SUMMER-15 EXAMINATION

Model Answer

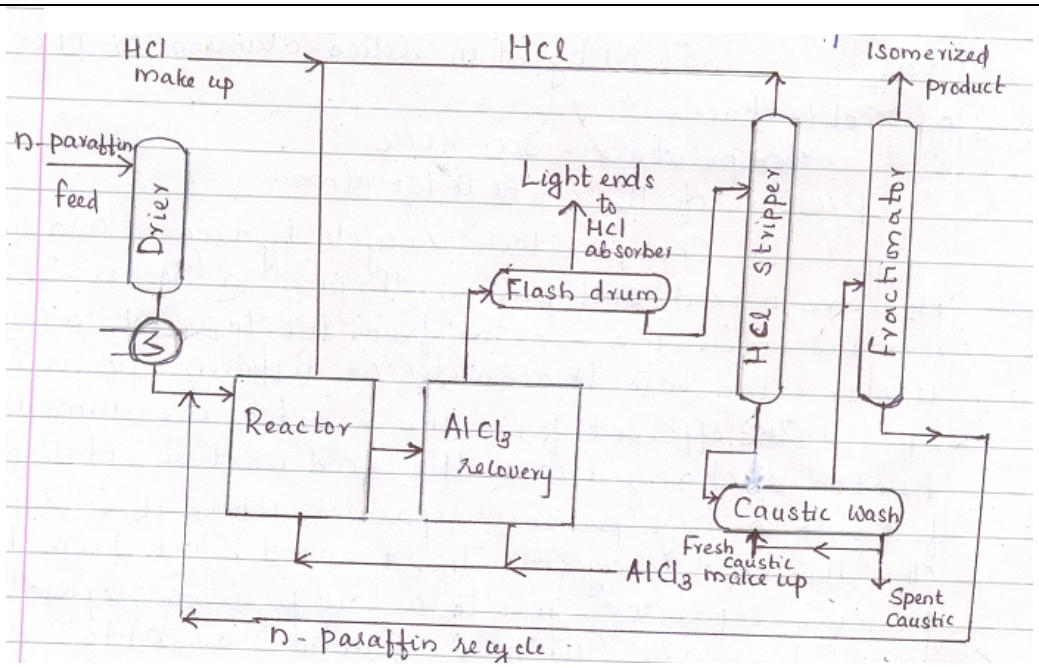
Subject code :(17651)

Important Instructions to examiners:

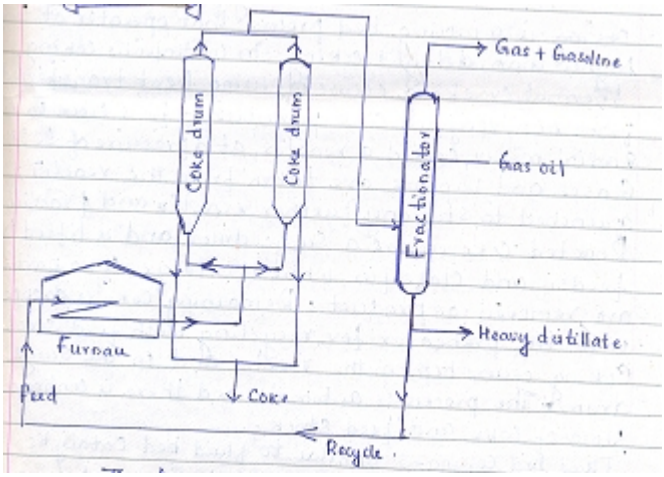
1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling 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
1a-i	**OPEC:** OPEC is Organization of Petroleum Exporting Countries. 43% of world crude produced is shared among the group members. **Names of six major crude oil Producers with their percentage share** Russia - 14% Saudi Arabia - 13% United States - 9% China - 5% Iran - 4.14% Canada - 4%	2 2	4
1-a-ii	**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
1a-iii	**BTX** BTX is benzene, toluene and xylene **Uses of benzene**: In the production of phenol, styrene, aniline, sulfonated detergents, chlorobenzene,maleic anhydride (any two) **Uses of toluene**: In the production of detergents, benzoic acid, used as plasticizer, solvents	1 1 1	4

	for paint, rubber etc (any two) **Uses of xylene**: Solvent for alkyd resins, in the production of phthalic anhydride, dimethyl terephthalate(anytwo)	1	
1a-iv	**Isomerization process** **Description:** Isomerization is used to convert normal paraffins to isoparaffins Catalyst: Aluminium trichloride, 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 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 HCl stripping , caustic wash and fractionation are the standard procedures performed to produce isomerized gasoline **Flow sheet**	2	4

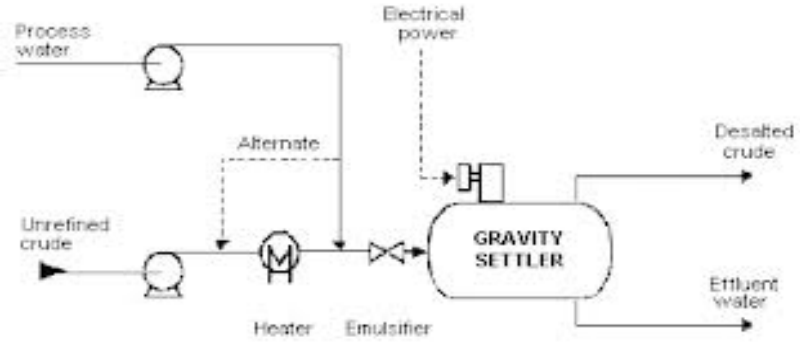
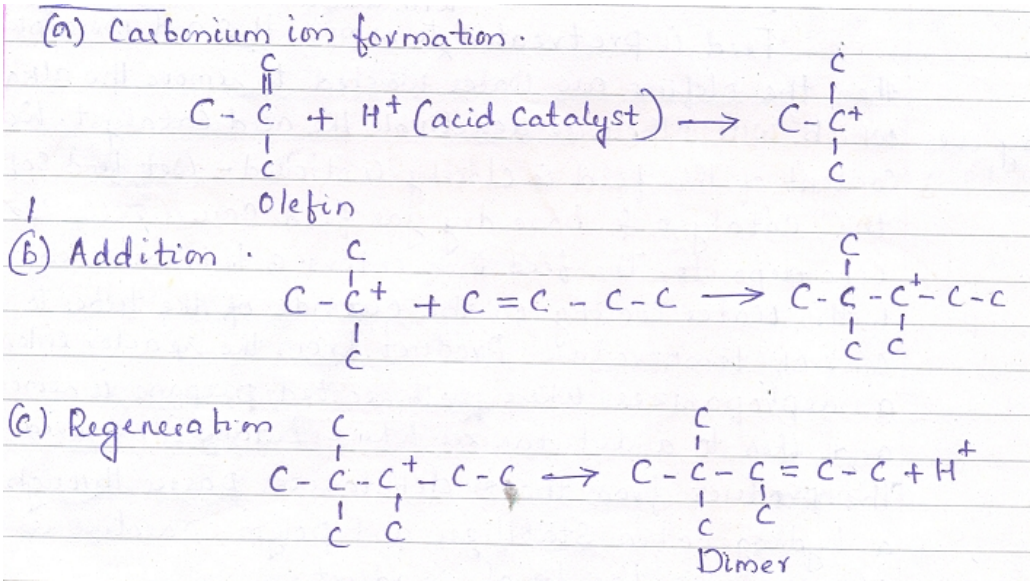
	 ***(Any other type of isomerization process should be given due consideration.)***	2	
1b-i	**Constituents of crude petroleum** Crude oil is made up of the following elements 1. carbon-84% 2. hydrogen -14% 3. sulphur-1-3% 4. nitrogen, oxygen, metals, salts- <1% The major compounds present in crude oil are: A. hydrcarbon i)Paraffins ii)Aromatics iii) Napthenes iv) dienes B. Non hydrocarbon	2	6

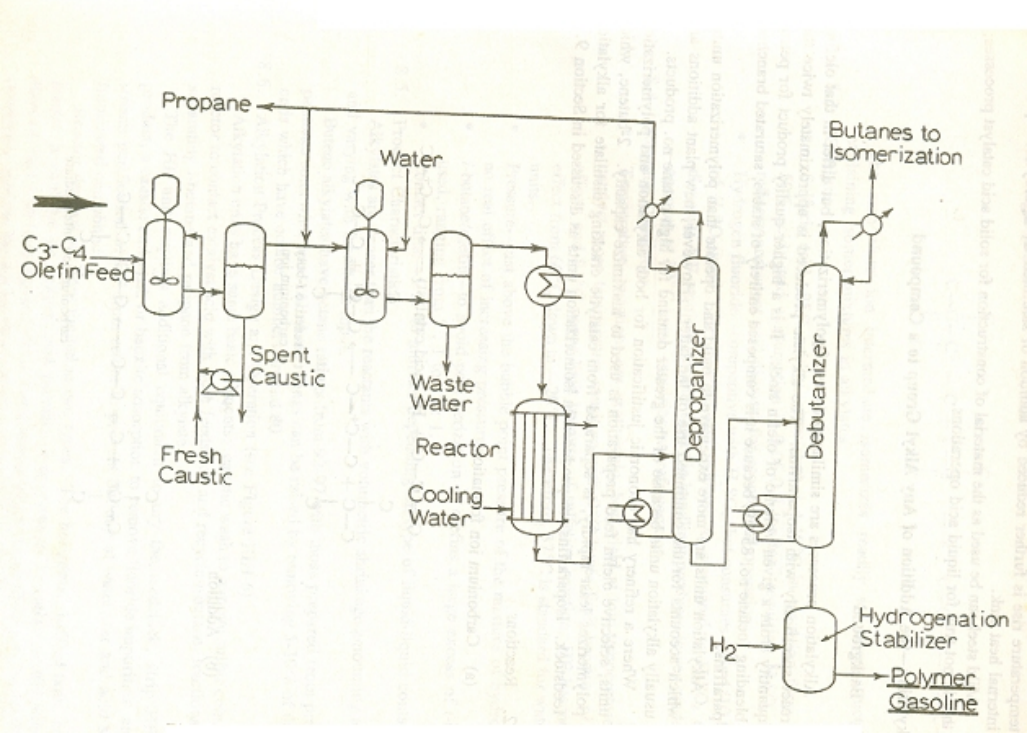
	i) S compounds ii)O_2 compounds iii)N_2 compounds C. Metallic compounds **Characterstics(Properties) of crude oil -:(any four)** 1.Crude is an yellowish black oily complex mixture 2. Flash point: below 10^0C 3. Kinematic viscosity: above 9.5 cSt 4. Pour point; 21^0C 5. Density: 0.83-0.9 gm/ml 6. API 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. **Unit operations involved in refining process(any four)** Distillation, absorption, extraction, adsorption, crystallization	2 2	
1b-ii	**Description of 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. **Delayed coking** In this method the heated charge is transferred to large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion. Initially the heavy feedstock is fed to a furnace which heats the residuum to high temp.(480-510^{o}c) at low pressures (25-30 psi) and is designed & controlled to prevent premature coking in the heater tubes. The	2 2	6

	mixture is passed from the heater to one or more coker drums where the hot materials is held for 24 hours until it cracks into lighter products. Vapours from the drums are returned to a fractionator where gas, naphtha separated out.  ***(Due weightage should be given for visbreaking, steam cracking,continuous coking etc)***	2	
2-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 four points	4

Thermal cracking	Catalytic cracking
1.High temperature, high pressure	Low temperature, low pressure
2. No catalyst used	Catalyst 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

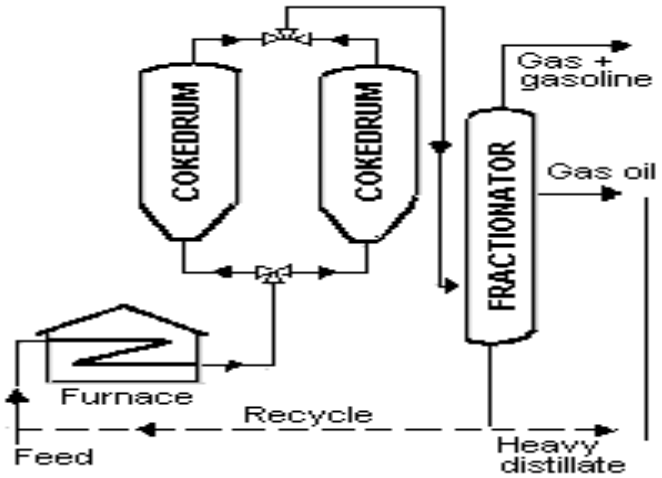
	6. selective cracking is difficult	Selective cracking is possible	
2-b	**Difference between petroleum refinery and petrochemical industry.**	1 mark each	4
	Petroleum refinery	**Petrochemical industry**	
	1)Process crude oil into different fractions.	It is a chemical plant that uses a petroleum based 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	
	4) All refineries have more or less similar unit operations and unit processes	The process depends on the product to be produced.	
2-c	**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	1	4
	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	3	

	agglomerates into a stream entrapping all the salts in the process. The desalted crude is continuously drawn from the top of settling tanks & sent to the crude distillation tower  ***(Description of chemical treatment should also be given due consideration)***		
2-d	**Polymerisation Process:** **Reaction:**  **Flow Sheet:**	1	4

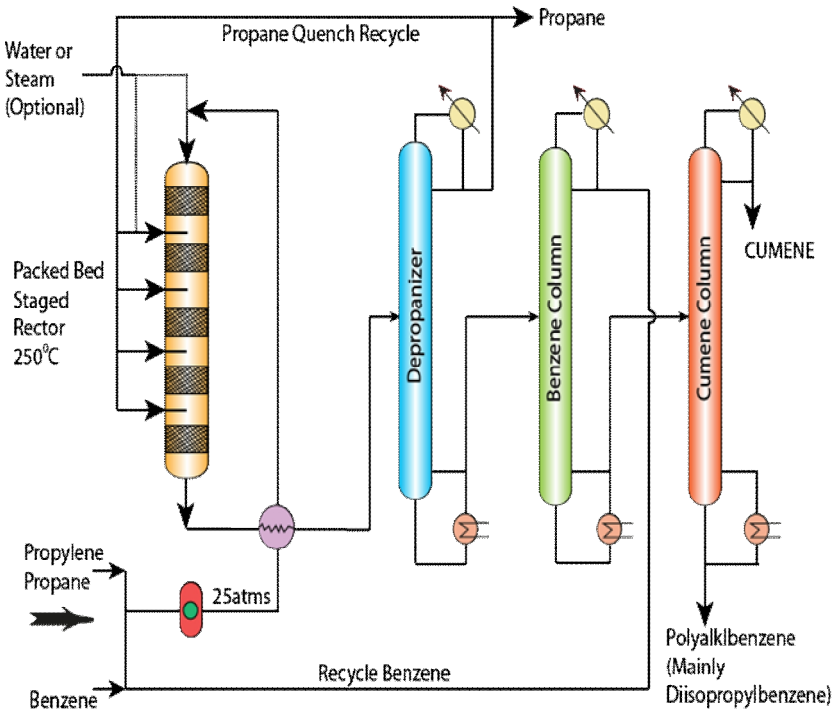
	 **Description:** Temperature: 150-220^{0}c Pressure: 25-100 atms Feed (C3-C4 olefin) is pretreated with alkali to remove H_2S and mercaptans. Then the olefins are water washed to remove the alkali which which will otherwise deactivate the acid catalyst. Water content of the feed is closely controlled. The feed then enters a water cooled tubular reactor. Product from the reactor enters a depropanizer where un reacted propane is removed and then to a debutanizer where unreacted butane is removed. The product from the debutanizer passes through a hydrogenation stabilizer and polymer gasoline is obtained as the final product.	2 1	
2-e	**Characteristics of waste water produced in petrochemical plant:** Free oil: 2000-3000 mg/ l	4	4

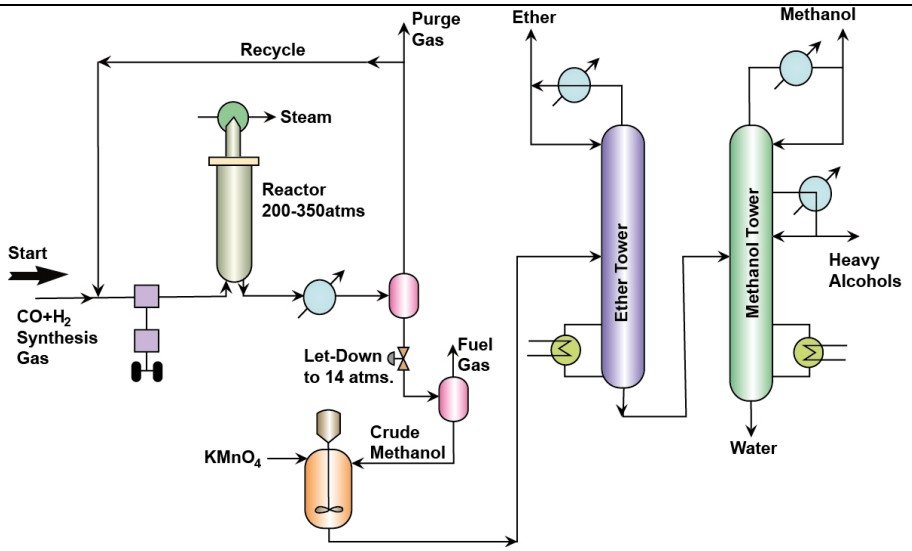
	H_2S and sulphides: 10-220 mg / l Phenol : 12-30 mg / l Suspended solids: 200-400 mg / l 5 day BOD at 20^0c : 100-300 mg / l Alkalinity: 10-250 mg / l		
2-f	**Reason for considering crude oil as black gold:** Crude oil is yellowish black oil that is extracted from under the surface of the earth. It is 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 1 1	4
3-a	**Application of vacuum distillation in crude oil refining:** To recover additional heavy distillates from this residue from atmospheric distillation, it may be piped to a second distillation column where the process is repeated under vacuum, called vacuum distillation. The principle of vacuum distillation resemble those of fractional distillation except that larger diameter columns are	4	4

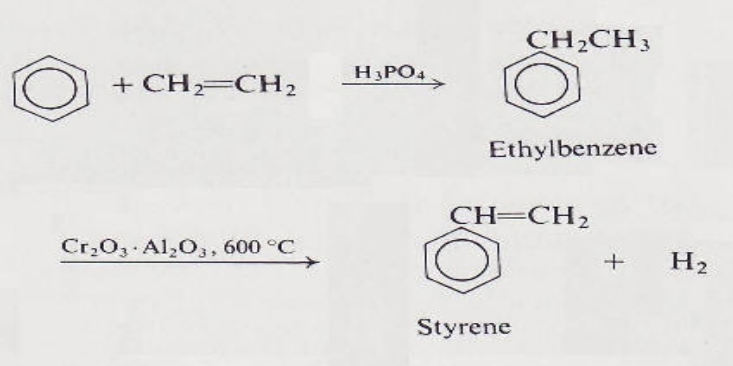
	used to maintain comparable vapour velocities at the reduced pressure .This vacuum distillation process has become an important chain in maximising the upgrading of crude oil. The residue from vacuum distillation can be used as feedstock for further upgrading, or as bitumen feedstock or as fuel component. The main objective of vacuum distillation is to maximise 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 & temp. conditions are vacuum distilled.		
3-b	**The steps of fractional distillation** 1. Heating of mixture. 2. The mixture boils, forming vapours. 3. The vapour enters to the bottom of the fractional distillation column that is 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 as the vapours are condensed. 9. In this way crude oil is separated by fractional distillation.	4	4
3-c	**Use of:** **1. Jet Fuel** :- Used for aviation turbine power units ,aviation industry 2**. Naphtha**:- Production of motor spirit, important feed stock for fertilizer manufacture. 3. **Motor Gasoline**:- Fuel for land based spark ignition engines, used in internal combustion engines such as motor vehicles 4**. Aviation gasoline:** - used in spark-ignited internal-combustion engines in	 1 1 1 1	4

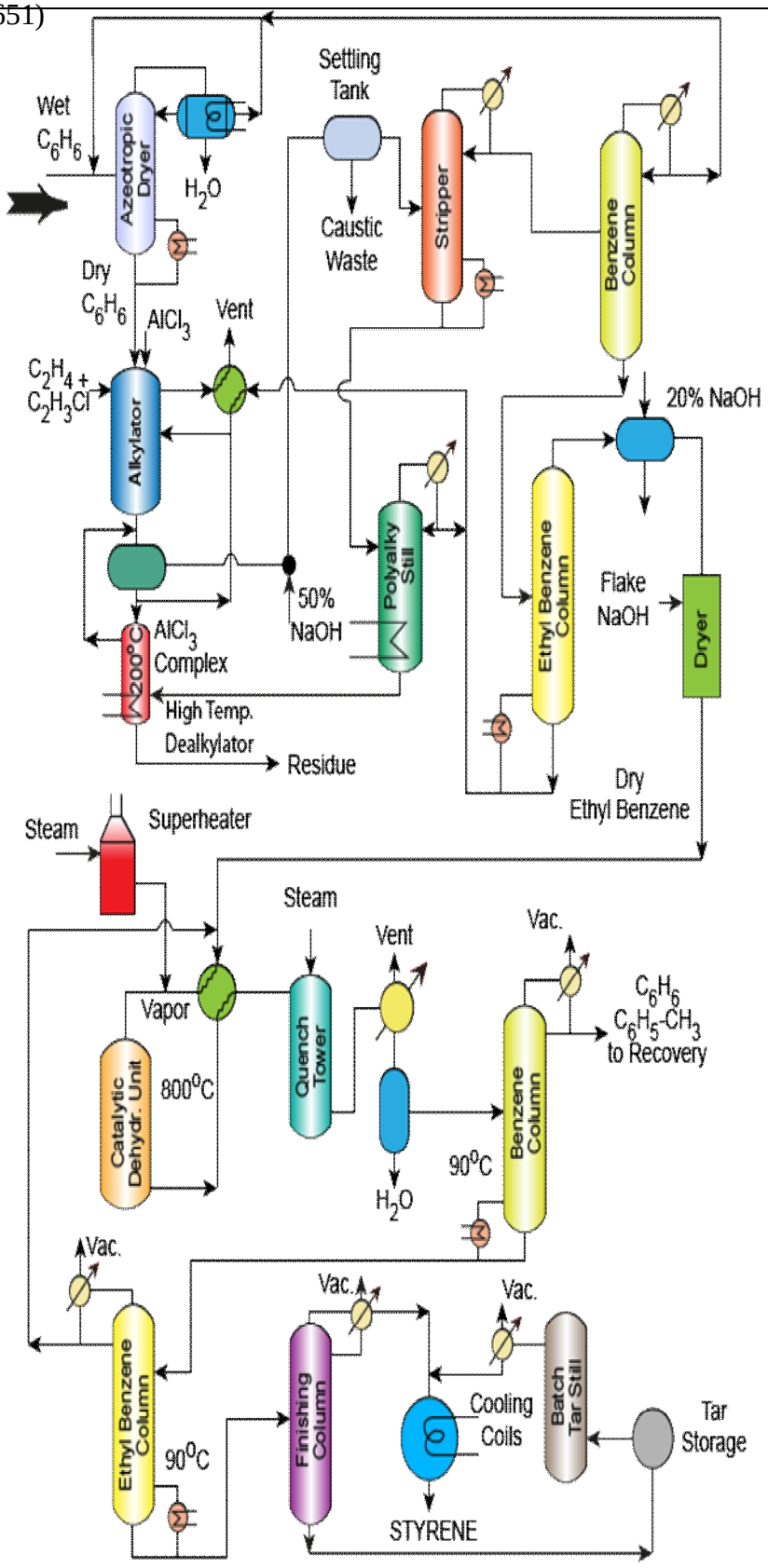
	aircraft, fuel for piston engine aircraft		
3-d	**Delayed coking process:** **Description:-** Heated charge residue from atmospheric distillation is transferred to large coke drums which provides the long residence time needed to allow the cracking reaction. Initially heavy feed stock is fed to a furnace 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	4
3-e	**Hydration reaction:** It is addition of water .Synthetic ethyl alcohol is made by hydration of ethylene. $3H_2C=CH_2 + 2H_2SO_4 \text{ -------} \rightarrow C_2H_5HSO_4+(C_2H_5)_2SO_4$ $C_2H_5HSO_4+(C_2H_5)2SO4+H_2O \text{---} \rightarrow 3C_2H_5OH+2H_2SO_4(dil.aq.)$ An older process dissolves in sulphuric acid to form ethyl sulphate, then	4	4

	hydrolyses this to form ethanol. There is always some by-product which can be either sold or recirculated. A direct hydration method is currently use for over 85% of production. $CH_2=CH_2+H_2O$---------→C2H5OH The catalyst use is H_3PO_4. Temp.-300 ^{0}c		
4a-i	1.**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 **2. Formaldehyde** i oxidation $CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O$ ii. Pyrolysis $CH_3OH \rightarrow HCHO + H_2$ iii. $CH_3OH + 3/2\ O_2 \rightarrow 2H_2O + CO_2$	2 2	4
4-a-ii	**Refinery**-It is composed of a group of chemical engg.unit processes & unit operations used for refining certain material into products of value. **Types of refineries-** 1.Primary refinery 2.Intermediate refinery 3. Complex refinery **Oil refining**-Crude oil contains hundreds of different types of hydrocarbons. So separation of the components by using the difference in their boiling point is done in oil refining.	1 2 1	4
4a-iii	**Manufacturing of cumene**: Propylene-propane feedstock from refinery off gases of a naphtha steam cracking plant	2	4

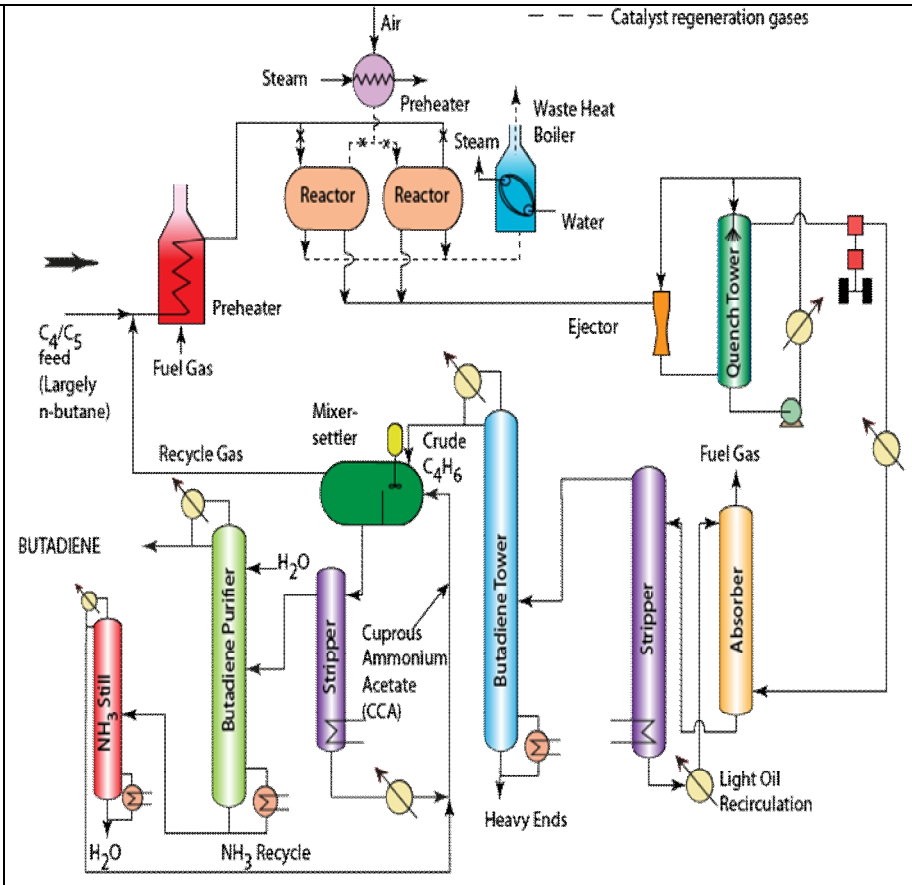
	Is mixed with benzene & pumped at 25 atms. the top of reactor packed with H3PO4 impregnated catalyst. The temp is maintained at 2500c by adding cold propane at each stage to absorb the heat of reaction. The reactor effluent is depropanised & the propane split into quench. Reaction- C6H6 + CH3CH=CH2-→C6H5.C3H7  ***Since cumene manufacture is not mentioned in G scheme curriculum, due consideration should be given***	2	

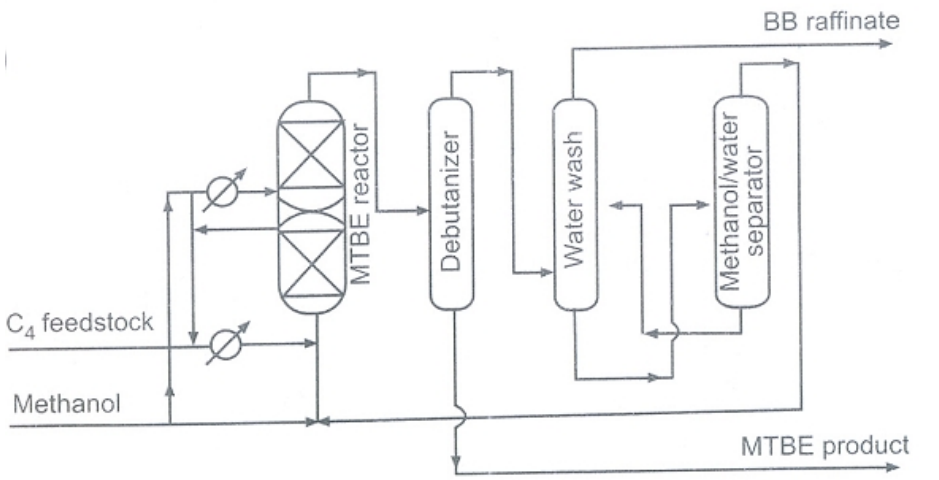
4a-iv	 **Methanol via synthesis gas route**	4	4
4b-i	**Manufacturing of styrene**-Benzene is alkylated with ethylene using aluminium chloride or acid type catalyst. The resulting ethylbenzene is catalytically dehydrogenated in steam or excess benzene atmosphere to give styrene. All benzene feed must 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 zinc,chromium,iron.Reaction product is cooled in the feed preheated ,then by steam quenching. Hydrocarbon mixture is passed into a series of vacuum distillation column to allow the	2	6

	separation of impurities at low temp to avoid polymerisation of styrene. The second column at 35mm & 900c reboiler temp separate styrene from ethyl benzene. **Reaction-**  	13 2	

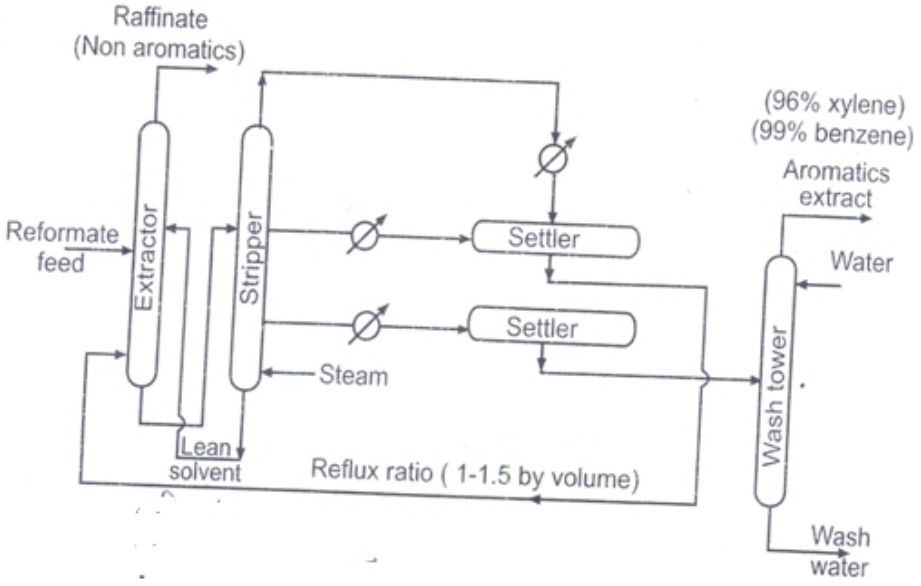

Wet
C_6H_6
Azeotropic Dryer
H_2O
Settling Tank
Caustic Waste
Stripper
Benzene Column
Dry
C_6H_6
$AlCl_3$
Vent
C_2H_4 +
C_2H_3Cl
Alkylator
20% NaOH
Polyalky Still
50% NaOH
Ethyl Benzene Column
Flake NaOH
Dryer
200°C
$AlCl_3$ Complex
High Temp. Dealkylator
Residue
Dry Ethyl Benzene
Steam
Superheater
Steam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

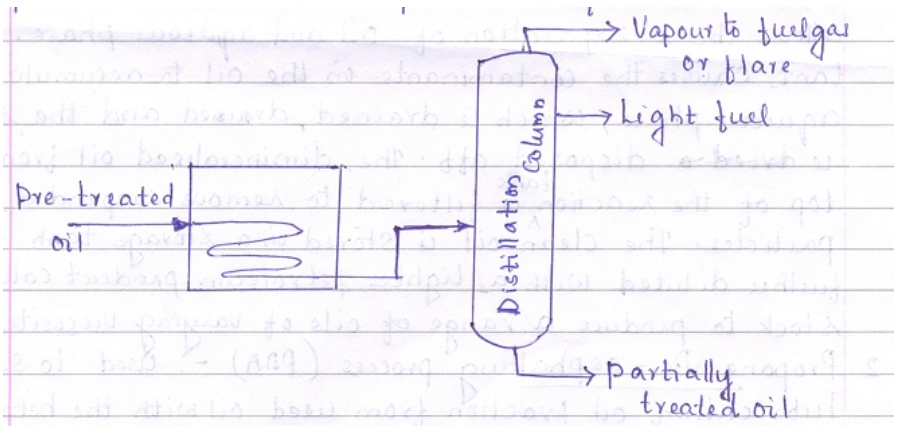
4b-ii	**Manufacturing of butadiene**-A refinery gas of c4/c5 cut is mixed with recycle gas & preheated to reac. Temp.Apair of reactor forms an adiabatic cycle with the heat of reaction required during the 5-15 min.make period equal to that supplied by the combustion of carbon deposit on the cayalyst 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	2 1	6

		3	
5-a	**MTBE Manufacture**		8

	 MTBE via catalytic etherification Chemical Reaction: $(CH_3)_2C=CH_2+ CH_3OH \rightarrow (CH_3)_2 C\text{-}O\text{-}CH_3$ **Process description:** Two stage reactor in which the first reactor is in the recycle mode. With this method a slight expansion of the catalyst bed is achieved which ensures very uniform concentration within the reactor and avoids hot spot formation. Side reaction minimize, temp. is 45^0C at start and run to about 60^0C . Catalyst may be replaced in each reactor separately. Catalyst used is carbon exchange resin and is available easily. MTBE is recovered as bottom product. Methanol rich C4 is sent to methanol recovery. Water is used to extract excess methanol.	4 1 3	
5-b	**Manufacture of acetone** **Chemical Reaction:** $(CH_3)_2CHOH \rightarrow CH_3COCH_3 + H_2$ $(CH_3)_2CHOH + ½\ O_2 \rightarrow CH_3COCH_3 + H_2O$ **Process Description:** Isopronanol vapour compressed to 3 atm is preheated by reactor effluent heat	2	8

	exchange and passed through a tubular catalytic reactor maintained at 500^0C with the catalyst consisting of copper or brass deposited on porous carrier. This hot reaction gases passes through a water cooled condenser and then into a water scrubber where final traces of isopropanol and acetone are removed from hydrogen. Condensate and water scrub liquor are fractionated to give product grade acetone as over head and dilute isopropanol as bottom. ***Since acetone manufacture is not mentioned in G scheme curriculum, due consideration should be given***	6	
5-c	**Udex process** Reformat as a feed is send to extraction colomn where it is heated at 140-150^{o}C in presence of solvent. During heating we get two phases extract and raffinate .a extract contain aromatic compound while raffinate contain non aromatic. A solvent is used to extract aromatic compound and then send to sripper colomn. In stripping recovery of solvent takes place from the bottom. Extract is removed from the top cooled, and send to settler .From the settler part is recycled and part is fed to wash tower where dissolved impurities are removed higher percentage concentrated aromatic extract withdrawn from the top which contain 99% benzene 96% xylene and water from the bottom side. The aromatic mixture containing BTX is fractionated separately .	5	8

	 **Products obtained from BTX:** **1.** Benzene- styrene, phenol, dodecylebenzene 2. Toluene – dichlorotoluene, benzoicacid, solvents 3. xylene- From o-xylene- phthalic anhydride From p-xylene – dimethylterephthalate From m-xylene – isophthalic acid	3	
6-a	**Definition:** **(i)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. **(ii) Cetane no:** It is defined as the percentage volume of n-cetane in a mixture of n-cetane and heptamethyl nonane that gives the same ignition delay as the fuel under consideration. **(iii)FlashPoint:** It is the minimum temperature at which oil will give enough vapours for giving a momentary flash when a flame is brought near it. **(iv) Fire Point:** It is the minimum temperature at which oil will give enough	1 1 1 1	4

	vapours which will burn continuously for at least 5 seconds when a flame is brought near it.		
6-b	**Atmospheric distillation process for waste water treatment:** It is carried out at normal atmospheric pressure and with temperature upto300^{o}c. Water containing used oil is heated and charged to a distillation tower. Low boiling hydrocarbons and water are collected at the top of the tower. Temperature is restricted to limit the thermal cracking of higher hydrocarbons, the partially treated oil is sent to vacuum distillation unit.  	4	4
6-c	**Test for determining properties of crude oil:** 1. API gravity: A low API gravity indicates a heavier crude or a petroleum product. API=[141.5/(sp.gr)]- 131.5 2. Specific gravity: Sp.gr of crude roughly ranges from 0.82 for lighter crude to higher for heavier crudes. 3. Salt content: The salt content expressed as milligrams of sodium chloride per litre oil indicates the amount of salt dissolved in water. A high salt content in a crude oil presents serious corrosion problems during the refining process. A salt content higher than 10 lb/1000 barrel requires desalting.	1 mark each for any 4	4

	4. Sulfur content: The amount of sulfur indicates the type of treatment required for the distillates. To determine sulfur content, a weighed crude sample is burned in an air stream. All sulfur compounds are oxidized to SO_2 which is further oxidized to SO_3 and finally titrated with a standard alkali. 5. Pour point: It is the lowest temperature at which an oil is observed to flow under the conditions of the test. It indicates the amount of long chain paraffins found in a crude oil. Ash content: This test indicates the amount of metallic constituents in a crude oil.		
6-d	**Four process of waste water treatment:** i. Primary treatment ii. Secondary treatment iii. Tertiary treatment iv. pretreatment **Primary treatment:** This treatment consists of oil removal in two stages by physical methods. The first stage of oil removal is done in smallponds or basin where major portion of the oil is removed by using baffles, floatation and skimming methods. The second stage of oil removal is mainly by API separator or other gravity separator. **Secondary treatment**: This includes chemical method and biological method. The main purpose of chemical method is to remove emulsified oil with addition of flocculating agents and also to remove suspended soilds and toxic substances thereby conditioning the effluent for further treatment by biological methods. Biological treatment aims at the removal of all oxidisable and organic matter from the waste water. **Tertiary treatment:** This treatment removes specific pollutants to meet	2 1mark each for any 2	4

	regulatory discharge requirement. This includes chlorination, ion exchange, reverse osmosis, activated carbon etc. **Pretreatment:** It is done to remove water from the used oil. Water plus used oil is placed in large settling tanks which separates oil and water.		
6-e	**Vinyl Chloride:** **Properties:** Molecular weight: 62.5 Melting point: -153.8^{o}C Boiling point:-13.81^{0}C Density: 0.983gm/cc Soluble in CCl_4, $(C_2H_5)_2O$ and alcohol Flash point:-77 ^{0}C Maximum toxicity limit:500ppm **Method of production:** 1. Ethylene dichloride thermal pyrolysis 2. Acetylene- HCl reaction 3. Ethylene dichloride-causticreaction **Chemical reaction(Ethylene dichloride thermal pyrolysis)** CH2Cl- CH2Cl → CH2=CHCl + HCl ***Since vinyl chlorie is not mentioned in G scheme curriculum, due consideration should be given***	1 mark each for any 2 1 1	4