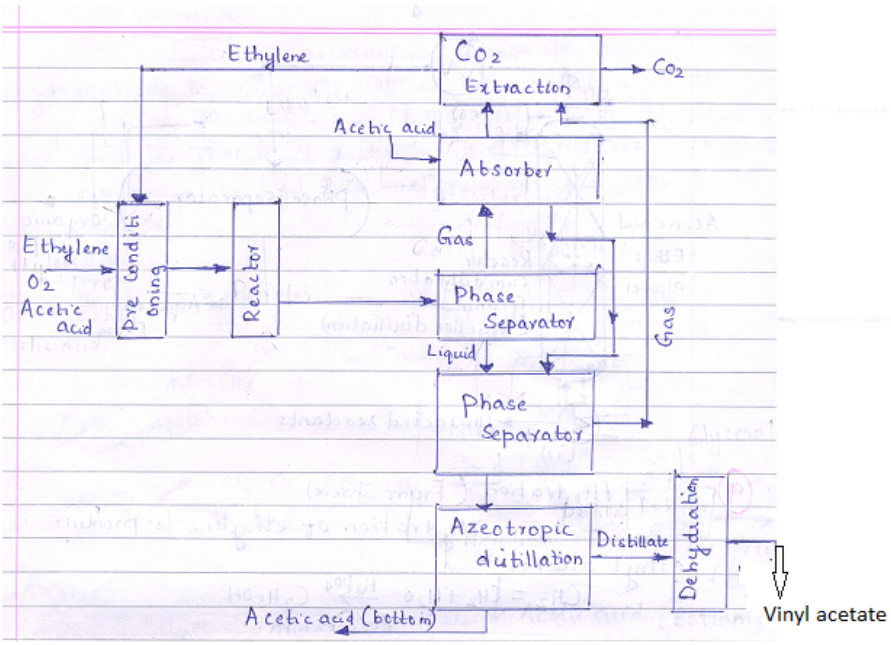
3-e	**Importance of distillation in oil refining operation:** The crude oil distillation unit (CDU) is the first processing unit in virtually all petroleum refineries. The CDU distills the incoming crude oil into various fractions of different boiling ranges, each of which are then processed further in the other refinery processing units. Crude oil contains various constituents such as diesel, petrol, asphalt, waxes etc.So for efficient separation of all hydrocarbons distillation is very important.	4	4
3-f	**Two Chemicals derived from C3 hydrocarbon with their uses** Acetaldehyde, acetone, glycerin Acetaldehyde-used in manufacture of acetic acid, acetic anhydride Acetone-used as solvent,manufacture of bisphenol Glycerin: used for making alkyl resins, plastics, explosives, food and pharmaceuticals **Two Chemicals derived from C4hydrocarbon with their uses** MTBE,Butadiene, butanol MTBE-It is a gasoline additive used to increase octane no. that is produced from methanol & isobutylene, used as a fuel component in fuel for gasoline engines. Butadiene-used in wide variety of synthetic rubbers & polymer resins. Butanol : used as a blended additive to diesel fuel, solvent for textile and chemical processes.	1/2 mark each for any two 1/2 mark each for any two 1/2 mark each for any two 1/2 mark each for any two	4
4	**Attempt any FOUR of the following**		
4-a	**Separation of crude oil by fractional distillation:** The steps of fractional distillation 1. Heating of mixture is done. 2. The mixture boils, forming vapours. 3. The vapour enters to the bottom of the fractional distillation column that is	2	4

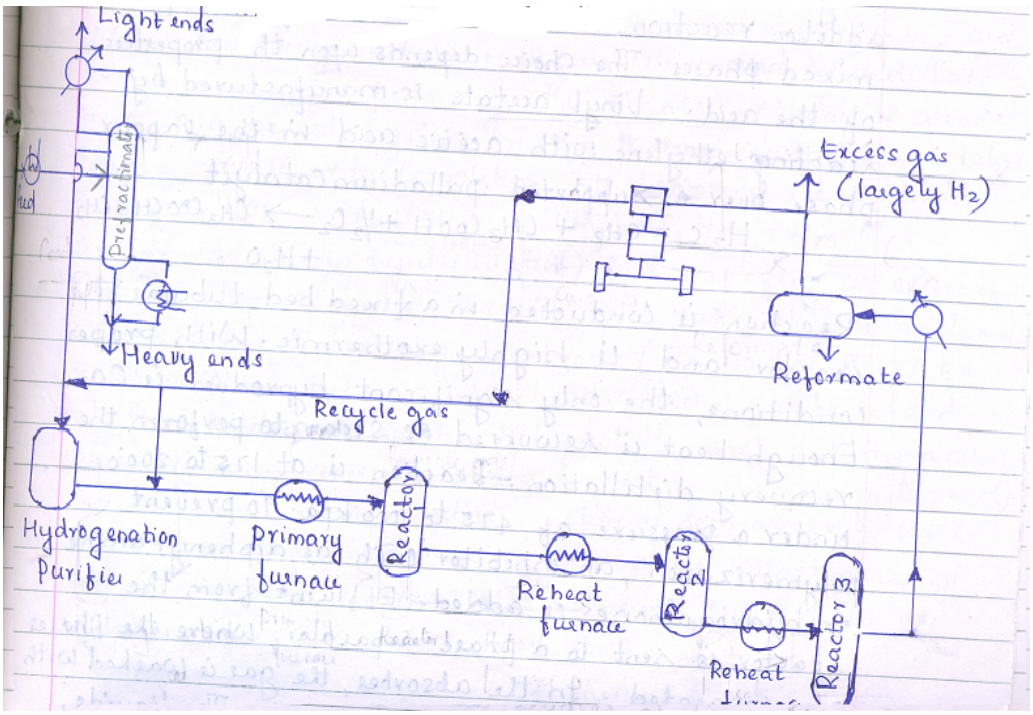
	fitted with trays. 4. The vapour rises in the column. 5. The trays have bubble caps in them to allow the vapour to pass through. 6. The trays increases contact time between the vapour& liquid. 7. The vapour rises in the column. As the vapour rises in the column, it becomes cool. 8. So the trays collect various liquid fractions & the vapours are condensed. 9. In this way crude oil is separated by fractional distillation. 	2	
4-b	**Flow diagram for the manufacture of MTBE**		4

		4	
4-c	**Udex process for recovery of BTX from reformate gasoline:** Reformate as a feed can be send to the extraction column where reformate is heated to about 140-150^{0}c in presence of lean solvent. During extraction we get two phases extract phase &raffinate phase. Extract phase contains aromatic compounds &raffinate phase contains non aromatic compounds. Solvent is used to extract aromatic compounds from reformate feed & then it send to the stripper .In stripping column ,recovery of solvent takes place which is removed from bottom side ,aromatic extract can be exist from top side. Aromatic extract phase is cooled & then sentto settler. Two settlers can be used, part of one settler is feed back again to extraction column as a reflux .Now the remaining part of aromatic extract phase is fed to wash tower, for washing with water. Higher % of conc. aromatic extract component can be withdrawn from top as a product, where water with impurity can be obtained from bottom side.	4	4

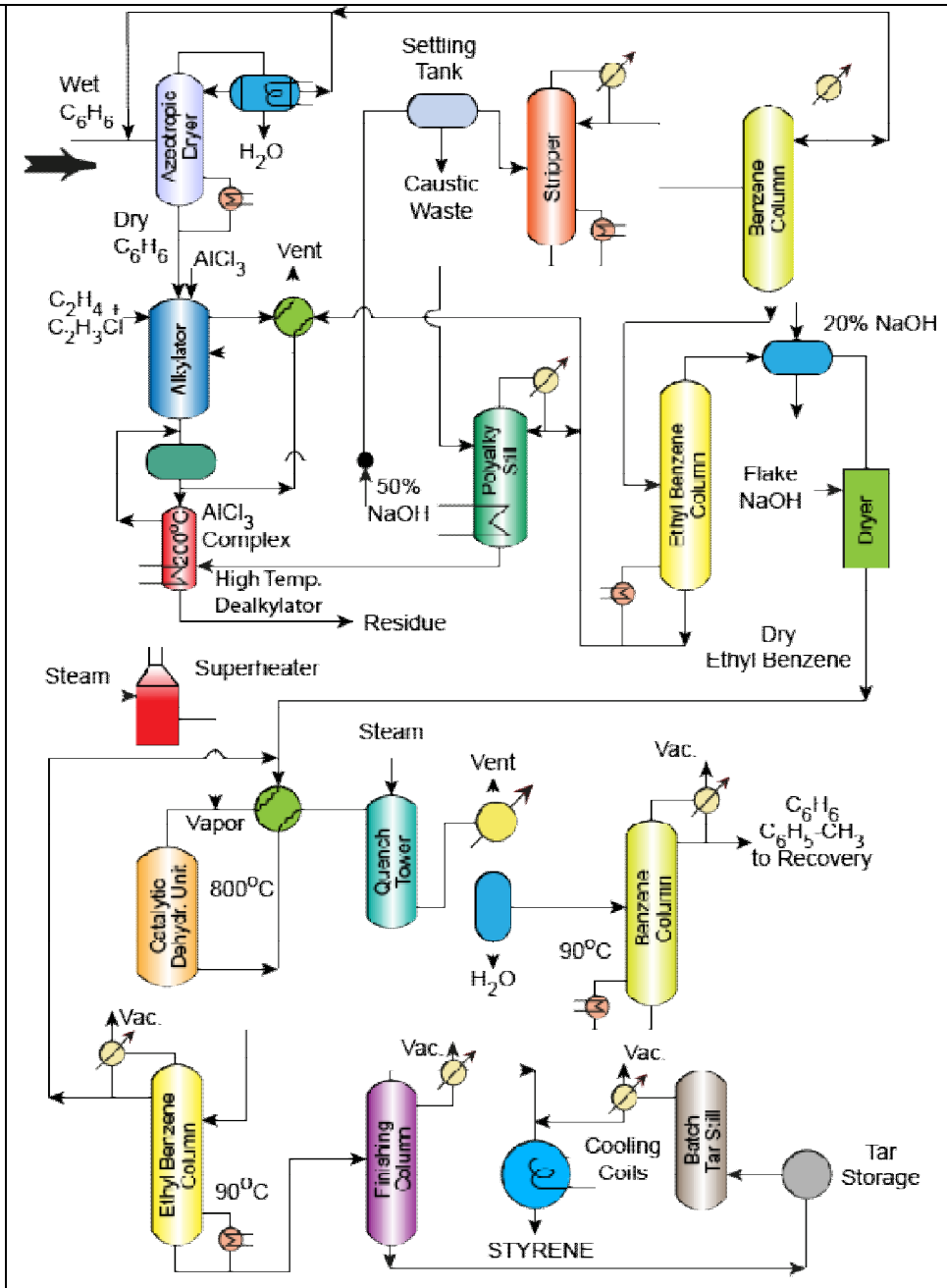
			
4-d	**Working of vacuum distillation unit:** Heavier fractions from atmospheric distillation unit that cannot be distilled without cracking under its pressure & temp. Conditions are vacuum distilled. Vacuum distillation is simply distillation of petroleum fractions at very low pressure to increase volatilization & separation. In most system vacuum inside the fractionators is maintained with steam ejector & vacuum pumps, barometric condensers or surface condensers. The injection of superheated steam at the base of vacuum fractionators further reduces the partial pressure of hydrocarbons in the tower, facilitating vaporization & separation. 	2 2	4

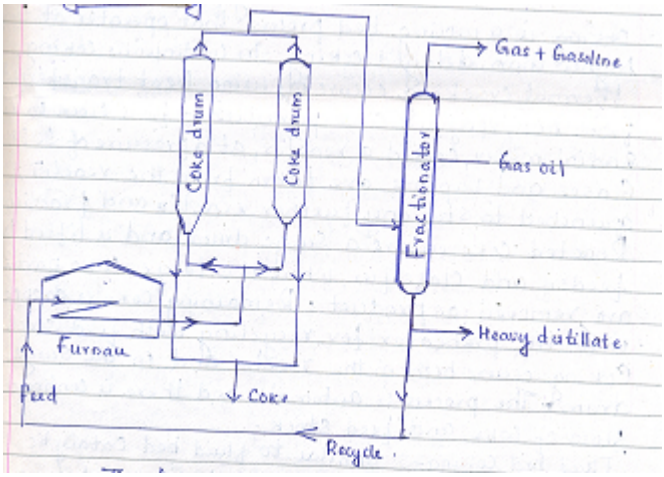
4-e	**Steps in waste water treatment in petrochemical industry.** *Primary treatment* -this treatment is the separation of oil, water, hydrocarbon solids from waste water in two stages .During the first stage, an API separator, a corrugated plate interceptor, or other separator design is used.Wastewater moves very slowly through separator allowing the free oil to float to the surface & be skimmed off &solids to settle to the bottom & be scraped off to a sludge collecting hopper. *Secondary treatment* –In secondary process, dissolved oil & other organic pollutants may be consumed biologically by microorganism..These processes biologically degrade & oxidized soluble organic matter by the use of activated sludge, unaerated or aerated lagoons, trickling filter methods. Materials with high adsorption are used in fixed bed filters or added to the wastewater to form slurry which is removed by sedimentation or filtration. *Tertiary treatment*-It removes specific pollutants to meet regulatory discharge requirements. These treatment includes chlorination, ozonations, ion exchange, reverse osmosis, activated carbon adsorption etc. *Pre treatment (dewatering)*-Dewatering means removing water from oil. This is simple process relying on the separation of aq. & oil phases over time under the influence of gravity.It involves following steps-a. Filtering & demineralization b. Propane Deasphalting process & Distillation.	4	4
4-f	**Importance of vacuum distillation in refining operation:** The main objective of vacuum distillation is to maximize the recovery of valuable distillate & to reduce the energy consumption of the units. Heavier fractions from atmospheric distillation unit that cannot be distilled without cracking under its pressure & temperature conditions are vacuum distilled.	4	4
5	**Attempt any FOUR of the following**		**16**
5-a	**Esterification process in refineries.**		4

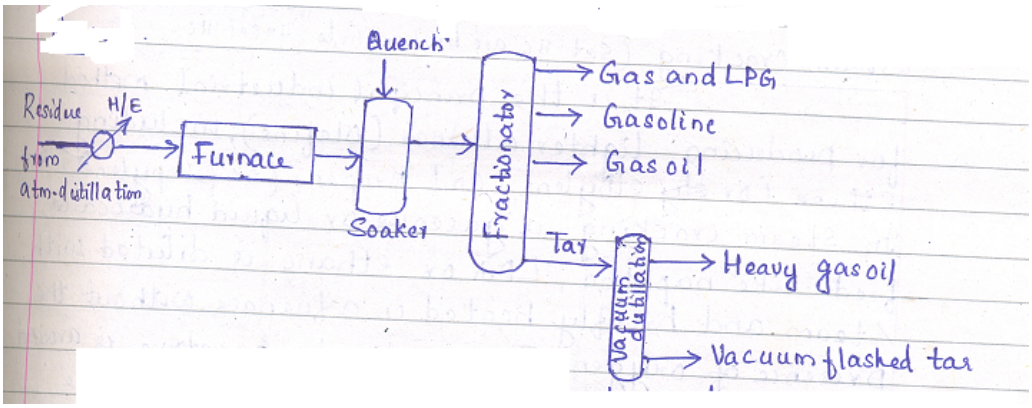
	 It is the reaction between alcohol and carboxylic acid to form ester.Unsaturated vinyl ester for use in polymerization reactions are made by the esterification of olefins. Vinyl acetate is made by reacting ethylene with acetic acid in the vapour phase over a supported palladium catalyst. $CH_2=CH_2 + CH_3COOH + 1/2\ O_2 \rightarrow CH_3COOCH=CH_2 + H_2O$ Reaction takes place in a fixed bed tubular reactor at 175-200^{0}c and 400-1000KPa and is highly exothermic. Effluent from the reactor is sent to a phase separator and the phases are separated. In the absorber the gas is washed with acetic acid to recover the vinyl acetate.	4	
5-b	**Reforming** **Description:** Catalytic reforming is used to convert hydrocarbonsto aromatics which have high octane rating. Naphtha feed is prepared in a fractionator. It is pretreated by mild hydrogenation to remove the impurities which will poison the platinum catalyst	2	4

	and then mixed with recycle stream, preheated and charged to 3 or more cylindrical fixed bed catalytic reactors in series. Reheat interstages are required since the overall reaction is endothermic. **Flowsheet**  	2	
5-c	**Manufacturing of styrene:** **Description** 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	2	4

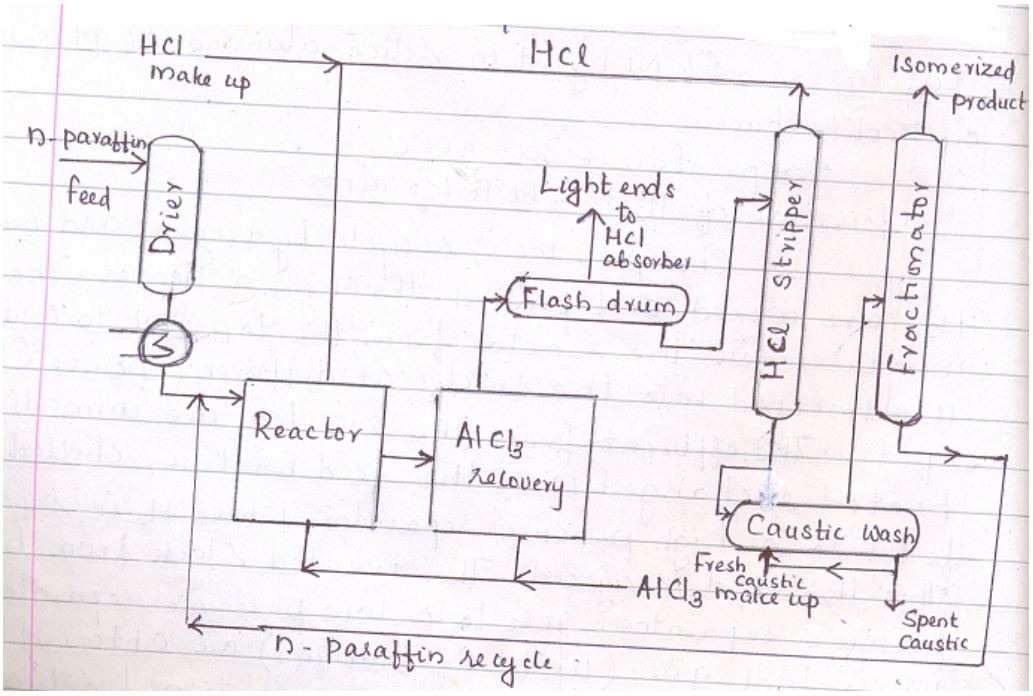
	overhead sent to benzene column which separates wet benzene from ethyl benzene. Dehydrogenation of ethyl benzene is the step which produces styrene The mixed feed passes through the preheated to achieve an input temp. Of 5000c.The dehydrogenation catalyst is promoted Zinc,chromium,iron.Reactionproduct is cooled in the feed preheater ,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. **Flowsheet**		

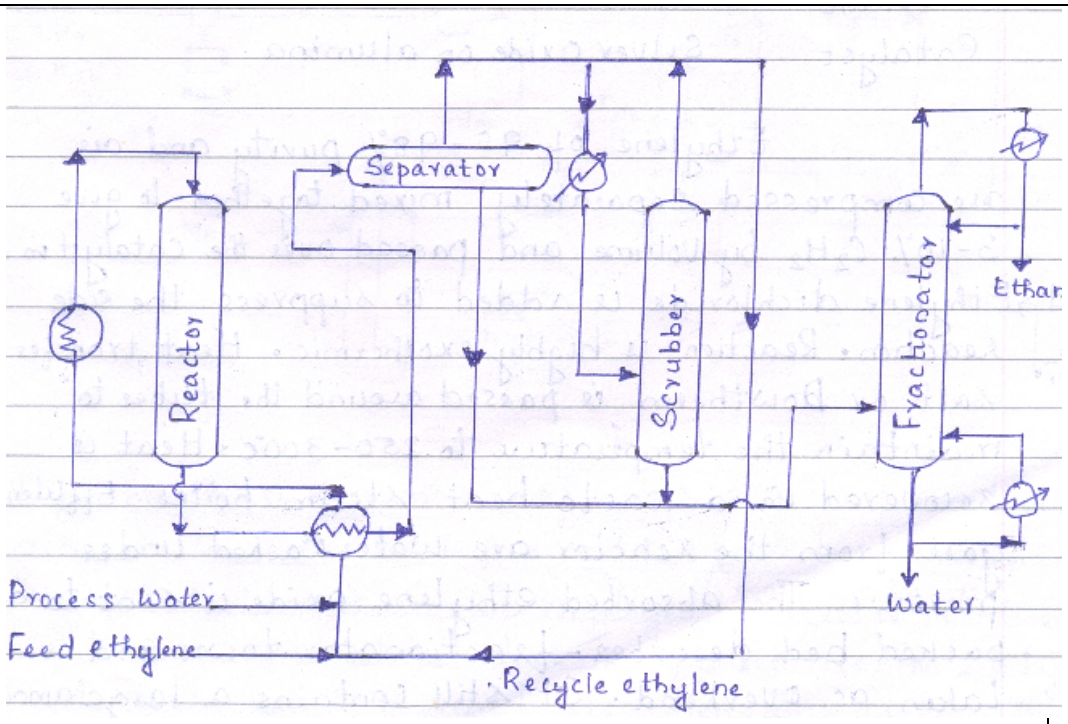
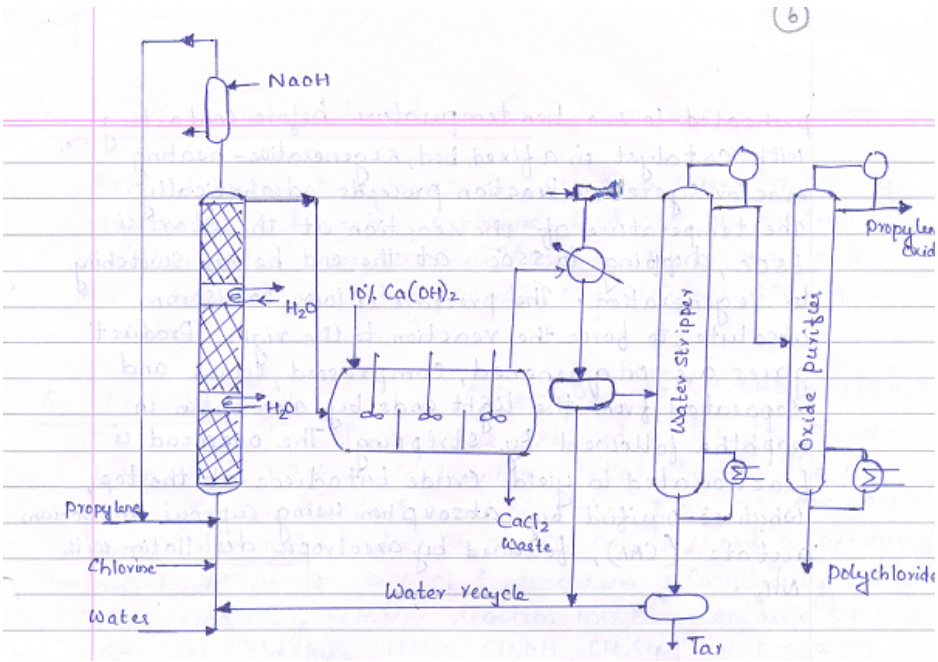
	 Wet C_6H_6 Azeotropic Dryer H_2O Settling Tank Caustic Waste Stripper Benzene Column Dry C_6H_6 $AlCl_3$ Vent C_2H_4 + C_2H_3Cl Alkylator 20% NaOH Polyalky Stl 50% NaOH Ethyl Benzene Column Flake NaOH Dryer 200°C $AlCl_3$ Complex High Temp. Dealkylator Residue Dry Ethyl Benzene Steam Superheater Steam 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	2	

5-d	**Coking Process:**  Initially the heavy feedstock (residue from atmospheric distillation unit) is fed to a furnace which heats it to high temperature (480-510^{o}c) at low pressures (25-30 psi) and is designed & controlled to prevent premature coking in the heater tubes. The hot mixture is passed from the heater to one or more coker drums where it is held for approximately 24 hours until it cracks into lighter products. Vapours from the drums are returned to fractionators, where gas, naphtha etc are separated out. After the coke reaches predetermined level in one drum, the flow is diverted to another drum to maintain continuous operation. Full drum is steam stripped to remove to remove uncracked hydrocarbons, cooled by water injection and decoked by mechanical or hydraulic methods. ***(Any other type of coking should be given due consideration)***	4	4
5-e	**Thermal cracking process:** Thermal cracking is a refining process in which heat (□ 800^{o}c) and pressure (□ 700KPa) are used to break down, rearrange hydrocarbon molecules. Visbreaking, steam cracking, coking are applications of thermal cracking. Visbreaking: It is a mild form of thermal cracking which cracks large hydrocarbon molecules	4	4

	in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons. Residue from the atmospheric distillation tower is heated in a heat exchanger to 250^{o}C and then heated to 425-510^{0}c at atmospheric pressure and mildly cracked in a heater. It is then quenched with cool gas oil to control over cracking and flashed in a distillation tower. The thermally cracked residue tar which accumulates at the bottom of the tower is vacuum flashed in a stripper and the distillate recycled.  ***Due weightage should be given forsteam cracking, delayed coking, continuous coking etc)***		
5-f	**Constituents of crude oil:** Crude oil is made up of the following elements 1. carbon-84% 2. hydrogen -14% 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	2	4

<table>
<tr><td></td><td>B. Non hydrocarbon
i) S compounds
ii)O_2 compounds
iii)N_2 compounds
C. Metallic compounds.
Four unit operation involved in refining process:
Distillation, extraction, absorption ,adsorption.</td><td>1/2 mark each</td><td></td></tr>
<tr><td>6</td><td>Attempt any FOUR of the following</td><td></td><td>16</td></tr>
<tr><td>6-a</td><td>Difference between petroleum refinery and petrochemical industry.
<table>
<tr><th>Petroleum refinery</th><th>Petrochemical industry</th></tr>
<tr><td>1)Process crude oil into different fractions.</td><td>It is a chemical plant that uses a petroleum based feedstock from petroleum refinery to produce a petrochemical product</td></tr>
<tr><td>2)Feed stock is crude oil from mines</td><td>Feed stock is product obtained from Petroleum refinery</td></tr>
<tr><td>3)Product obtained from Refinery are kerosene, gasoline, diesel, LPG etc</td><td>Product obtained from petrochemical industry are plastic, different hydrocarbons</td></tr>
<tr><td>4) All refineries have more or less similar unit operations and unit processes</td><td>The process depends on the product to be produced.</td></tr>
</table></td><td>1 mark each</td><td>4</td></tr>
<tr><td>6-b</td><td>Types of refineries.
1.Primary refinery
2. Intermediate refinery
3. Complex refinery</td><td>4</td><td>4</td></tr>
<tr><td>6-c</td><td>Isomerization: Isomerization is used to convert n-paraffins to isoparaffins.
Description: Feed stock is dried preheated and fed to a reactor where efficient contact between reactants and catalysts takes place. Catalyst is HCl promoted</td><td>1</td><td>4</td></tr>
</table>

	aluminiumtrichloride and reaction temperature is 100-150^{0}c and pressure 17 to 27 atm. Removal of light ends by flashing , followed by HCl stripping, caustic washing and fractionation are the standard operations performed to produce isomerized gasoline. **Flowsheet** 	1.5 1.5	
6-d	**Oetane number:** Octane number 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 **Cetane number:** It is defined as the percentage volume of n-cetane in a mixture of n-cetane and heptamethylnonane that gives the same ignition delay as the fuel under consideration.	2 2	4
6-e	**Flow sheet for the manufacture of ethanol:**		4

		4	
6-f	**Flow sheet for the manufacture of propylene oxide.** 	4	4