WINTER-17 EXAMINATION

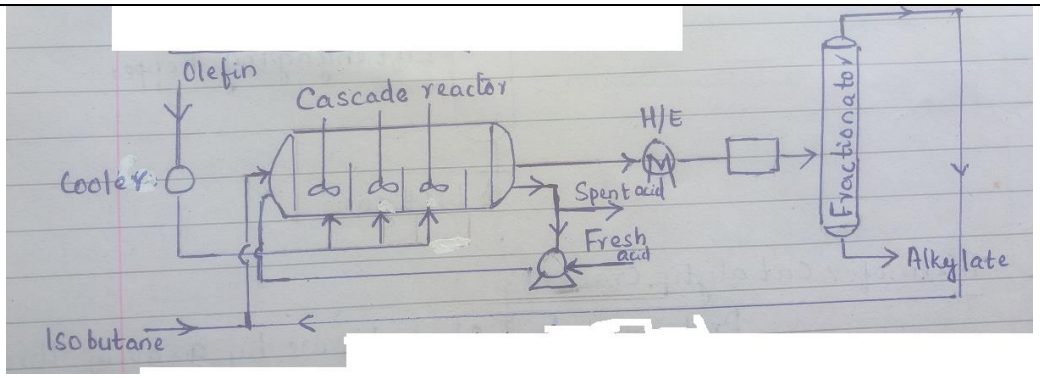
Model Answer

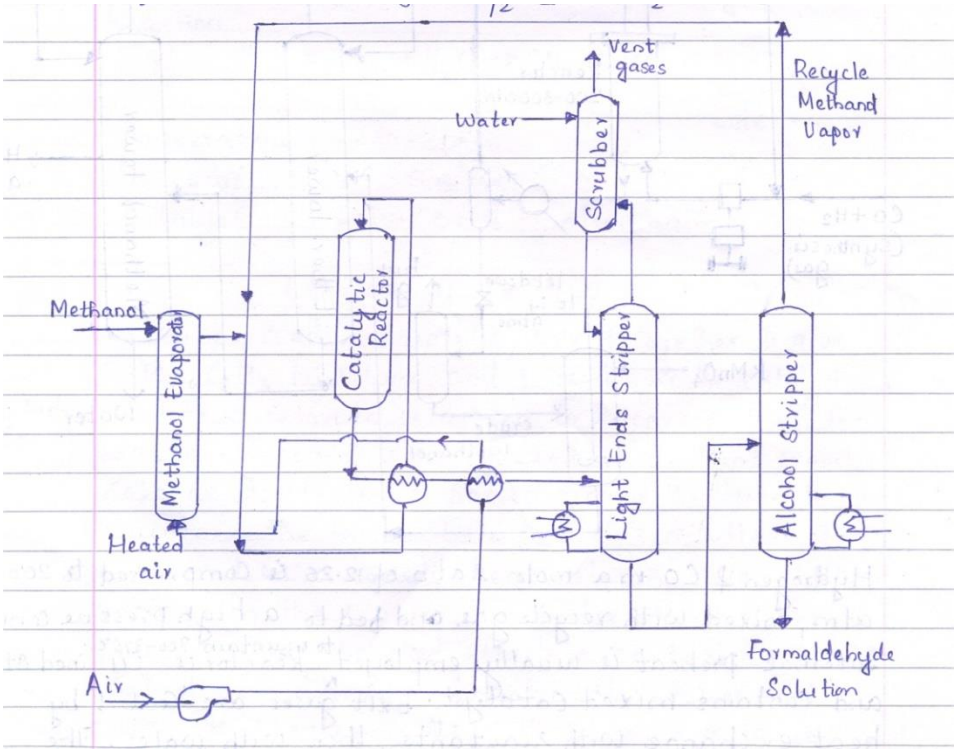
Important Instructions to examiners:

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.

Q No.	Answer	Marks
1a	**Attempt any three of the following**	**12**
1a-i	**OPEC:** OPEC is Organization of Petroleum Exporting Countries. 43% of world crude produced is shared among the group members. **List of six major oil producing countries in the world** Saudi Arabia - 13% United States - 12% Russia - 11.64% China - 5% Iran - 4.14% Canada – 4%	1 3
1a-ii	**Classification of crude:** Refinery crude petroleum classification is as follows 1. Paraffin base: Predominantly open chain compounds 2. Naphthene base: Cyclic compound predominates. 3. Intermediate (mixed) crude: large amount of both paraffinic and naphthenic Compounds Petroleum industry generally classifies crude oil by its geographical location, API gravity and its sulphur content. Crude oil is considered light if it has low density or heavy if it has high density. It is referred to as sweet if it contains relatively little sulphur or sour if it contains substantial amount of sulphur	4
1a-iii	**Octane number:** Octane number is defined as the percentage volume of isooctane in a mixture of isooctane and – heptane that gives the same knocking characteristics as the fuel under consideration **Calorific value:** Calorific value is the quantity of heat released per quantity of	2

	fuel when it is burned completely with oxygen and the products of combustion returned to ambient temperature.	2
1a-iv	**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 the Uses. 1 maark each for listing and writing the uses.
1b	**Attempt any ONE of the following**	6
1b-i	**Sulphuric acid alkylation process:** **Flowsheet:**	

	 **Explanation:** 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. ***(Due consideration should be given for hydrofluoric acid alkylation)***	3 3
1b-ii	**Flow sheet for the 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	3

	endothermic dehydrogenation and exothermic oxidation at 450-500^{o}C. Some complete combustion also takes place. Product gases are absorbed in a water scrubber and then fractionated to recover unreacted methanol which is recycled.  	3
2	**Attempt any FOUR of the following**	**16**
2-a	**Properties of crude oil (any four):** 1.Crude is an yellowish black oily complex mixture 2. Flash point: below 10^{0}C 3. Kinematic viscosity: above 9.5 cSt 4. Pour point; 21^{0}C 5. Density: 0.83-0.9 gm/ml 6. API gravity:41 7. Specific heat: Lighter fractions have higher value 8. Heat of combustion : value decreases from paraffins to aromatics.	1 mark each

9. Viscosity index: Paraffinic base oils have high viscosity index and naphthenic base oils have low viscosity index.

10.Paraffins have less ignition temperature and aromatics have high ignition temperature.

2-b **Difference between petroleum refinery and petrochemical industry:** — 1 mark each for any two points

Petroleum refinery	**Petrochemical industry**
1)Process crude oil into different fractions.	It is a chemical plant that uses a petroleum based feedstock from petroleum refinery to produce a petrochemical product
2)Feed stock is crude oil from mines	Feed stock is product obtained from Petroleum refinery
3)Product obtained from Refinery are kerosene, gasoline, diesel, LPG etc	Product obtained from petrochemical industry are plastic, different hydrocarbons etc
4) All refineries have more or less similar unit operations and unit processes	The process depends on the product to be produced.

List of petroleum refinery (any two) — ½ mark each

1.Reliance petroleum Ltd, Jamnagar.

2. Indian Oil Corporation Limited(IOCL), Koyali in Gujarat.

3. Manglore Refinery and Petrochemicals Ltd, Manglore in Karnataka.

4. Hindustan Petroleum Corporation Ltd (HPCL), Mumbai.

5. Bharat Petroleum Corporation Ltd (BPCL), Mumbai**.**

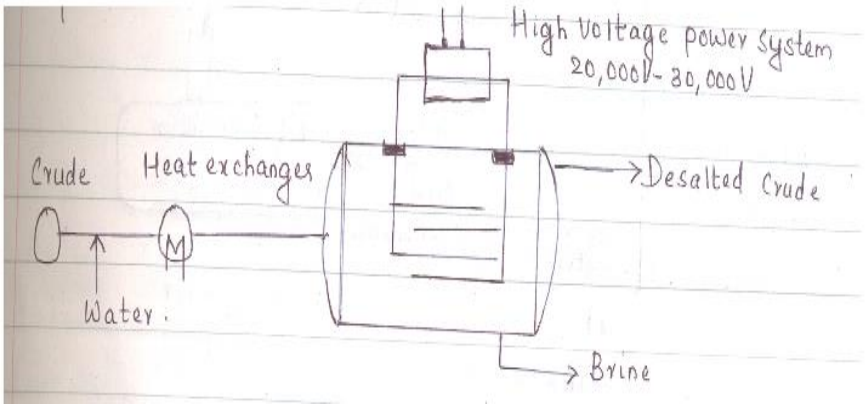
6. Indian Oil Corporation Limited, Panipat in Haryana.

	7. Indian Oil Corporation Limited, Barauni in Bihar. **List of petrochemical industry (any two)** 1. Reliance petrochemicals Ltd, Patalganga 2. Haldia petrochemicals,Mumbai. 3. IGPL, Mumbai 4. Deepak Ferrilizers and Petrochemicals Ltd. ***Any other refineries and petrochemical industry should be given due consideration.***	½ mark each
2-c	**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 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.	1 mark each for any 4 points

2-d	**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 commodity. Any fluctuation in the crude oil prices can have direct and indirect influence on the economy of the counties. **Advantages of crude oil over other energy sources:** 1. It is one of the most abundant energy resources. 2. Liquid form of oil makes it easy to transport and reuse. 3. Oil has high heating value. 4.No new technology needed for use. **Disadvantages of crude oil over other energy sources**: 1. Oil burning leads to carbon emission. 2. Oil recovery process not efficient enough. 3. Oil drilling endangers the environment and ecosystem 4.Oil transportation by ships can lead to spills causing environmental and ecological damage.	2 ½ mark each for any two points ½ mark each for any two points
2-e	**Fractions obtained from crude oil with their boiling point range**	4

Fractions	Boiling point range
1. Uncondensed gases	< 30^{o}C
2. Petroleum ether	30-70^{o}C
3.Gasoline or petrol or motor spirit	40-120^{o}C
4. Naphtha	120-180^{o}C
5. Kerosene oil	180-250^{o}C
6. Diesel oil	250-320^{o}C

		7.Heavy oil On vacuum distillation of heavy oil gives lubricating oil, petroleum jelly, greases, p raffin wax etc.	320-400^{o}C		
		8.Residue	> 400^{o}C		
2-f	**Desalting of crude oil:** 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:** **Explanation:** The feedstock crude is heated between 150^{0} & 350^{0}F 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. **Diagram**				1 2



(Description of chemical treatment should also be given due consideration)

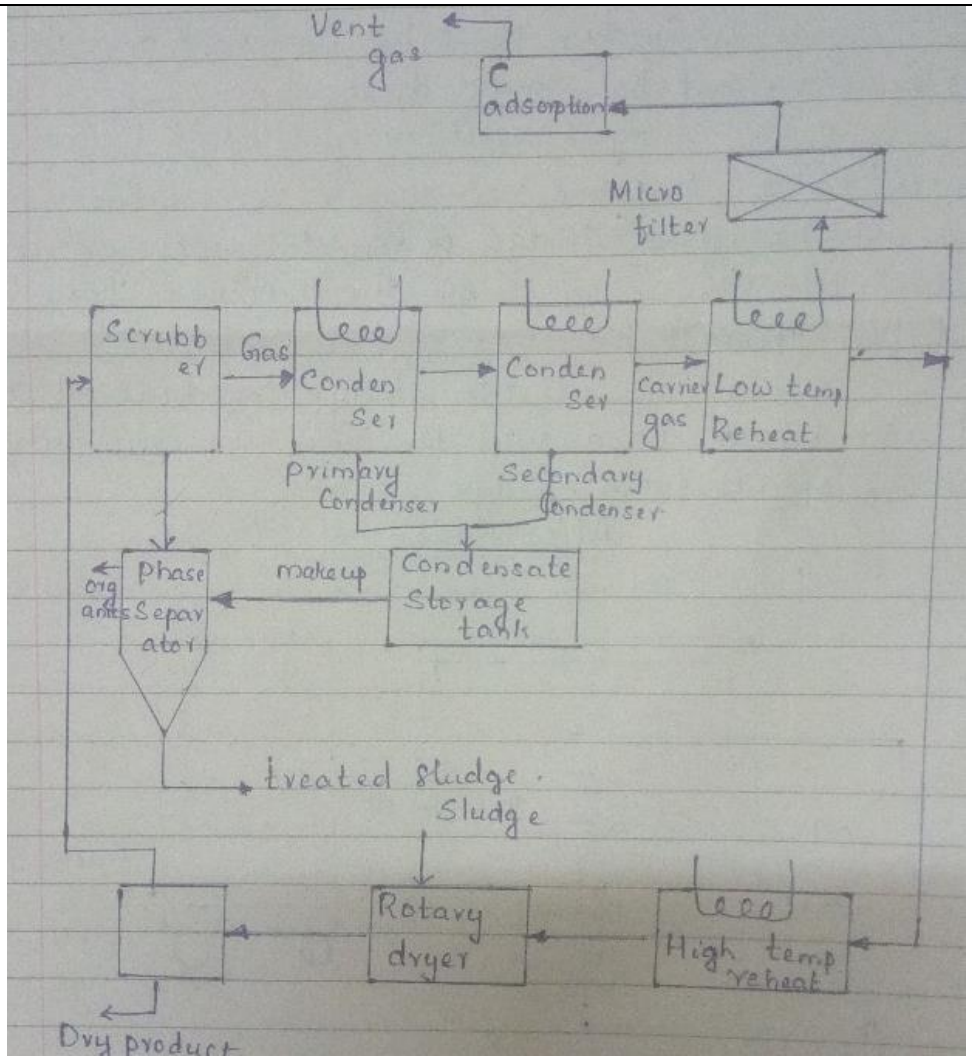
1

3	**Attempt any FOUR of the following**	**16**
3-a	**Fractions obtained from crude oil with their boiling point range and uses**	1 mark each for naming the fraction and writing one application (any four)

Fractions	**Uses**
1. Uncondensed gases	Domestic fuel, synthesis of organic chemicals
2. Petroleum ether	Solvent for fats, essential oils, used in dry cleaning.
3.Gasoline or petrol or motor spirit	As a motor fuel for IC engines, solvent, in dry cleaning.
4. Naphtha	As a solvent and in dry cleaning, feed stock for petrochemicals.
5. Kerosene oil	Illuminant, fuel for stoves
6. Diesel oil	Diesel engine fuels, carbureting of water gas

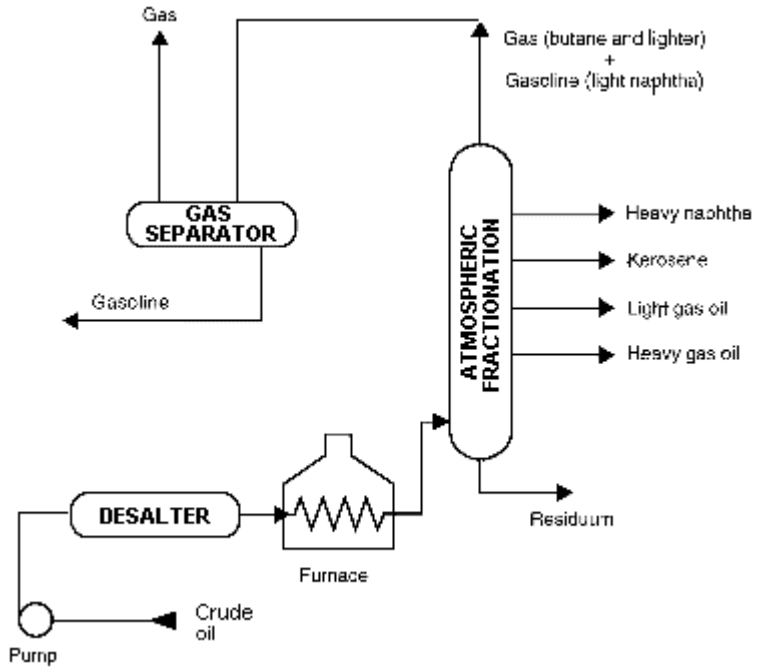
		7.Heavy oil On vacuum distillation of heavy oil gives lubricating oil, petroleum jelly, greases, paraffin wax etc.	Fuel for ships, metallurgical furnaces, feed stock for cracking processes.	
		8.Residue	Used for making roads and water proofing roof, as a fuel, for moulding electrode rods.	
3-b	**Unit operatons carried out in separation process of of petroleum refining:** 1Crude Oil Pretreatment (Desalting) Crude oil often contains water, inorganic salts, suspended solids, and water-soluble trace metals. As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in processing units, these contaminants must be removed by desalting (dehydration) 2. Atmospheric Distillation The desaled crude oil is preheated to 350-380^{o}C in tubular furnace known as pipe still. Hot vapours plus liquid are passed through a tall fractionating column, called bubble tower. 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 or burned as a fuel or used as a feed stock for cracking units. 3.Vacuum Distillation: 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 tower may produce gas		1 mark each

	oils, lubricating-oil base stocks, and heavy residues. Vacuum towers are typically used to separate catalytic cracking feedstock from surplus residuum. 4.Solvent Extraction and Dewaxing Solvent treating is a widely used method of refining lubricating oils as well as a host of other refinery stocks. Solvent refining processes including solvent extraction and solvent dewaxing usually remove the undesirables like compounds containing sulfur, nitrogen, and oxygen; inorganic salts and dissolved metals;, wax etc at intermediate refining stages or just before sending the product to storage.	
3-c	**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 is 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.)

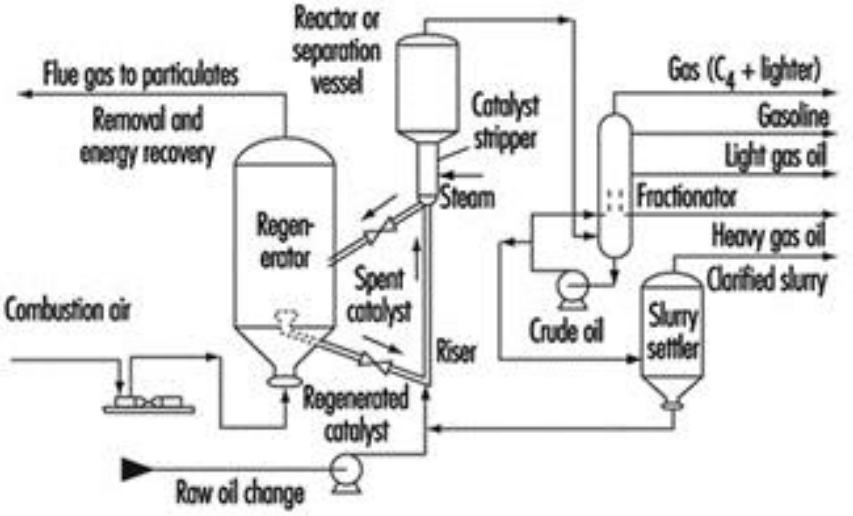
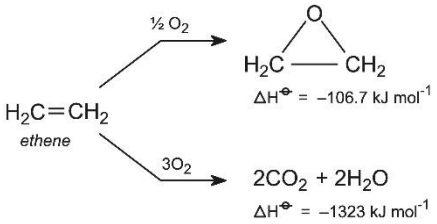
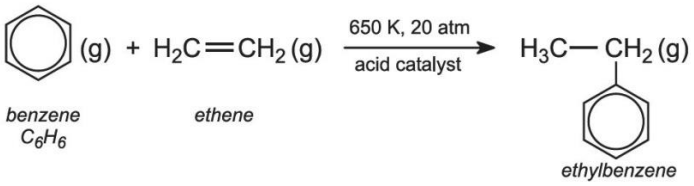
3-d	**Reasons for carrying out vacuum distillation in crude oil refining process:** In atmospheric distillation of crude oil, it is important not to subject the crude oil to temperature above 370 to 380^{o}C because the high molecular weight components will undergo thermal cracking and form petroleum coke at	2

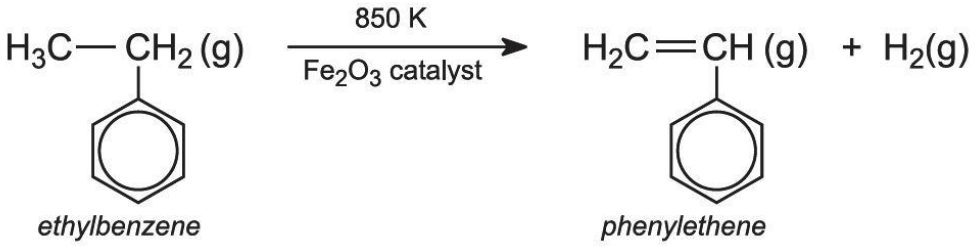
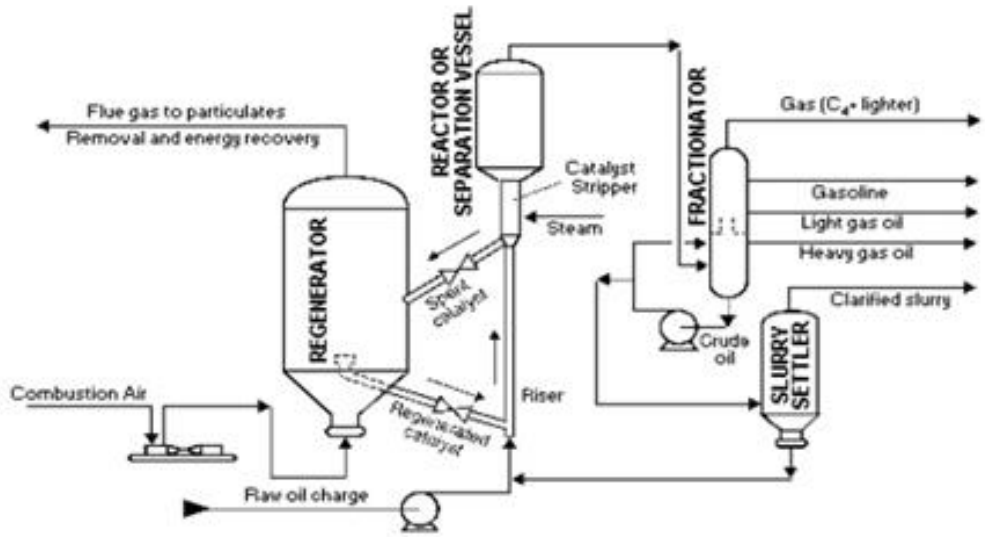
	temperature above that. Formation of coke results in the plugging of pipings and furnace tubes and hence coke formation is not desirable. The residue from the atmospheric distillation unit consists entirely of hydrocarbons that boil above 370 to 380°C. This is send to vacuum distillation unit, where distillation is carried out at an absolute pressure of 10 to 40 mm of Hg so as to limit the operating temperature to less than 370 to 380°C. vacuum distillation helps to maximize the recovery of valuable distillates **Reason for preferring low sulphur crude:** Low sulphur crude is easier to refine and safer to extract and transport than high sulphur crude. Because sulfur is corrosive, low sulphur crude also causes less damage to refineries and thus results in lower maintenance costs over time.	2
3-e	**Atmospheric distillation process:**  The crude oil is preheated to 350-380°C in tubular furnace known as pipe still.	2

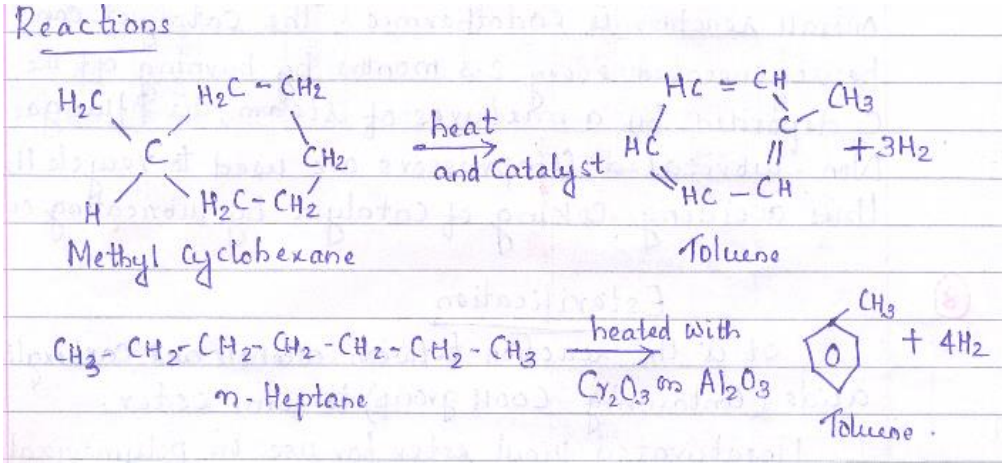
	Hot vapours plus liquid are passed through a tall fractionating column, called bubble tower. It consists of a number of bubble cap trays which provide intimate contact between escaping vapours and down coming liquid. Heavier hydrocarbons condense more quickly and settle in lower trays and lighter hydrocarbons 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 or burned as a fuel or used as a feed stock for cracking units.	2
4a	**Attempt any THREE of the following**	**12**
4-a-i	**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 **Advantages of catalytic cracking:** 1. Produces high quality petrol from any crude. 2. More selective cracking and less light ends. 3. More isomerization. 4. Greater portion of aromatics 5. Less polymerization. 6. Relatively little coke. 7. Greater ability to tolerate high sulphur feed stocks. 8. Uniformity of temperature and pressure control	2 ½ mark each for any 4 points
4a-ii	**Ploymerisation in petroleum industry**: It is the combination of two or more olefinic molecules to yield larger molecules. C3 and C4 olefins from catalytic cracking can be converted to liquid hydrocarbon of the dimer and trimer type.	2

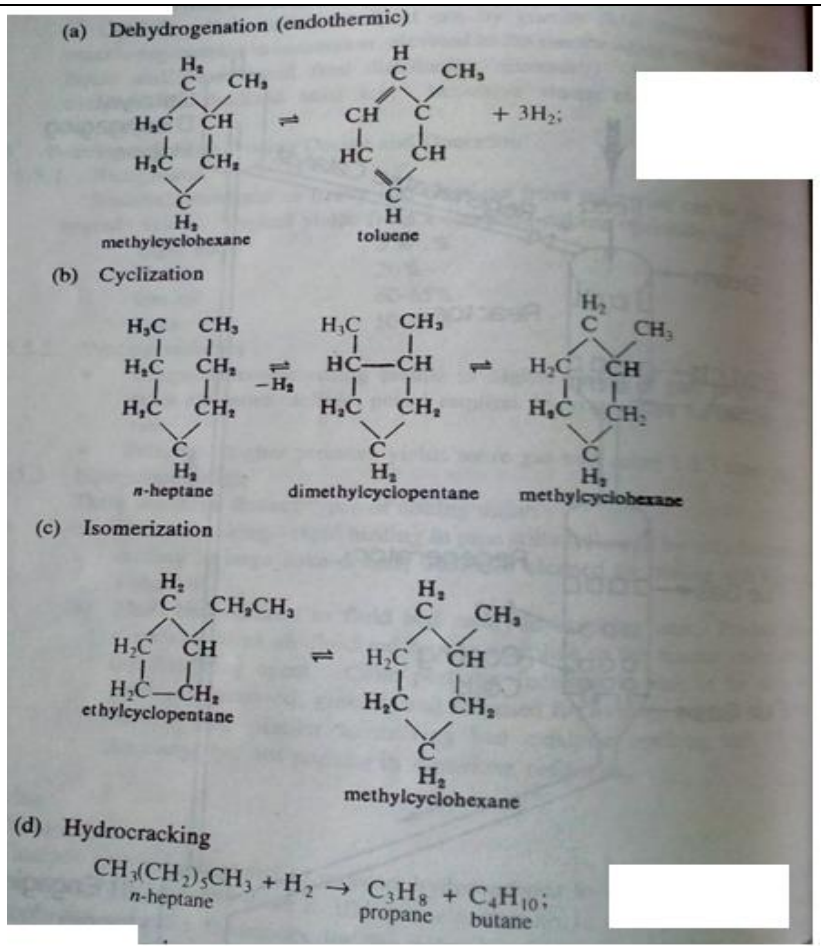
	Methods of polymerization: Methods of polymerization can be classified into condensation or step-growth polymerization and addition or chain growth polymerization. Addition polymerization can be further classified as homogeneous polymerization and heterogeneous polymerization. Homogeneous polymerization is of two types- bulk polymerization and solution polymerization. Heterogeneous polymerization can be classified into emulsion polymerization and suspension polymerization.	2
4a-iii	**BTX:** BTX refers 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 1 1 1
4a-iv	**Products obtained from C4 hydrocarbons:** Butadiene, MTBE, butyl acetate, butanol, isobutane (any 4) **Uses:((2 uses each)** 1. Butadiene Butadiene is used primarily as a chemical intermediate and as a monomer in the	1 3

	manufacture of polymers such as synthetic rubbers or elastomers, including styrene-butadiene rubber (SBR),polybutadiene rubber (PBR), polychloroprene (Neoprene) and nitrile rubber (NR), used as a solvent in the manufacture of cyclo alkanes and cyclo alkenes (any two). 2. MTBE: Best suited for lead in gasoline, as a solvent for paint. 3. Butyl acetate: Used as a solvent in the production of lacquers, synthetic fruit flavor in candies, in the manufacture of artificial leather, photographic films, safety glass 4. Butanol Used as a blended additive to diesel fuel to reduce suit emission, solvent for chemical and textile processes, base for perfumes, salts of butanol are chemical intermediates. 5. Isobutane As a gas for refrigeration systems, especially in domestic refrigerators and freezers, and as a propellant in aerosol sprays.	
4b	**Attempt any ONE of the following**	**6**
4b-i	**Moving bed catalytic cracking** The catalyst is in the form of pellets instead of fine powder. The pellets move continuously by conveyor or pneumatic lift tubes to a storage hopper at the top of the unit, and then flow downward by gravity through the reactor to a regenerator. The regenerator and hopper are isolated from the reactor by steam seals. The cracked product is separated into recycle gas, oil, clarified oil, distillate, naphtha and wet gas.	3

		3
4b-ii	**Reaction involved in the formation of ethylene oxide:** Direct oxidation of ethylene  Temperature: 250-300^{o}C Pressure: 4-5 atms Catalyst: Silver oxide on alumina **Reaction involved in the formation of styrene:** 1. Alkylation of benzene 	3 1.5

	2. Dehydrogenation of ethyl benzene  	1.5
5	**Attempt any TWO of the following**	**16**
5-a	**Fluidized bed catalytic cracking:**  Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality & quantity of lighter & more desirable products. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions. A typical FCC process involves mixing of a preheated hydrocarbon charge with hot, regenerated catalyst .The charge is combined with a recycle stream	3

	within the riser ,vapourized & raised to the reactor temp. (480 to 540^{0}c)by the hot catalyst. As the mixture travels up the raiser ,the charge is cracked. The cracking continues as the oil vapours are separated from the catalyst in the reactor cyclone. The resultant product stream is then charged to a fractionating column where it is separated into fractions & some of the heavy oil is recycled to the riser. Spent catalyst flows through the catalyst stripper to the regenerator where most of the coke deposit burn off at the bottom where preheated air & spent catalyst are mixed . Fresh catalyst are added & worn out catalyst is removed to optimize cracking process.	5
5-b	**Reforming process** 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 + $3H_2$ n-Heptane → (heated with Cr_2O_3 on Al_2O_3) → Toluene + $4H_2$ **OR**	2



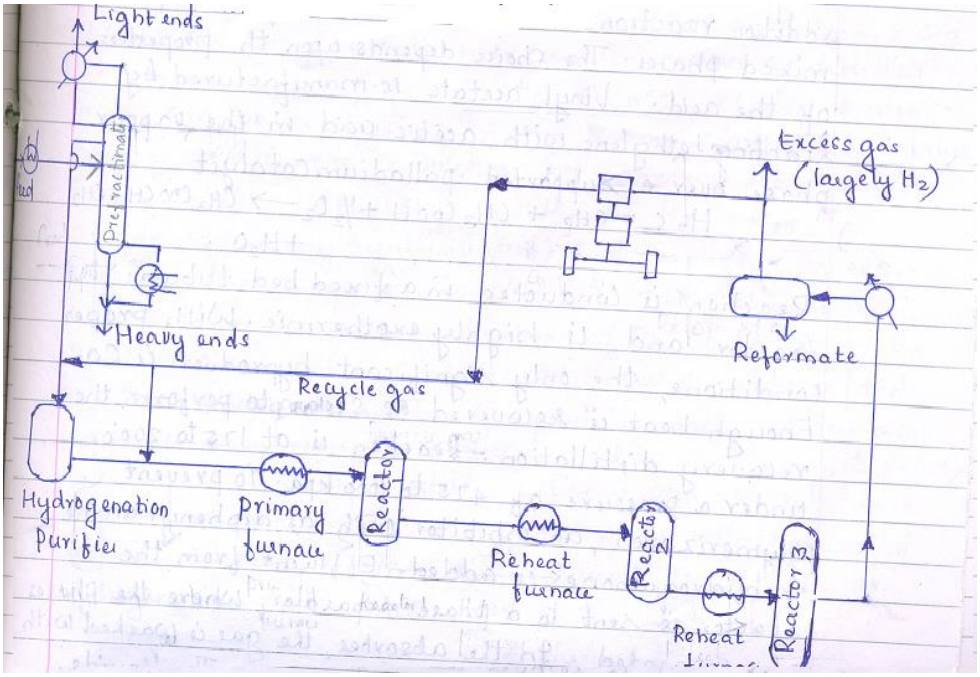
Catalyst: Platinum

Pressure: 15-50 atms

Temperature: 470-525^{0}C

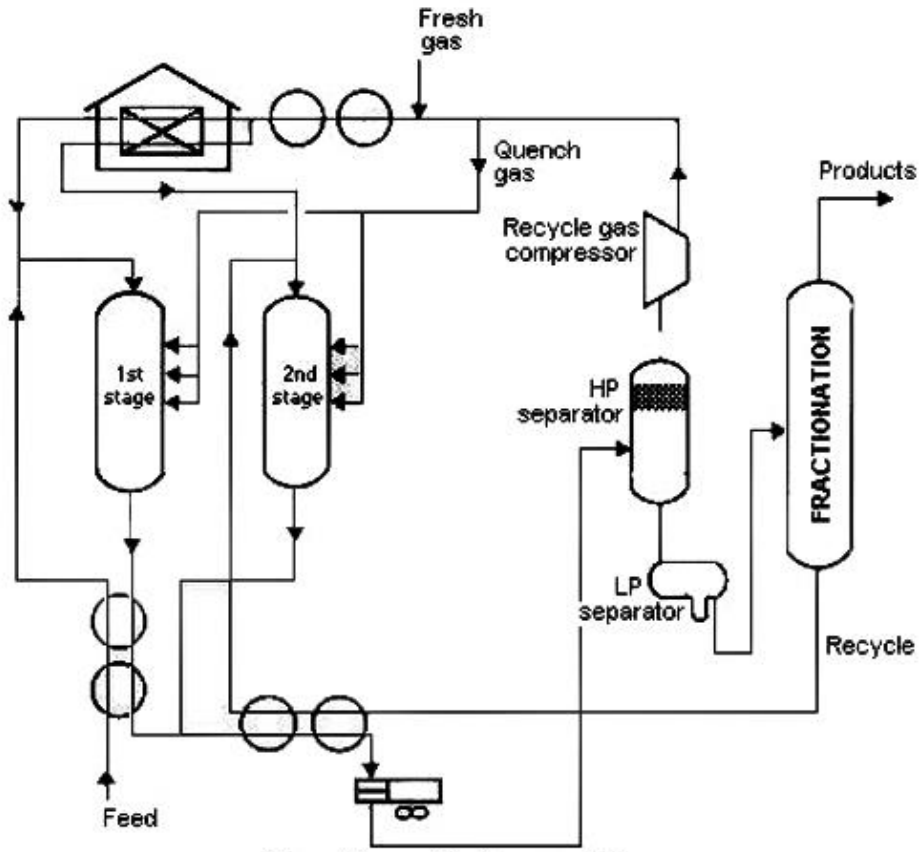
3

Naphtha feedstock is preheated by mild hydrogenation, high temperature .bauxite reaction to remove sulphur, nitrogen & metal which lower pt catalyst activity. The treated feed is mixed with recycle H_2, preheated & charged to three or more cylindrical reactors in series .Reheat interstages are required since overall reactions is endothermic. The catalyst can be regenerated every 2-3

	months by burning off the carbonaceous deposit with mixture of stream, air & flue gas. Smaller particles catalyst gives higher activity per unit volume but causes greater pressure drop in a given sized reactor.  	3
5-c	**Hydrocracking** **Description** 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	3

fractions from the bottom are sent to fractionators where distillates are separated and heavy oil from the bottom is recycled.

Flow Sheet

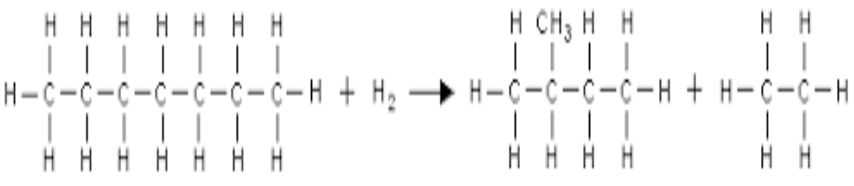


Two Stage Hydrocracking

3

Reaction:

n-Heptane + H_2 → Isopentane + Ethane



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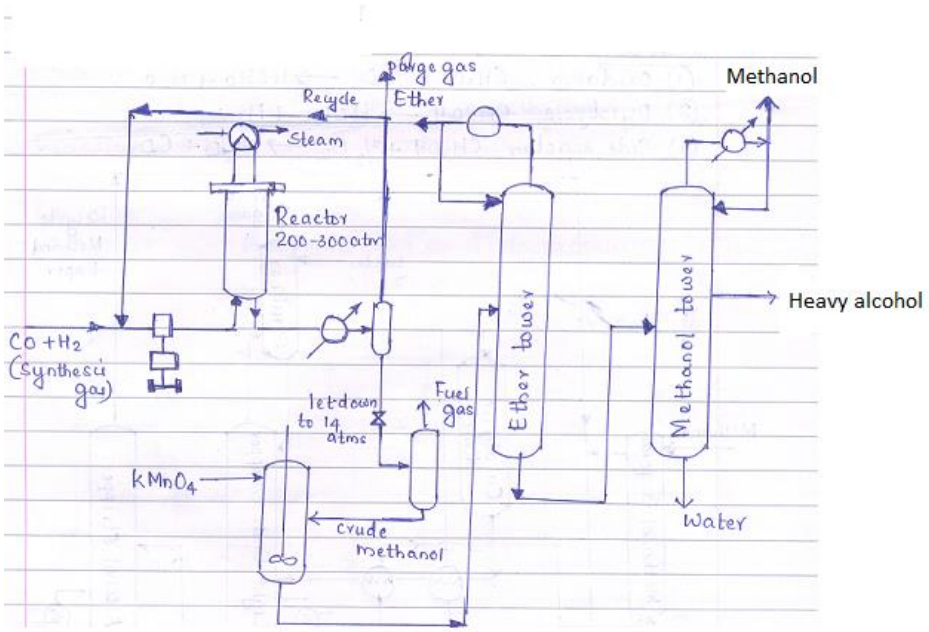
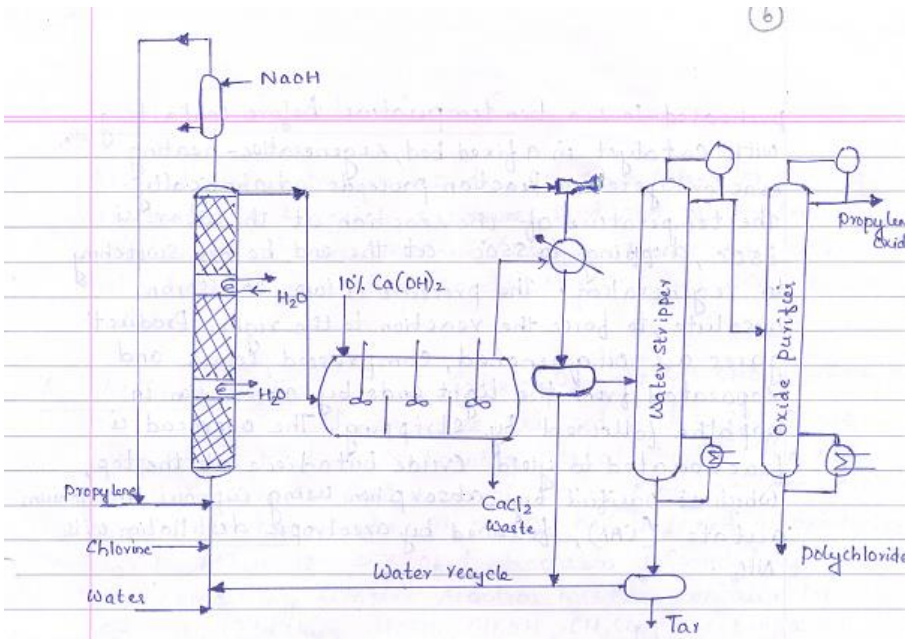
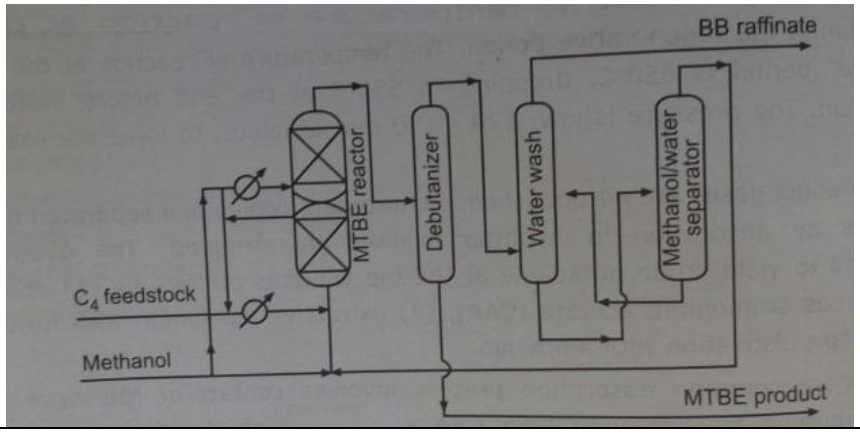
6	**Attempt any FOUR of the following**	**16**
6-a	**Flow sheet for the manufacture of methanol** 	4
6-b	**Propylene oxide:** 	2

	Propylene, chlorine & water are introduced into the bottom of a packed tower where reaction forms the chlorhydrin .The reaction mechanism is formation of hypochlorous acid which reacts rapidly with propylene. The chlorine-propylene ratio of gaseous feed to the tower is chosen so that the liquid effluent contains 4-5% chlorhydrin. The reaction is exothermic & maximum tower temp.is 50^0c.Unreacted propylene is scrubbed with caustic to remove HCl & then recycled.	2
6-c	**Petrochemicals derived from C3 hydrocarbon:** 1. Acetaldehyde: Used in the manufacture of acetic acid, acetic anhydride. 2. Propylene oxide: Used in the manufacture of propylene glycol, glycerin. 3. Acetone: Used in the manufacture of pharmaceuticals, pesticides. 4. Glycerin: Used in the manufacture of alkyl resins and plastics, explosives, food and pharmaceuticals	1mark each for naming and writing the use
6-d	**Flowsheet for the manufacture of MTBE** 	4
6-e	**Udex process** 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	4

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.