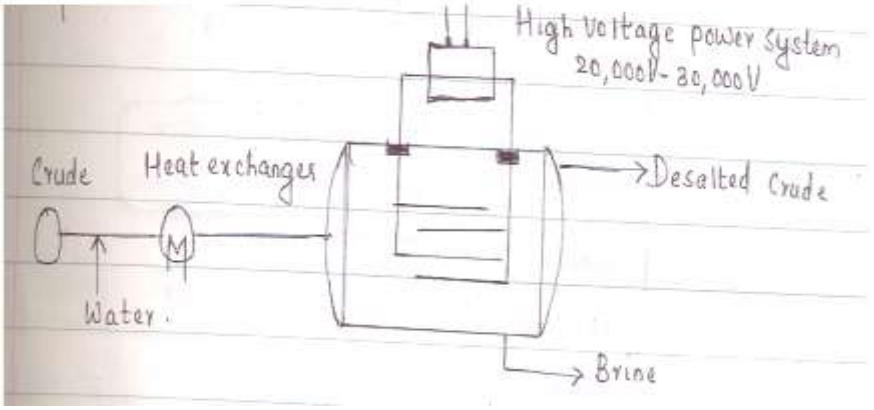
Important Instructions to examiners:

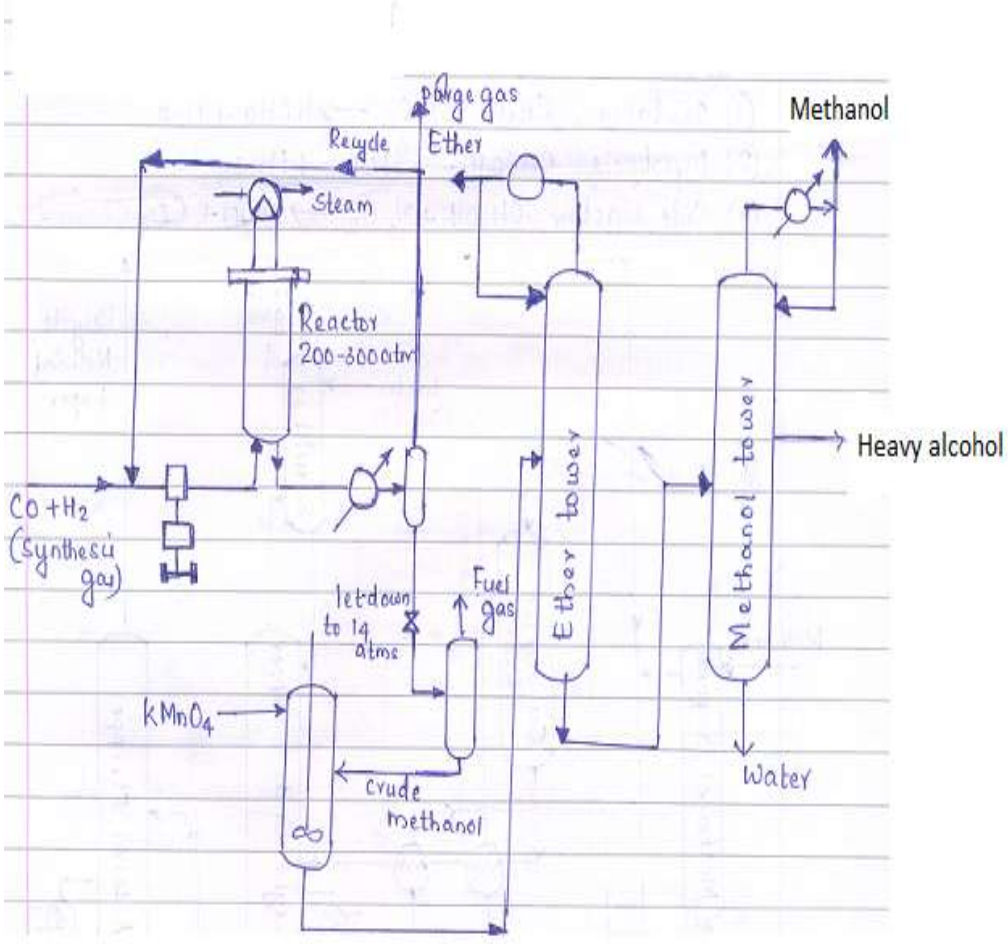
1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling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

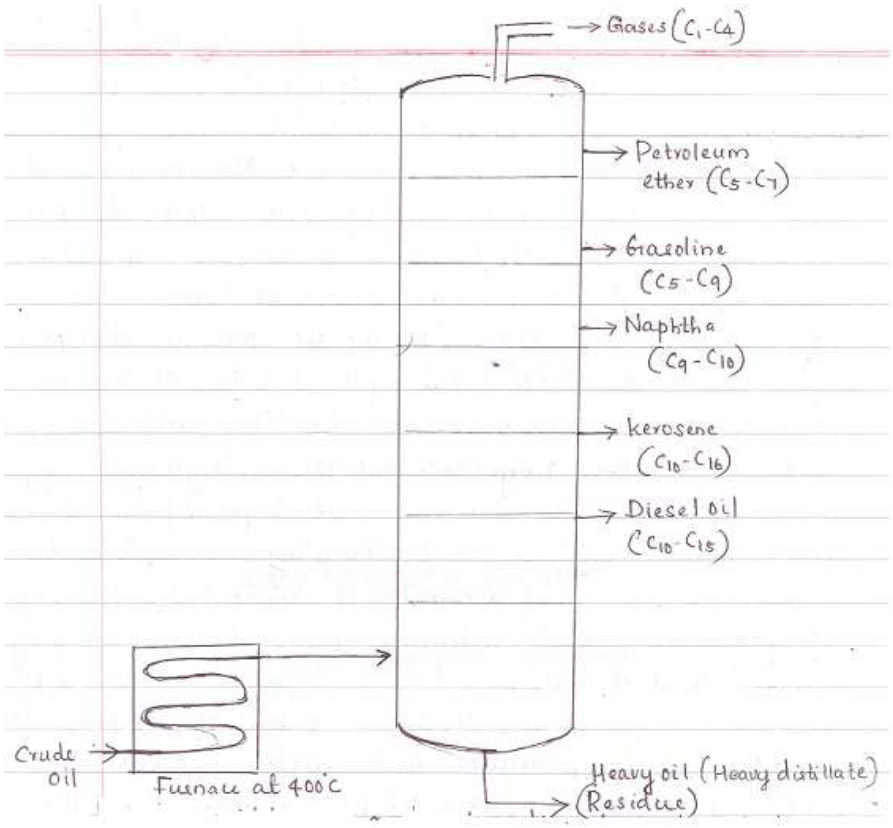
Q No.	Answer	Marks
1	**Attempt any FIVE of the following**	**20**
1-a	**List of OPEC countries with their percentage crude oil production:** OPEC is a 14 member body consisting of 1. Algeria – 1.8% 2. Iran - 4.14% 3. Iraq – 5% 4. Saudi Arabia-13% 5. Gabon - 1% 6. Kuwait -3.5% 7. Ecuador - 1% 8. Libya- 1.9% 9. Equatorial Guinea - 1% 10. Nigeria – 2% 11. Qatar – 2.5 12. UAE – 4.2% 13. Venzuela -2.8% 14. Angola – 1%	4
1-b	**List of Indian refinery with their capacity(any four)**	1 mark each for listing the name with their capacity.

Name	**Location**	**Capacity (MMTPA)**
Reliance petroleum Ltd	Jamnagar	33
Indian Oil Corporation Limited	Koyali in Gujarat	13.7
Manglore Refinery and Petrochemicals Ltd	Manglore in Karnataka	9.69
Chennai Petroleum Corporation Ltd	Manali	9.5
Indian Oil Corporation Limited.	Mathura in Uttar Pradesh	8.0
Cochin Refineries Ltd.	Cochin , Kerala.	7.5
Hindustan Petroleum Corporation Ltd.	Visakhapattanam in Andhra Pradesh	7.5

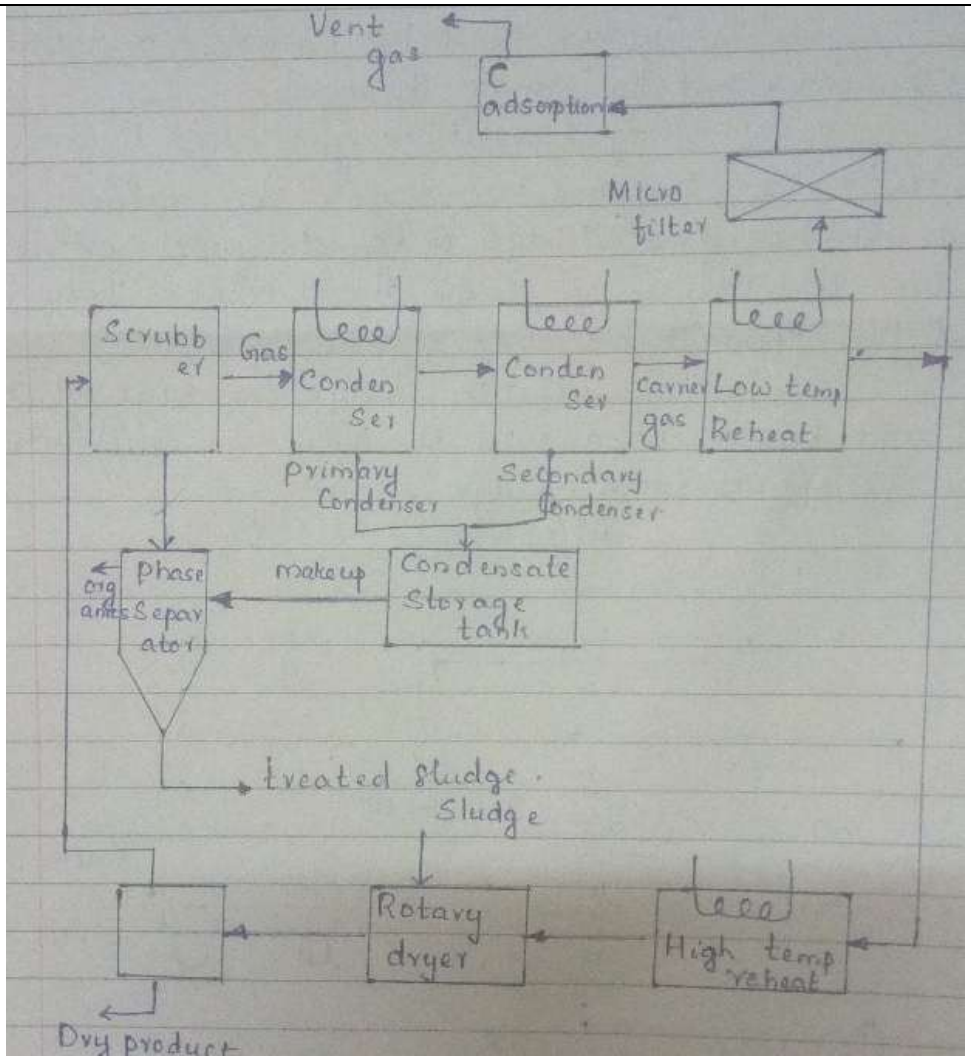
		Bharat Petroleum Corporation Ltd.	Mumbai.	6.9	
		Indian Oil Corporation Limited	Panipat in Haryana	6.0	
		Indian Oil Corporation Limited	Barauni in Bihar	6.0	
		Hindustan Petroleum Corporation Ltd.	Mumbai	5.5	
	Note: ***Any other Indian refineries should be given due consideration***				
1-c	**Constituents 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)Paraffinsii)Aromatics iii) Napthenesiv) dienes B. Non hydrocarbon i) S compounds ii)O_2 compounds iii)N_2 compounds C. Metallic compounds. **Characteristics of crude oil:** 1.Crude is an yellowish black oily complex mixture 2. Flash point: below 10^0C 3. Kinematic viscosity: above 9.5 cSt 4. Pour point; 21^0C 5. Density: 0.83-0.9 gm/ml				2

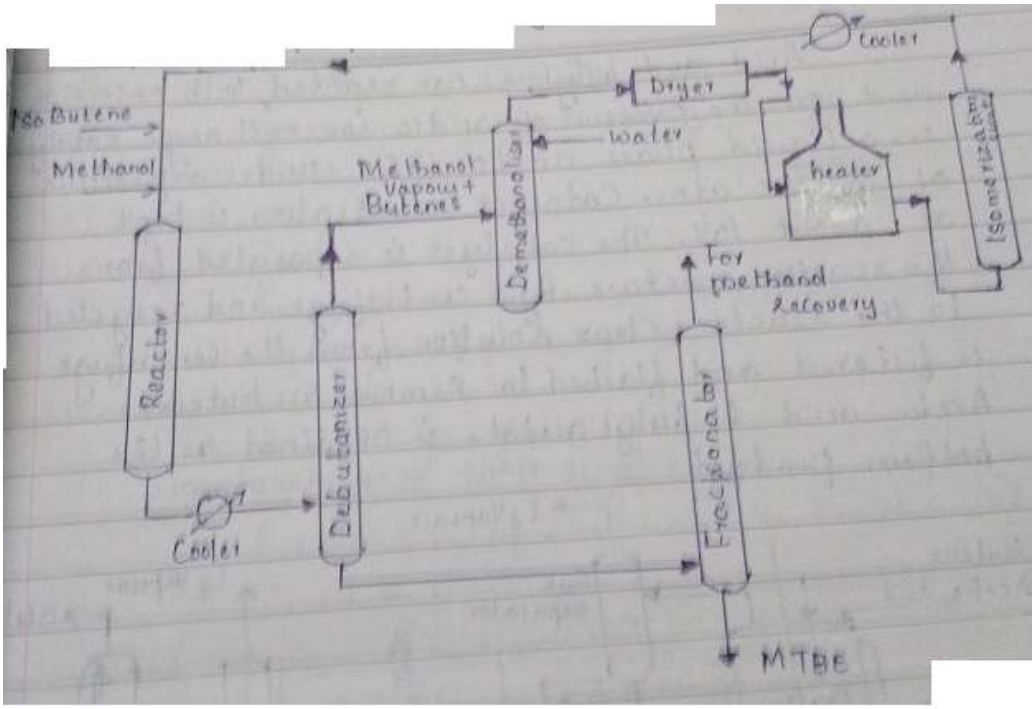
	6. API gravity:41 7. Specific heat: Lighter fractions have higher value 8. Heat of combustion : value decreases from paraffins to aromatics. 9. Viscosity index: Paraffinic base oils have high viscosity index and naphthenic base oils have low viscosity index.	½ mark each for any four
1-d	**Desalting of crude oil:** Desalting of crude oil is the removal of corrosive salts and water from the crude which will otherwise cause corrosion, plugging & catalyst poisoning. **Electric desalting:** **Explanation:** 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.  	4

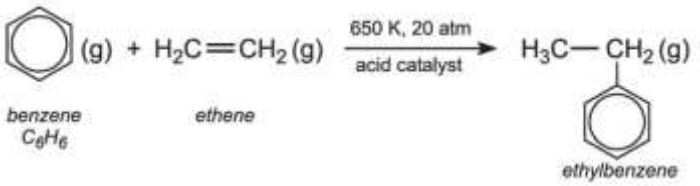
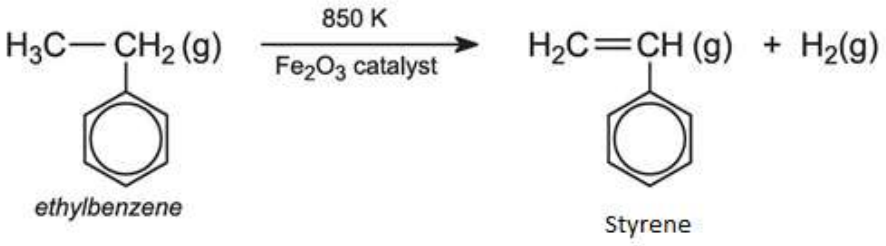
	(Description of chemical treatment should also be given due consideration	
1-e	**Reason for crude oil being known as black gold:** Crude oil is yellowish black oil that is extracted from under the surface of the earth. It is one of the most necessitated worldwide required commodities. Any fluctuation in the crude oil prices can have direct and indirect influence on the economy of the countries. That is why crude oil is called black gold.	4
1-f	**Products obtained from C4 hydrocarbons(any 4):** Butadiene, MTBE, butyl acetate, butanol, isobutane	1 mark each
1-g	**Flow sheet for the manufacture of methanol:** 	4

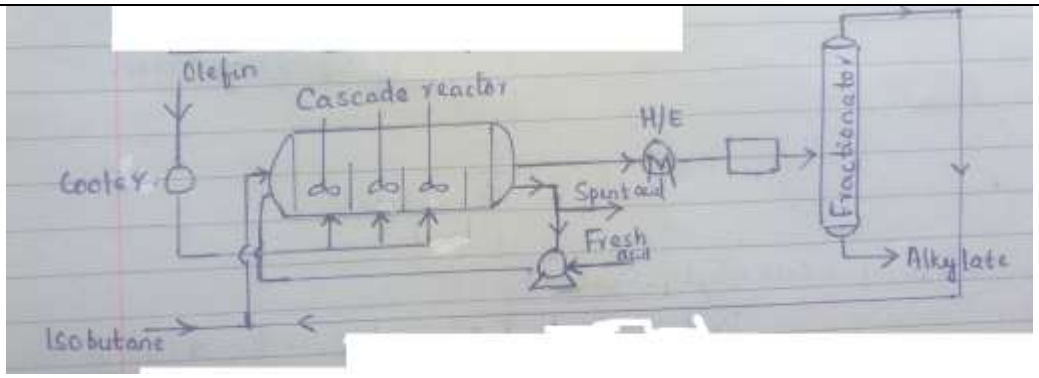
2	**Attempt any FOUR of the following**	**16**
2-a	**Atmospheric distillation process:**  The crude oil is preheated to 350-380°C in tubular furnace known as pipe still. Hot vapours plus liquid are passed through a tall fractionating column, called bubble tower. It consists of a number of bubble cap trays which provide intimate contact between escaping vapours and down coming liquid. Heavier hydrocarbons condense more quickly and settle in lower trays and lighter hydrocarbons remain as vapour for a long time and condense on higher trays. Light gases like methane, ethane etc pass out from the top of the column, petrol are formed in the top trays, kerosene and gas oils in the middle and fuel oils at the bottom. Residue drawn from the bottom is send to a vacuum distillation unit	2 2

	or burned as a fuel or used as a feed stock for cracking units.	
2-b	**Hazardous waste treatment:** **Low temperature thermal treatment process:** At low temperature of 250-450^{o}C, hazardous waste like polychlorinated biphenyls (PCB) are removed. The process uses an indirectly heated rotary drier to volatilize water and organic compounds in a sealed system. Hot treated solids are cooled and wetted to reduce dust formation. An inert gas carrier (N_2) transports the volatilized compound to a gas treatment train which removes entrained solid particles with a scrubber and cools entire gas to less than 5^{o}C to condense organic compound. These can be recycled or disposed. The carrier gas is reheated to 315^{o}C and recycled to the drier. Very small quantities of the carrier gas are passed through a micro filter and a carbon adsorption system before discharging to atmosphere.	4

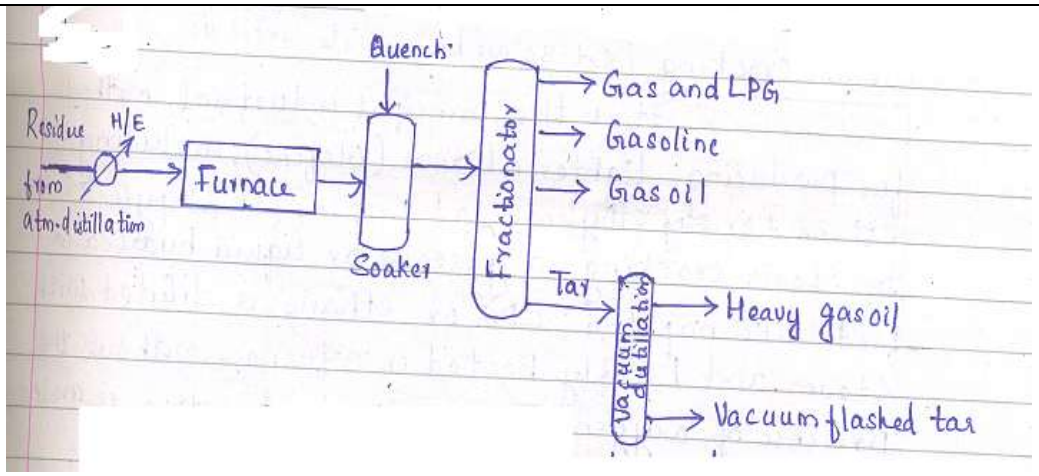
	 ***(Any other method of hazardous waste treatment should be given due consideration.)***	
2-c	**Definitions:** **(i)Octane number:** Octane number is defined as the percentage volume of isooctane in a mixture of isooctane and – n heptane that gives the same knocking characteristics as the fuel under consideration **(ii)Cetane number:**	2

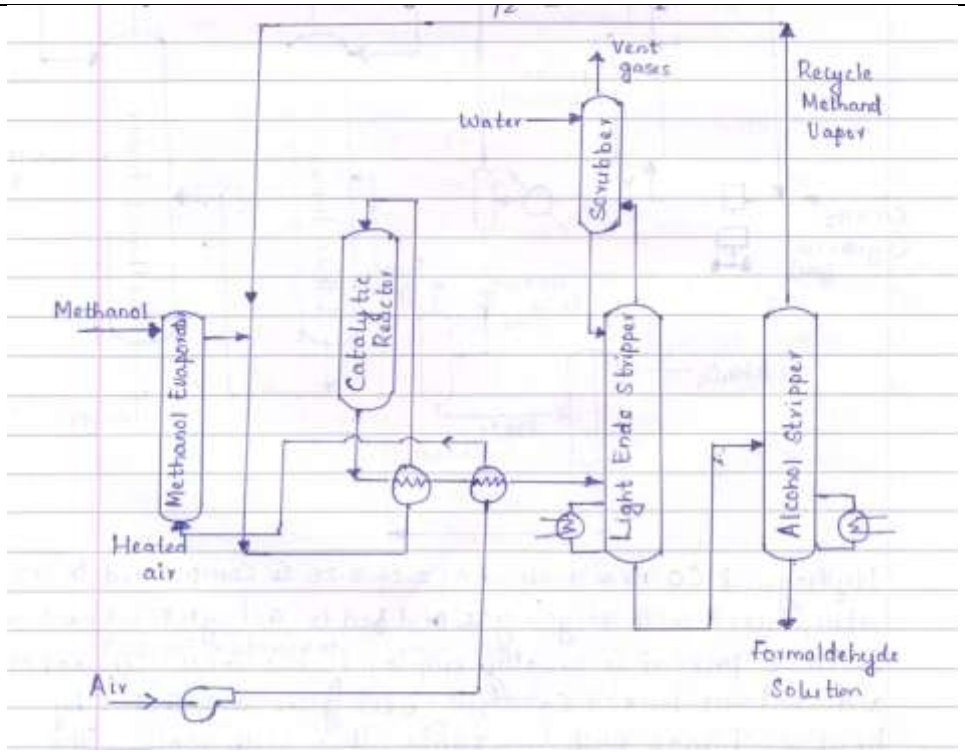
	It is defined as the percentage volume of n-cetane in a mixture of n-cetane and heptamethylnonane that gives the same ignition delay as the fuel under consideration.	2
2-d	**Manufacturing of MTBE**  MTBE is produced by the addition reaction between methanol and butylene Reaction: $(CH_3)_2C= CH_2 + CH_3OH \rightarrow (CH_3)_3CO\text{-}CH_3$ Isobutene and methanol enters a fixed bed reactor, where 90% of butene is consumed. The products are cooled to 20^0C, whereby unreacted methanol and MTBE are condensed. Butenes are separated first from the reactor mix by distillation (debutanizer). Methanol and MTBE mixture is obtained from the bottom of the column which is again distilled in a separate column to obtain MTBE as the bottom product. The gas phase containing methanol vapours is washed with water in a demethanolizer, dried, heated to about 300^oC and	4

	admitted to a isomerization unit where 2 and n-butene are converted into isobutene. Isobutene is cooled and then recycled.	
2-e	**Reaction involved in the manufacture of styrene:** 1. Alkylation of benzene  2. Dehydrogenation of ethyl benzene  	2 2
3	**Attempt any FOUR of the following**	**16**
3-a	**Sulphuric acid alkylation process:** **Explanation:** C_4H_8 + C_4H_{10} → C_8H_{18}(2,2,4 Trimethyl Pentane)	4

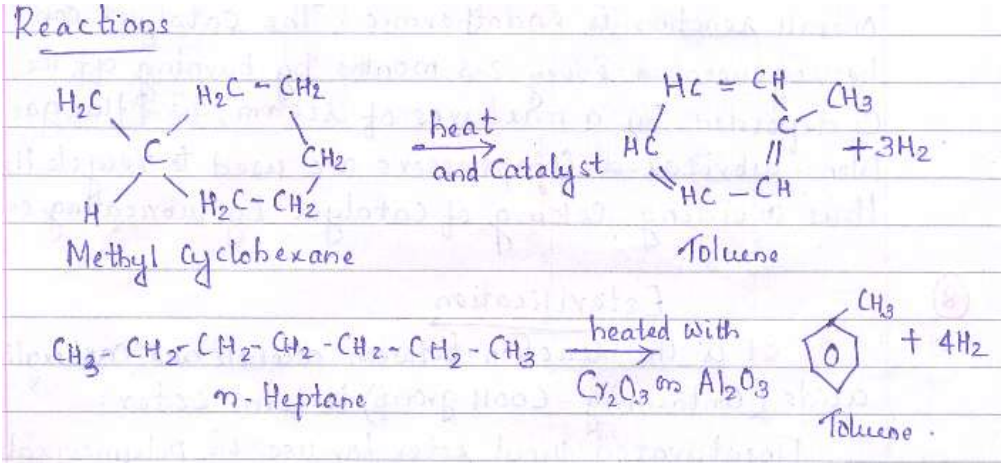
	 Feed stock (Propene, butene, isobutane) enters the multistage cascade reactor. Isobutane and acid passes from one stage to other cascading serially. Olefin is split and introduced into each cascade. To avoid polymerization of olefins, a large excess of isobutane is used, ranging from 5:1 to 15:1. Sulphuric acid as catalyst is introduced at 4-10^{o}C in emulsion form. Reactions are exothermic, best yield at lower temperatures. Alkylate formed is taken out from the reactor, cooled and fractionated. Isobutane from the fractionator is recycled. Acid from the bottom of the reactor is taken and kept in circulation. Propene evaporation causes self-refrigeration and maintains the temperature of alkylation at required low level.	
3-b	**Definitions:** **(i) Aniline point:** It is defined as the minimum temperature at which equal volumes of anhydrous aniline and oil mix together. **(ii) Pour point:** The temperature at which oil stops flowing or getting poured is called pour point of oil. **(iii) Cloud point**-When oil is cooled slowly, the temperature at which it becomes cloudy is called as cloud point. **(iv) Fire Point:** It is the minimum temperature at which oil will give enough vapours which will burn continuously for at least 5 seconds when a flame is brought near it.	1 mark each

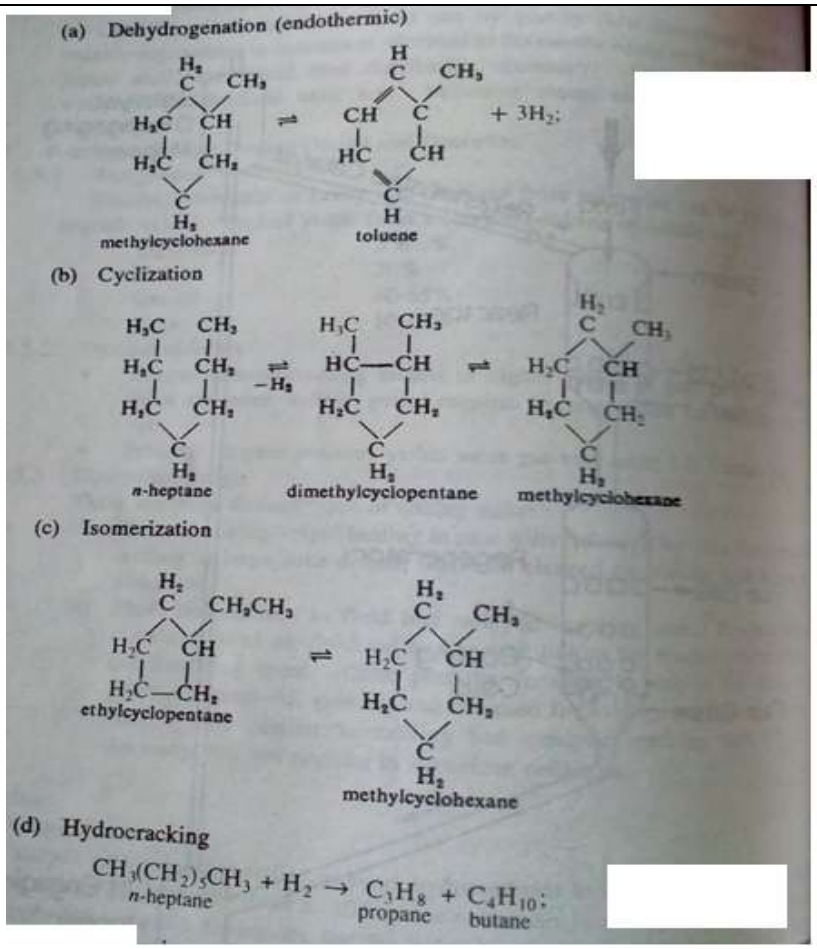
3-c	**BTX:** BTX refers to mixtures of benzene, toluene, and the three xylene isomers, all of which are aromatic hydrocarbons **Uses of benzene**: Used in the production of phenol, styrene, cyclohexane, aniline, sulfonated detergents, chlorobenzene,maleic anhydride (any two) **Uses of toluene**: Used in refinery streams such as gasoline for blending to improve the octane value. In the production of detergents, benzoic acid, used as plasticizer, solvents for paint, rubber etc (any two) **Uses of xylene**: Used in refinery streams for gasoline blending or further separated by isomers for chemical applications.Solvent for alkyd resins, in the production of phthalic anhydride, dimethyl terephthalate(any two).	1 ½ mark each for any 2 uses ½ mark each for any 2 uses ½ mark each for any 2 uses
3-d	**Visbreaking:** It is a mild form of thermal cracking which cracks large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons. **Description:** 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.	1 1

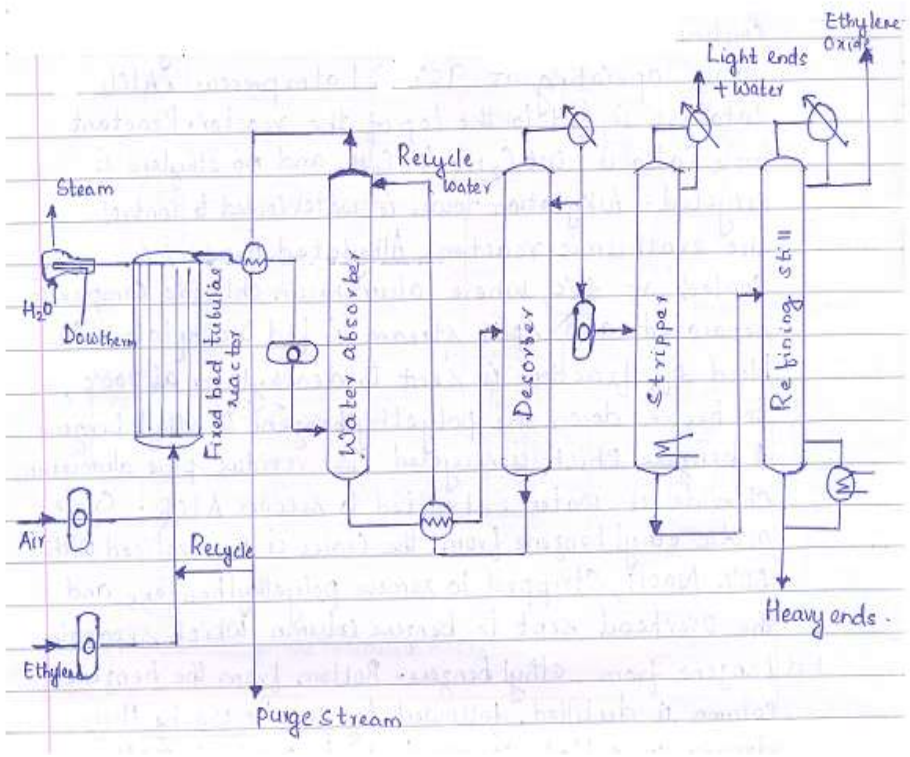
		2
3-e	**Manufacture of formaldehyde:** **Explanation:** Reaction : $CH_3OH + ½ O_2 \rightarrow HCHO + H_2O$ Non purified air compressed to about 1.2 atm is preheated by heat exchange with reacting gases and then conveyed to a methanol evaporator. Methanol to oxygen ratio is maintained in the 390-50% range. The mixed gases are preheated , sent to a reactor where Ag or Cu gauze or their oxides acts as catalysts. Catalyst activity is controlled to maintain a balance between the endothermic dehydrogenation and exothermic oxidation at 450-500^oC. Some complete combustion also takes place. Product gases are absorbed in a water scrubber and then fractionated to recover unreacted methanol which is recycled. **Flow sheet**	2

		2
4	**Attempt any FOUR of the following**	**12**
4-a	**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.	1 mark each for any 4 points

Thermal cracking	**Catalytic cracking**
1.High temperature, high pressure	Low temperature, low pressure
2. No catalyst used	Cata yst is used
3. More coke is produced	Little coke is produced
4. More polymerization	Less polymerization
5. Difficult to handle high sulphur feed stock	Can handle high sulphur feed stock

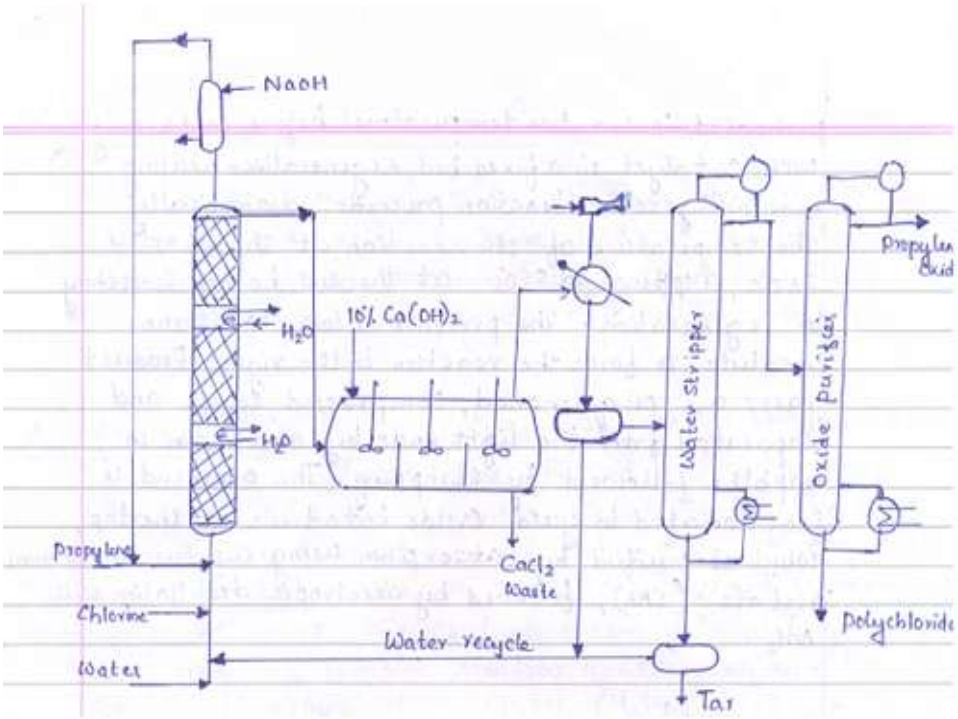
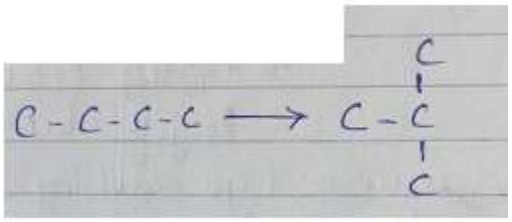
	6. selective cracking is difficult	Selective cracking is possible	
4-b	**Reforming process** Reforming is used to convert hydrocarbons to aromatics which have high octane rating. Reforming is an important process used to convert low octane naphtha into high octane gasoline blending components called reformates. Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, isomerization taking place simultaneously. Catalytic reformates make excellent blending stocks.  Reactions Methyl cyclohexane heat and Catalyst Toluene n-Heptane heated with Cr_2O_3 on Al_2O_3 Toluene. **OR**		2 2

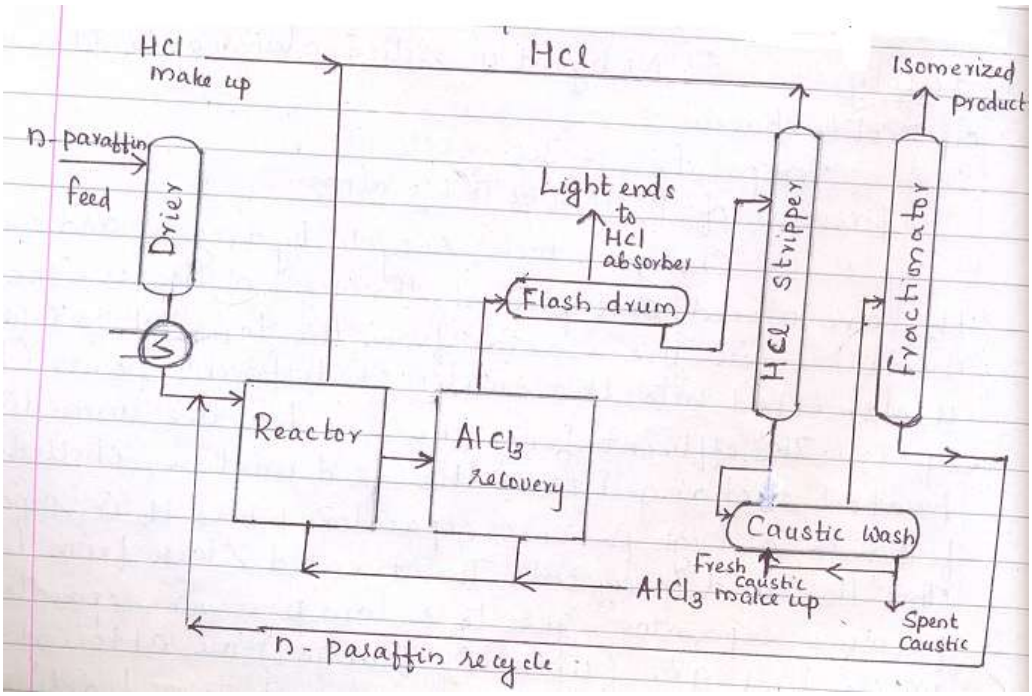
		
4-c	**Importance of vacuum distillation in petroleum refining:** In atmospheric distillation of crude oil, it is important not to subject the crude oil to temperature above 370 to 380^{o}C because the high molecular weight components will undergo thermal cracking and form petroleum coke at temperature above that. Formation of coke results in the plugging of pipings and furnace tubes and hence coke formation is not desirable. The residue from the atmospheric distillation unit consists entirely of hydrocarbons that boil above 370 to 380^{o}C. This is send to vacuum distillation unit, where distillation is carried out at an absolute pressure of 10 to 40 mm of Hg so as to limit the	4

	operating temperature to less than 370 to 380^{o}C. Vacuum distillation helps to maximize the recovery of valuable distillates & to reduce the energy consumption of the units. The residue from vacuum distillation can be used as feedstock for further upgrading, as bitumen feedstock or as fuel component.	
4-d	**Manufacture of ethylene oxide:**  $CH_2=CH_2 + 1/2\ O_2 \rightarrow C_2H_4O + (CO_2 + H_2O)$ Temperature- 250-300 ^{0}C Catalyst -Silver Oxide Ethylene of 95-98 % purity & air are compressed separately mixed together & passed over a catalyst of silver oxide on a porous inert carrier such as alumina.Ethylene dichloride is added to the feed to reduce the competitive oxidation reaction.The effluent gases from the reactor are water washed under pressure.The absorbed ethylene oxide is sent to packed bed desorber-	4

	fractionator tower & taken as overhead.It still contains large amount of water vapour plus some impurities.This stream is compressed to 4-5 atm.& fractionated twice to remove light ends,water& high boiling polymers.	
4-e	**Chemicals derived from C1 hydrocarbon(any two)** 1. Methanol – in the production of formaldehyde, drugs, pesticides, chemicals such as acetic acid, methyl amines, esters, component of gasoline-alcohol mixture for petrol engine (any two) 2. Formaldehyde – In the manufacture of phenolic, urea and melamine resins, in the manufacture of methylene diisosyanate, 1,4butandiol(any one) 3. Chloromethane-– in the production of silicones, tetra methyl lead, synthetic rubber, herbicides, amines(any two) 4. Methylene dichloride – Good paint removal solvent, good propellant for aerosols(any two) **Chemicals derived from C2 hydrocarbon (any two)** 1. Ethanol: Solvent in the manufacture of varnishes, in medicines and drugs, as a disinfectant (hand sanitizer), antidote to methanol poisoning 2. Ethylene oxide: Used in the production of ethylene glycol, non-ionic surfactants (detergents), ethanol amines, glycol ethers etc 3. Styrene : In the manufacture of polystyrene, styrene butadiene rubber, styrene acrylonitrile, polyester resins etc 4. Acetaldehyde: In the manufacture of acetic acid, acetic anhydride, ethyl acetate, n butanol, pyridines. ***(Due consideration should be given for any other chemical derived from C1 and C2 hydrocarbon)***	1 mark each for listing and writing any 2 uses. 1 mark each for listing and writing any 2 uses.
5	**Attempt any TWO of the following**	**16**
5-a	**Propylene oxide:** **Description:**	

	It is produced via chlorohydrins route. Reaction: 1. Chlorhydrination $CH_3CH= CH_2 + HOCl \rightarrow CH_3- CHCl- CH_2OH$ 2.Dehydrochlorination: $2CH_3- CHCl- CH_2OH + Ca(OH)_2 \rightarrow CH_3 CH CH_2O + CaCl_2 + 2H_2O$ Propylene, chlorine & water are introduced into the bottom of a packed tower where chlorohydrin is formed. The reaction mechanism is formation of hypochlorous acid which reacts rapidly with propylene. Reaction is exothermic and maximum tower temperature is held at 50^0C by admitting cold water. Unreacted propylene is scrubbed with NaOH to remove HCl. The liquid stream containing chlorohydrin is drawn and neutralized with lime. Then it is steam stripped to remove propylene oxide in to the overhead condenser. The condensate is a mixture of oxide, water and small amount of propylene dichloride and other organics. Then it is fractionated to separate propylene oxide. **Flowsheet**	4

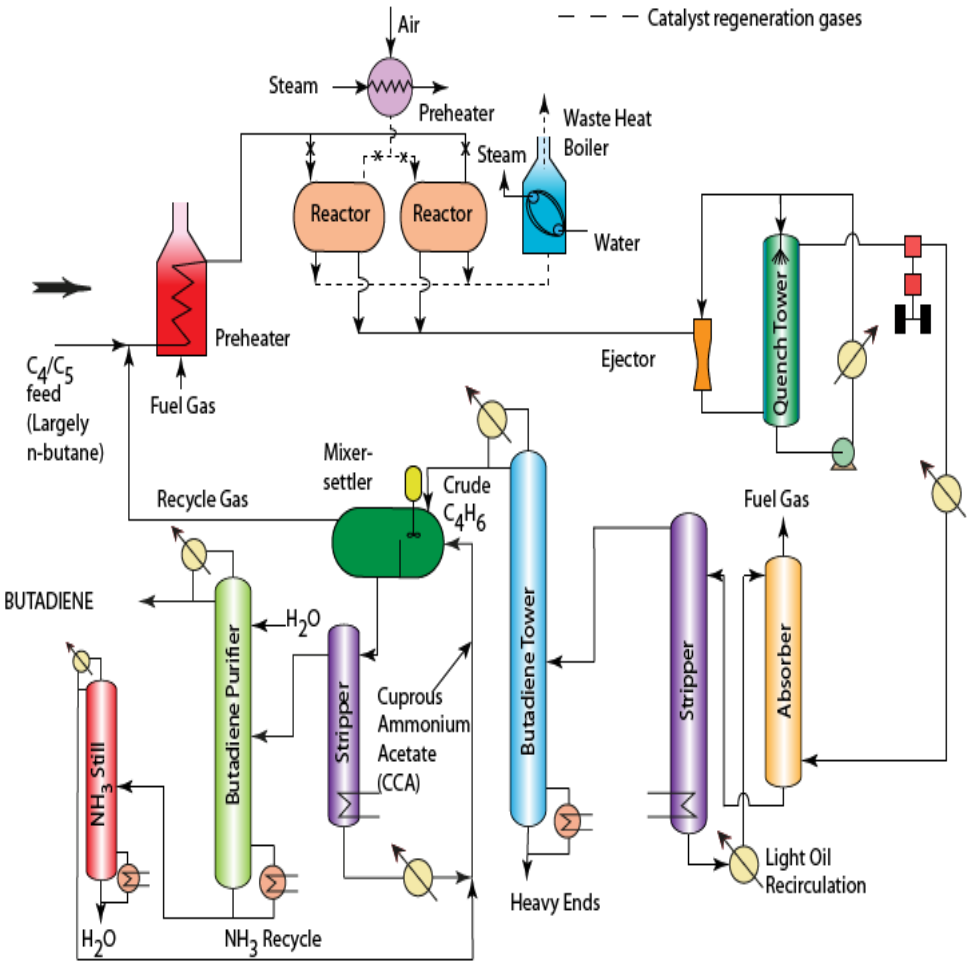
		4
5-b	**Isomerization process:** **Explanation:**  Isomerization is used to convert normal paraffins to isoparaffins Catalyst: Aluminiumtrichloride, HCl is the promoter. Temperature: 100-150^{0}C. Pressure: 17-27 atms Feed stock (n-paraffins) is dried, preheated and fed to a reactor where efficient	4

	contact between reactants and catalysts takes place. HCl and make up $AlCl_3$ are also added. $AlCl_3$ recovery by condensation or distillation is necessary because it is volatile in reactor conditions and slightly soluble in liquid hydrocarbons. Removal of light ends by flashing, followed by HClstripping , caustic wash and fractionation are the standard procedures performed to produce isomerized gasoline. **Flow sheet**  ***(Any other type of isomerization process should be given due consideration)***	4
5-c	**Fractions obtained from crude oil with their uses and boiling point range** **Fractions** | **Boiling point range** | **Uses** 1. Uncondensed gases | < 30°C | Domestic fuel, synthesis of organic	1 mark each

				chemicals.		
		2. Petroleum ether	30-70^{o}C	Solvent for fats, essential oils, used in dry cleaning.		
		3.Gasoline or petrol or motor spirit	40-120^{o}C	As a motor fuel for IC engines, solvent, in dry cleaning.		
		4. Naphtha	120-180^{o}C	As a solvent and in dry cleaning, feed stock for petrochemicals.		
		5. Kerosene oil	180-250^{o}C	Illuminant, fuel for stoves		
		6. Diesel oil	250-320^{o}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		

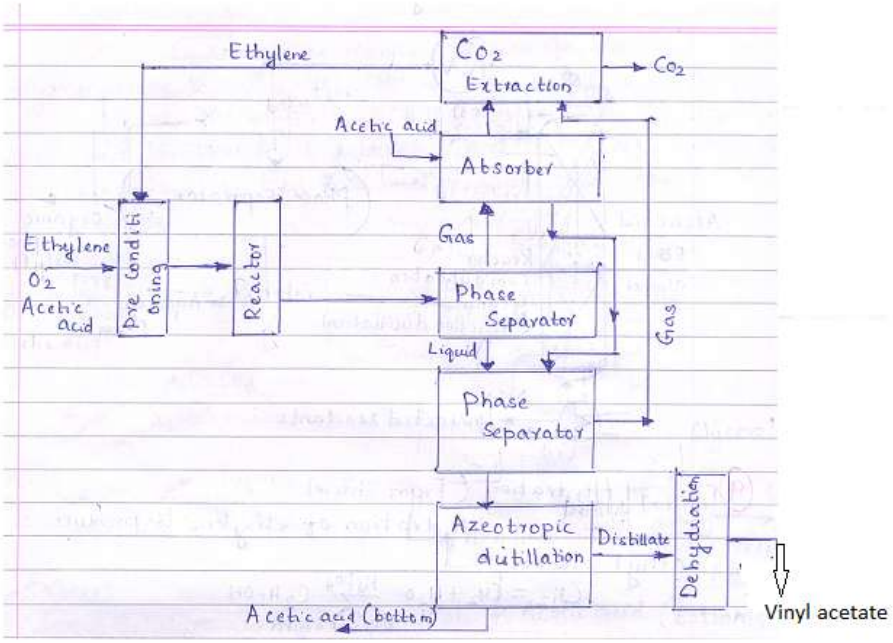
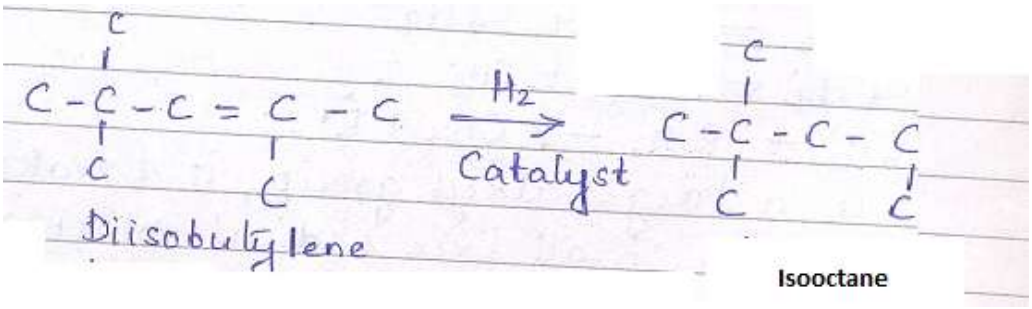
				processes.		
		8.Residue	> 400^{o}C	Used for making roads and water proofing roof, as a fuel, for moulding electrode rods.		
6	**Attempt any TWO of the following**					**16**
6-a	**Manufacture of butadiene:** **Explanation:** Main reaction-$C_4H_{10} \rightarrow CH_2=CH.CH=CH_2+2H_2$ Side reaction-$C_4H_{10} \rightarrow C_4H_8+H_2$ A refinery gas of C4/C5 containing n-butane with some isopentane is mixed with recycle gas & preheated to reaction temperature .prior to contact with catalyst in a fixed bed, regenerative heating reactor system. The temperature 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.					3

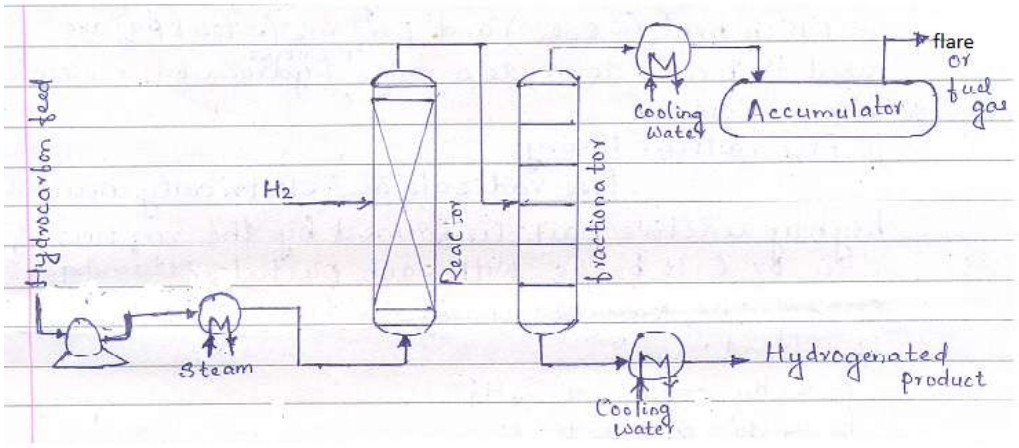
Flow sheet


Air
Catalyst regeneration gases
Steam
Preheater
Waste Heat Boiler
Steam
Reactor
Reactor
Water
Preheater
Ejector
Quench Tower
C_4/C_5 feed (Largely n-butane)
Fuel Gas
Mixer-settler
Crude C_4H_6
Recycle Gas
Fuel Gas
BUTADIENE
H_2O
Butadiene Purifier
Stripper
Cuprous Ammonium Acetate (CCA)
Butadiene Tower
Stripper
Absorber
NH_3 Still
Light Oil Recirculation
Heavy Ends
H_2O
NH_3 Recycle

5

6-b	**(i) Factors affecting the prices of crude oil (4 points):** 1. Production of crude oil: OPEC nations are the major producers of world's crude oil. Any decision by them to increase or decrease the 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 affects the 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 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. **(ii) Esterification process:** 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	1 mark each 4

	separator and the phases are separated. In the absorber the gas is washed with acetic acid to recover the vinyl acetate. 	
6-c	**(i) Hydrogenation:** **Explanation:** It is the addition of hydrogen to an olefin 	4



Hydrogen and hydrocarbon feed flows concurrently in a fixed bed reactor. Intimate mixing of hydrogen and reactants in the reactor bed is essential to make the best use of palladium catalyst. Poor hydrogen distribution results to inadequate diolefin hydrogenation. Additional equipment for high temperature hydrogen stripping is required for removal of polymer in order to extend the useful life of catalyst.

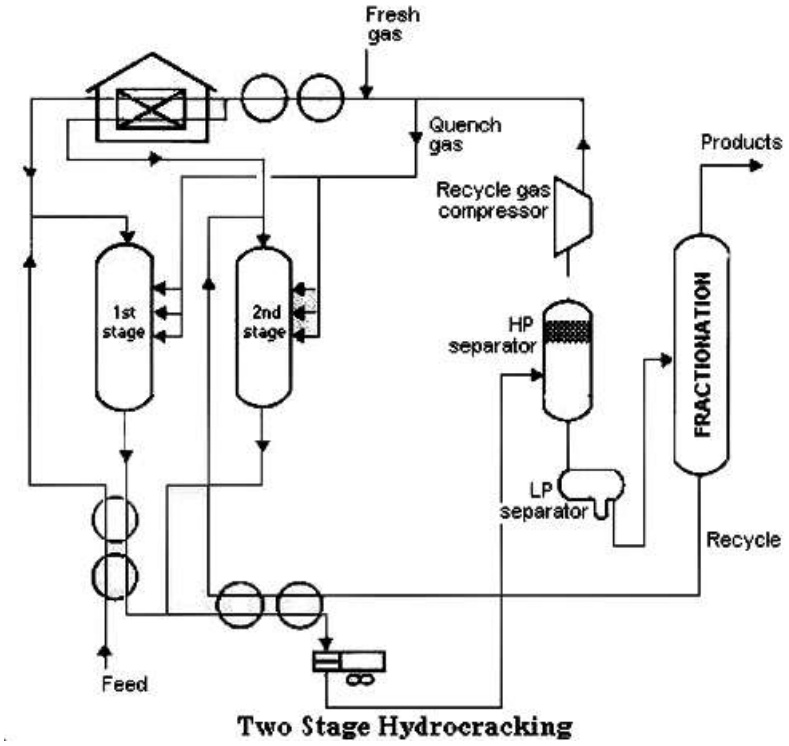
(ii) **Hydrocracking**

Explanation

Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feed stocks are cracked in the presence of hydrogen to produce more desirable products. Charge stock, recycle hydrogen and make up hydrogen are mixed and passed through a heater. The mixture enters the reactor from the top while cold hydrogen is admitted in to the reactor at different points. The effluent from the reactor is immediately heat exchanged with the feed mixture, chilled and fed in to a high pressure separator where hydrogen is separated and recycled. The treated stock from high pressure separator goes to low pressure separator where fuel gas are obtained. Liquid fractions from the bottom are sent to fractionators where distillates are separated and heavy oil from the bottom is recycled.

2

Flow Sheet



Two Stage Hydrocracking

2