SUMMER-14 EXAMINATION

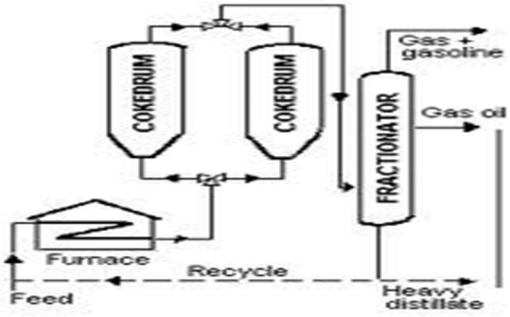
Model Answer

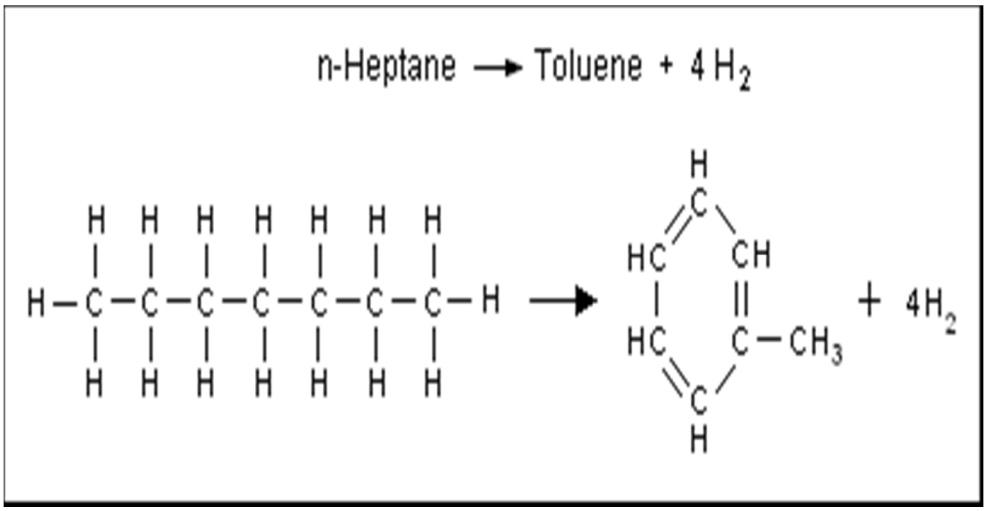
Important Instructions to examiners:

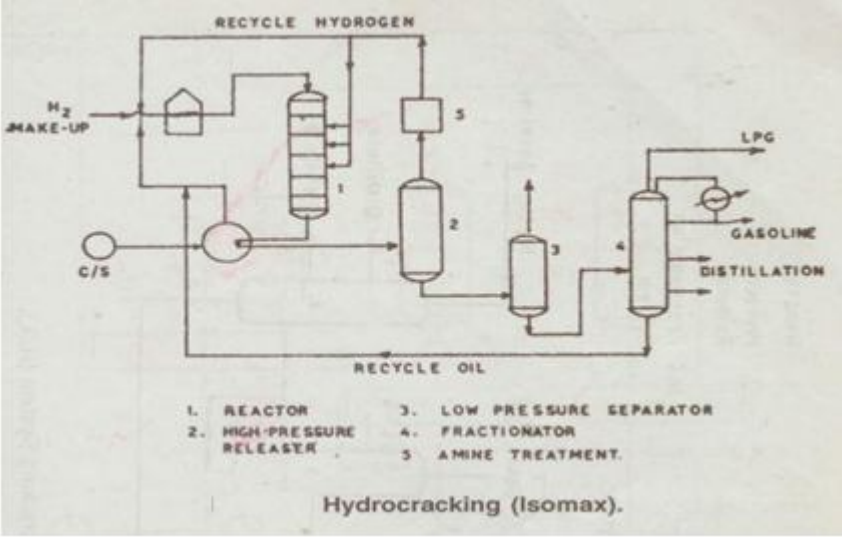
1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling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

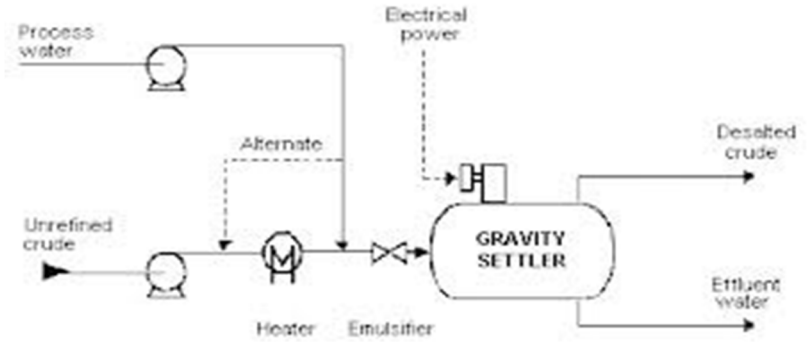
Q No.	Answer	marks	Total marks
1A-a	**Names of countries producing crude oil** Saudi Arabia Russia United states Iran China Norway **Saudi Arabia** is the leading producer of crude oil with the production figure of 10.37 million barrels per day	3 1	4
1A-b	Desalting, distillation, solvent extraction, absorption, adsorption **Solvent extraction**- The purpose of solvent extraction is to prevent corrosion & improve finished products by removing unsaturated aromatic hydrocarbons from lubricant & grease stocks. The feedstock is first dried & then treated using a continuous countercurrent solvent treatment operation .The feedstock is washed with a liquid in which the substances to be removed are more soluble than in the desired resultant product or selected solvent are added to cause impurities to precipitate out of the product. The solvent is separated by heating, evaporation etc. Most widely used extraction solvents are phenol, furfural. ***Marks should be given for any of the treatment methods***	1 3	4
1A-c	**Primary process** -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.	2	4

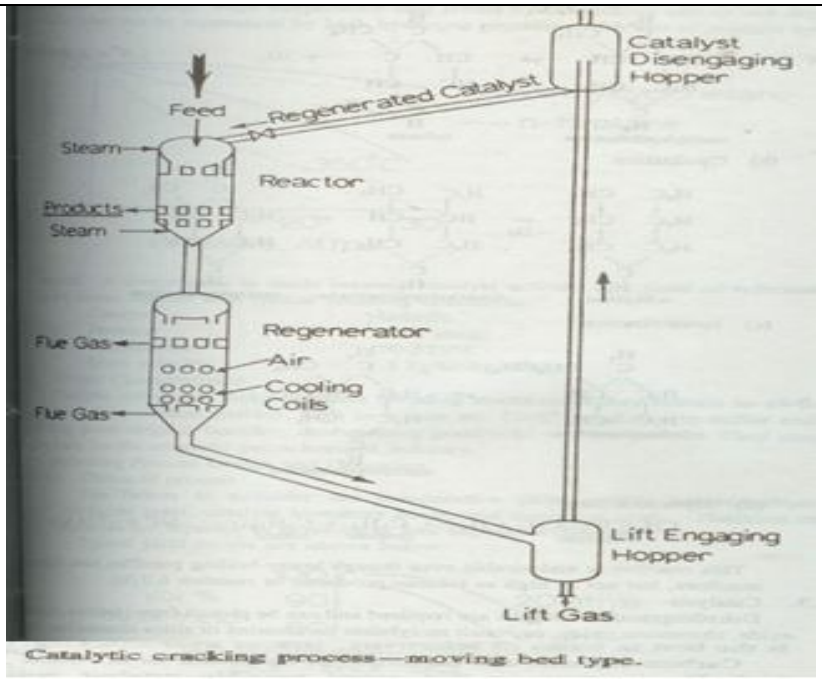
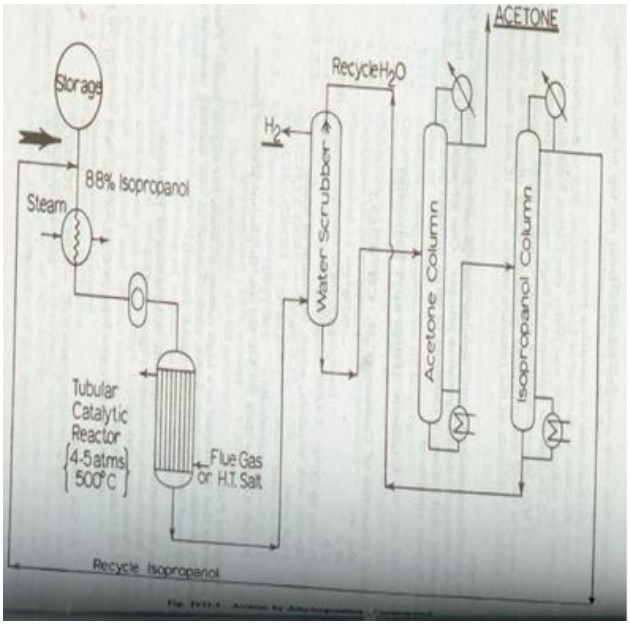
	Wastewater moves very slowly through separator allowing the free oil to float to the surface & be skimmed off & solids to settle to the bottom & be scraped off to a sludge collecting hopper. **Secondary process** – In secondary process ,dissolved oil & other organic pollutants may be consumed biologically by microorganism .Secondary treatment generates biomass waste which is typically treated anaerobically & then dewatered. 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.	2	
1A-d	**Accident** : Any unexpected or unplanned occurrence that interferes with the orderly progress of activity which leads to loss of life ,revenue & complete breakdown of plant & supplies of chemical vital to other industries. **Causes :** 1. poor design & construction of equipment & machinery. 2. unsafe personal conditions 3. unsafe act 4. exposure to harmful substances	2 2	4
1B-a	**Factors affecting price of crude oil:** 1. Production-OPEC nations are the major producers of crude oil. So any decision taken by OPEC nations impacts the price level of crude oil. 2. Natural causes- some natural causes also effect on price of crude oil. 3. Inventory –Any upward or downward movement in inventory level shoots up volatility in price index of crude oil, which generates lot of changing movement in Sensex. 4. Demand –the major gap created between demand & supply of crude oil	6	6

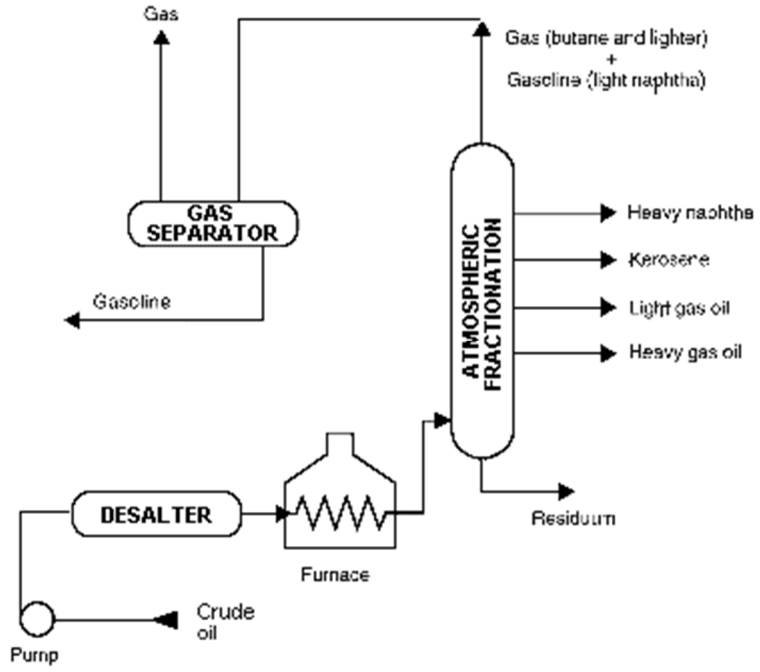
	is forcing the price curve of crude oil to rise in upward direction.		
1B-b	Delayed coking – In this method the heated charge is transferred to large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion. Initially the heavy feedstock is fed to a furnace which heats the residuum to high temp.(900-950F) at low pressures (25-30 psi) and is designed & controlled to prevent premature coking in the heater tubes.The 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.  **Types of coking process** Delayed coking Fluid coking Flexi coking	3 2 1	6
2-a	Crude oil is a mixture of various components (hydrocarbons).The first step in refining of crude oil is to separate all the components .The various components of the crude oil have different sizes ,weights & boiling temp. So the first step is to separate these components .Because they have different boiling temp. they can be separated easily by a process called distillation. So for conversion of crude oil components into useful product distillation is the major unit operation	4	4

	in refining process.		
2-b	**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. Boiling point range is broader. So used in making good cold weather petrol. To supply aromatic feedstock for petrochemical industry 	2 2	4
2-c	Hydrocracking	4	4

	 Hydrocracking (Isomax).		
2-d	**Desalting of crude oil:** **Description-:** To reduce corrosion, plugging & to prevent poisoning catalyst in processing units desalting is used. Electrical desalting applications of high voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids Method is continuous. The feedstock crude is heated between 150^0 & 350^0F to reduce viscosity & surface tension for easier mixing & separation of the water. The desalted crude is continuously drawn from the top of settling tanks & sent to the crude distillation tower	2	4

	 **Different methods:** Chemical desalting & electrical desalting are the methods of desalting.	1 1	
2-e	**Moving bed catalytic cracking process** – Catalyst pellets move at a fixed rate by gravity flow downward through the reactor-regenerator in succession , elevated to the reactor again by a gas lift. Uniform liquid & vapors liquid feed distribution necessary. Other design drawbacks are excessive steam requirement, poorer heat economy. The moving bed catalytic cracking process is similar to FCC process. The cracked products is separated into recycle gas ,oil, distillate ,naphtha.	2	4

	 Catalytic cracking process—moving bed type.	2	
2-f	Acetone 	4	4

3-a	**Atmospheric Distillation** The desalted crude feedstock is preheated using recovered process heat. The feedstock then flows to a direct-fired crude charge heater where it is fed into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 650° to 700° F (above these temperatures undesirable thermal cracking may occur). All but the heaviest fractions flash into vapor. As the hot vapor rises in the tower, its temperature is reduced. Heavy fuel oil or asphalt residue is taken from the bottom. At successively higher points on the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off.  	2 2	4

<table>
<tr><td>3-b</td><td>1) Catalytic cracking produces more gasoline of higher octane than thermal cracking.
2) Products of catalytic cracking are more stable than thermal cracking.
3) Reactions through catalytic cracking occur via carbocation intermediate compared to the free radical intermediates in thermal cracking.
4) Carbocations are longer lived & accordingly more selective than free radicals.</td><td>1 Marks each</td><td>4</td></tr>
<tr><td>3-c</td><td><table><tr><th>Distillation Fraction</th><th>Boiling point(^{0}C)</th></tr><tr><td>Gases</td><td>Below 30</td></tr><tr><td>Gasoline</td><td>30-210</td></tr><tr><td>Naphtha</td><td>100-200</td></tr><tr><td>Kerosene and Jet Fuel</td><td>150-250</td></tr><tr><td>Diesel and Fuel Oil</td><td>160-400</td></tr><tr><td>Atmospheric Gas Oil</td><td>220-345</td></tr><tr><td>Heavy Fuel Oil</td><td>315-540</td></tr><tr><td>Atmospheric Residue</td><td>Over 450</td></tr><tr><td>Vacuum Residue</td><td>Over 615</td></tr></table></td><td>4</td><td>4</td></tr>
<tr><td>3-d</td><td>Manufacturing of methanol</td><td>4</td><td>4</td></tr>
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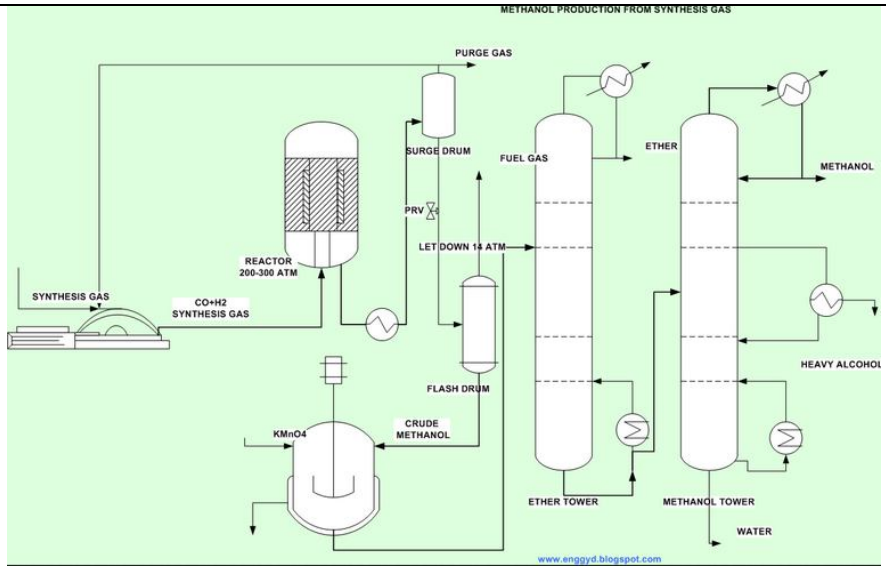
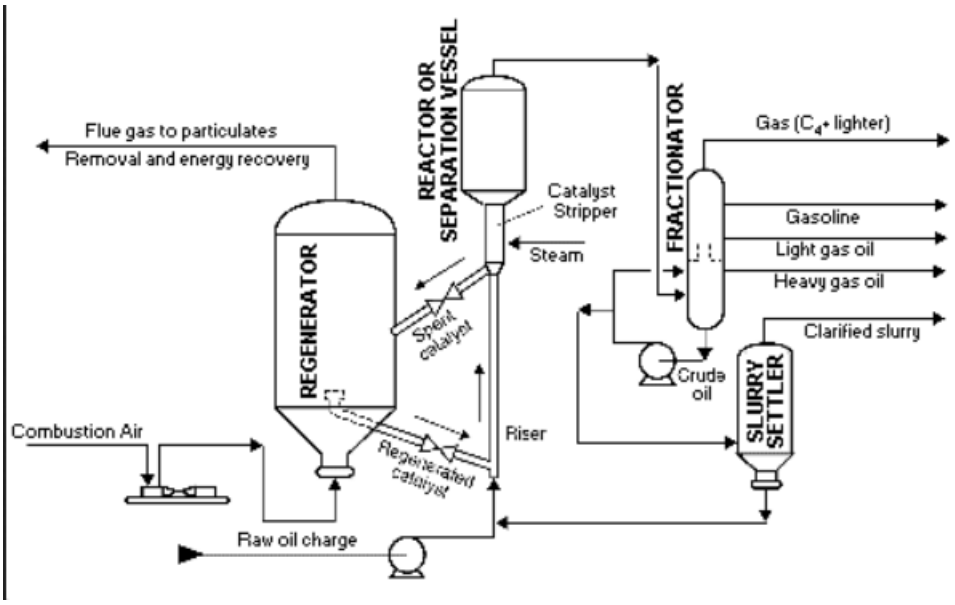
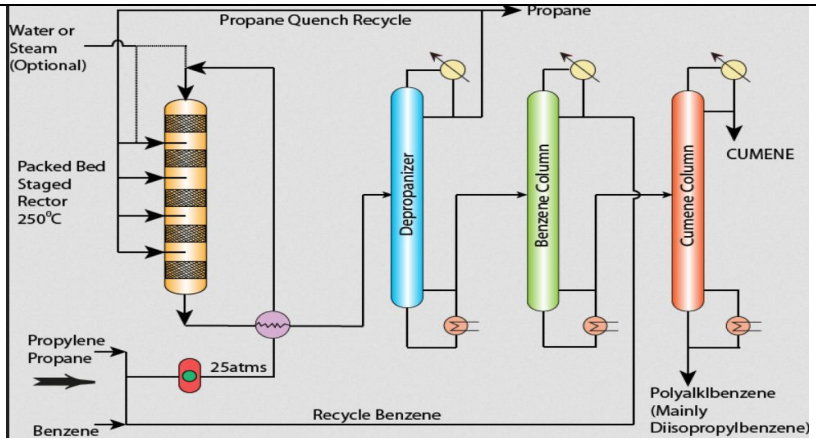
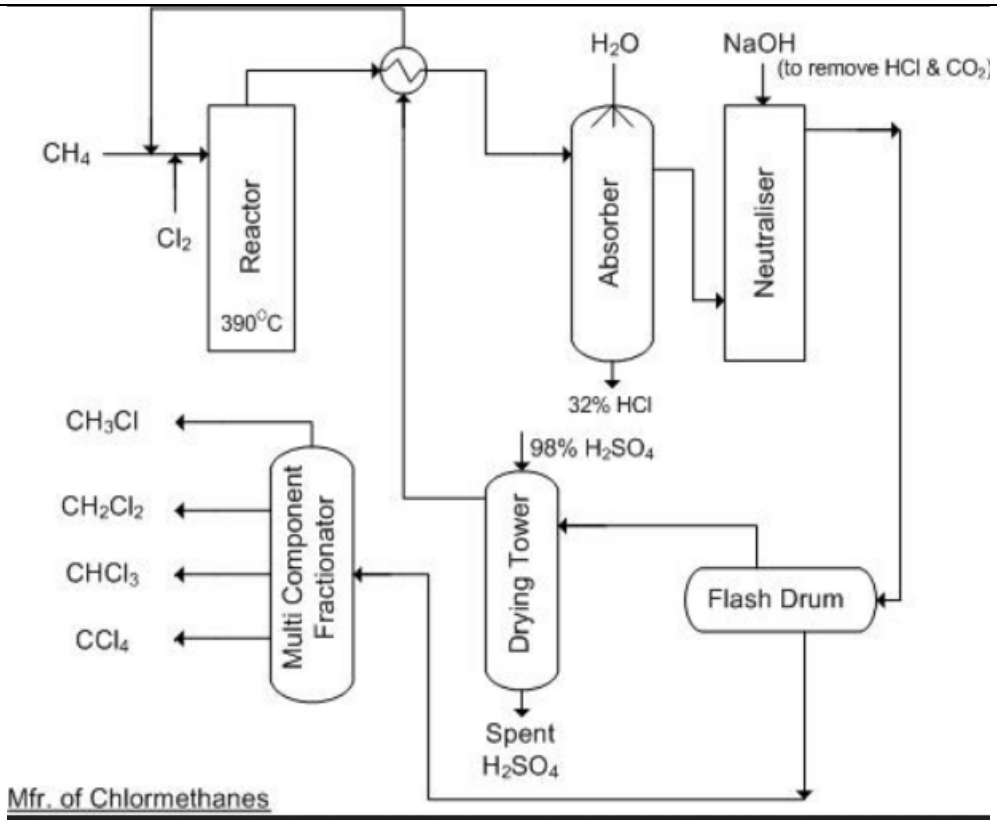
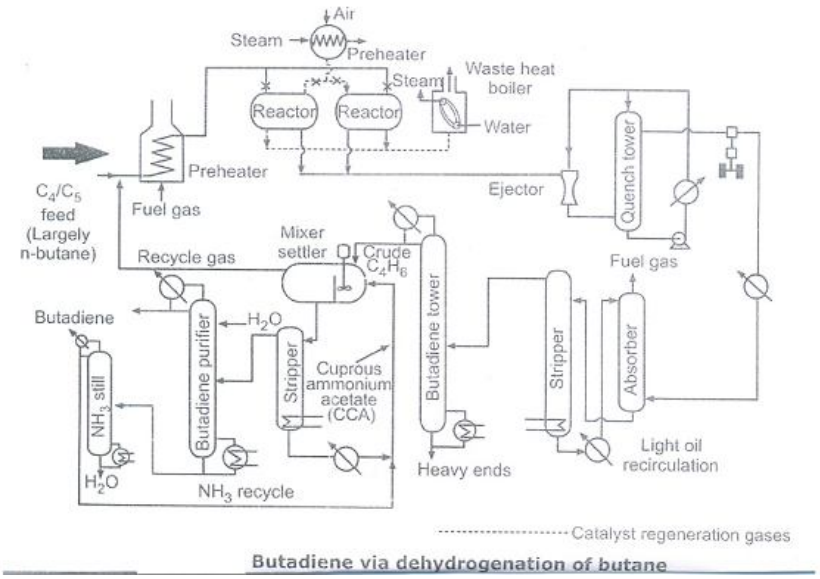
			
3-e	**Flow diagram for moving bed catalytic cracking process.** 	4	4
4A-a	**Refinery** – A refinery is composed of a group of Chemical engineering unit	2	4

	processes & unit operations used for refining certain materials. **Types of refineries** – 1. oil refinery 2. sugar refinery 3. salt refinery 4. natural gas processing plant	2	
4-A-b	**Air pollutants**: COx, SOx, CH4, NOx, Fluro-chloro methane etc **Water Pollutants**: Oil, grease, chelating agents, sulpher, lead, sulphides, phenolic group etc	2 2	4
4A-c	**Description of esterification process-** In this process, the alcohol & an acid are heated in presence of sulfuric acid, and the reaction is driven to completion by removing the products.in case of ethyl acetate esterification take place in a column which takes a ternary azoetrope overhead. Alcohol can be added to the condensed overhead liquid to wash out the Alcohol, which is then rectified & returned to the column to react. $CH_3COOH+C_2H_5OH$ -----→$CH_3COOC_2H_5+H_2O$ $CH_2=CH_2+CH_3COOH+1/2O_2$ -----→ $CH_3COOH=CH_2+H_2O$	2 Marks each for description and reaction	4
4A-d	 **Description**: Propylene-propane feedstock from refinery off gases from	2 2	4

	naptha steam cracking plant is mixed with benzene and pumped at 25 atms. Into the top of a reactor packed stagewise with H3PO4 impregnated catalyst. The reactor effluent is depropanised and the propane split into quench and the product stream obtained.		
4B-a	 **Description**: The methane and chlorine is send to reactor with fixed ratio. The chlorination takes place at 390 ^{O}C. The product then water absorbed to remove HCl and neutralize with NaOH to remove HCL and CO2. The washed product then send to flash drum to recover spent acid and product like CH3Cl etc.	3 3	6
4B-b	Safety means protection against any occurrence of accidents. Accidents do not	Relevant answer	6

	just happen, they are caused. The causes are the potential hazards and the risks involved in any plant. Safety starts with the identification of hazards that may involve fire, explosion, toxicity, break or crack, fall or slip, etc. The entire pathway of hazards leading to accidents has to be identified. The hazards involved with type of materials, hazards associated with the materials, hazards associated with the processing or production scheme, quantity in storage, and the layout of the plant and equipment. These are classified as 1. Material hazards and special material hazards 2. Process hazards and special process hazards 3. Quantity hazard 4. Layout hazards Some practices like 1) To establish a system to identify & manage all hazardous chemicals in the factory thorough the provision of material safety data sheets & procedures for proper use, storage, handling & movement of the hazardous chemicals internal & external safety audit should be done. 2) Personnel protection, motivation for safety. 3) Proper plant maintenance, Piping connected to a work area from vessels, pumps & other sources is isolated with a solid plate prior to the start of work. 4) Sewer cover must be in good condition with no openings for vapour flow.	should carry full marks as it is very general type of question	
5-a		4	8



Butadiene via dehydrogenation of butane

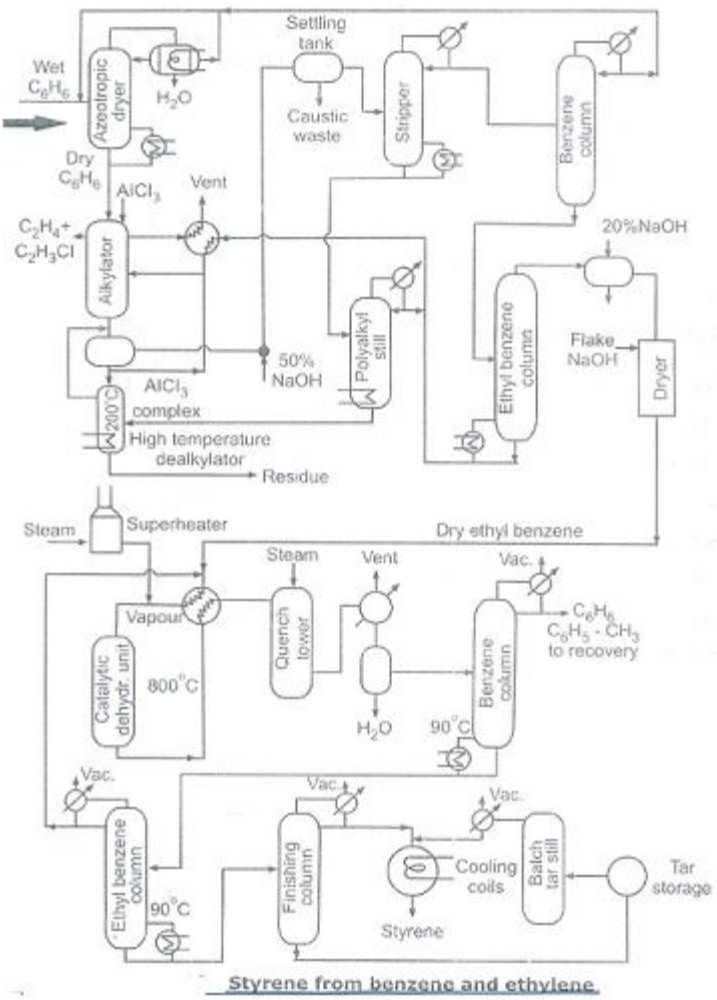
Process Description :

A refinery gas of C_4/C_5 cut containing predominantly n-butane with some isopentane is mixed with recycle gas and preheated to reaction temperature prior to contact with a catalyst in a fixed bed, regenerative-heating reactor system. 4

The temperature of reaction at the start of the "make" period is 650^oC, dropping to 550^oC at the end before switching to regeneration. The pressure is low, 120-150 mm absolute, to force the reaction to the right.

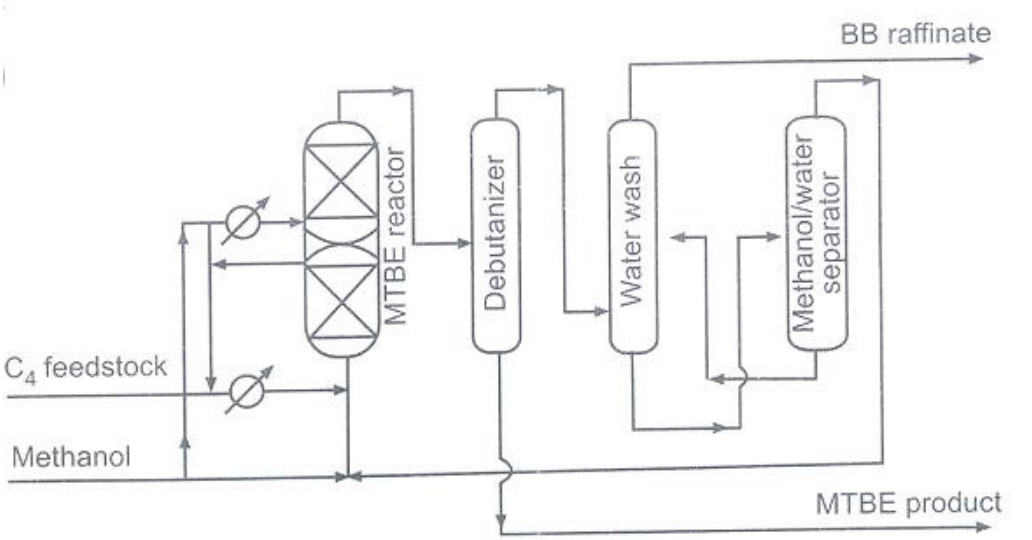
The product gases are oil-quenched, compressed, cooled and separated from the light ends by absorption in naphtha followed by stripping. The overhead is fractionated to yield crude butadiene at the top which is purified by (1) absorption using cuprous ammonium acetate (CAA), (2) extractive distillation with furfural, or (3) azeotropic distillation with ammonia.

The more common absorption process involves contact of the close boiling butadiene-butene fraction with lean CAA solution which dissolves butadiene. A desorption step at higher temperature is followed by distillation, compression

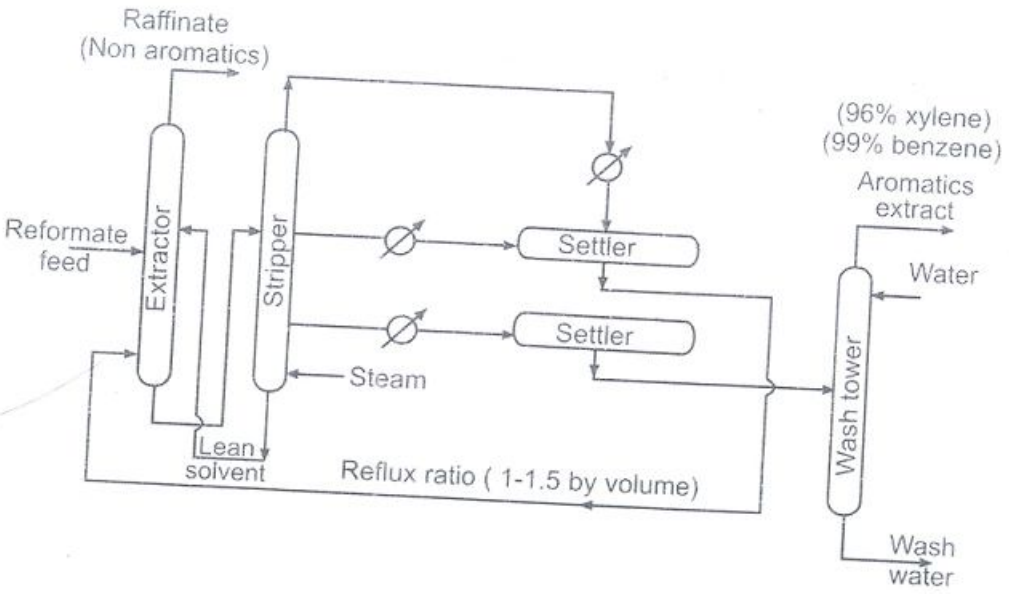
	and liquefaction of butadiene to give 98.99% product purity.		
5-b	 Styrene from benzene and ethylene **Description** : The alkylation operation must be done under very dry conditions with high purity feedstock to avoid activity loss of catalyst. All benzene feed must be	4	8

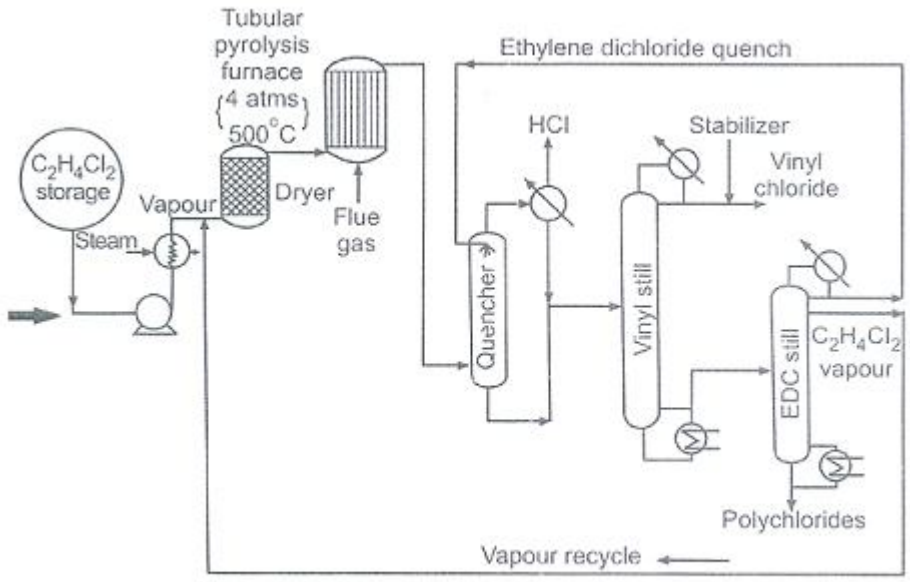
	dried by azeotropic distillation. Ethyl chloride, which serves ultimately as a source of hydrogen and chlorine free radicals for catalyst promotion, is added to ethylene which is fed continuously along with benzene to the alkylation tower operating at 95^{o}C and l1 atm. Pressure, Granular $AlCl_3$ catalyst is fed continuously at the top of the reactor,. The reactant mole ratio is 0.6 C_2H_4/1.0 C_6H_6 and no ethylene is recycled. The alkylation tower is water cooled to control the exothermic reaction. The alkylate products are pumped to a cooler at 40^{o}C where the aluminum chloride complex is separated and split stream is fed to alkylator. The bleed off fraction is pumped to a high temperature (200^{o}C) dealkylator to break down the poly ethyl benzenes to benzene and ethyl benzene which are returned to the system. The tar residue plus aluminum chloride is water extracted to recover 80-85% of $AlCl_3$. Crude acidic ethyl benzene from the coolers is neutralized with 50% NaOH solution, stripped to remove poly ethyl benzenes and the overhead sent to the benzene column which separates wet benzene from ethyl benzene. Final distillation is followed by 20% caustic wash, then drying by percolation in a flake caustic bed, produces 99% ethyl benzenes for dehydrogenation in yields averaging 95%. The resulting ethyl benzene is catalytically dehydrogenated in steam or excess benzene atmosphere to yield styrene.	4	
5-c	**Hydrocarbons**: 1. Aviation gasoline 2. Gas/Diesel oil 3. Heavy fuel oil residual 4. Kerosene	4	8

	5. Jet fuel 6. Liquefied petroleum gas 7. Motor Gasoline 8. Naphtha 9. Other petroleum products. **Uses** : 1. Aviation gasoline is used for aviation piston engines. 2. Diesel oil for train, trucks cars etc. 3. Kerosene for illumination 4. Jet fuel – used as aviation fuel. 5. Liquified Petroleum Gas for cooking 6. Motor gasoline –for internal combustion engine. 7. Naphtha – production of motor spirit 8. Heavy fuel oil residual for furnace 9. Other petroleum products-petcoke as fuel in cement kilns, tar for construction of roads.	4	
6-a	**Four fractions other than gas and gasoline.** i) Petroleum coke ii) Aviation Turbine Fuel. iii) High Speed Diesel iv) Light Diesel oil v) Fuel Oil vi) Bitumen vii) Kerosene viii) Naphtha	1 mark each for any 4	4

6-b	 MTBE via catalytic etherification The reactor inlet temperature ranges from 45°C at start-of-run to about 60°C at end-of-run conditions. One important factor of the two stage system is that the catalyst may be replaced in each reactor separately without shutting down the MTBE unit. The catalyst used in this process is a cation-exchange resin and is available from several catalyst manufacturers. Isobutene conversion of 97% are typical for FCC feed stocks. Higher conversions are attainable when processing steam-cracker C_4 cuts, which contain isobutene concentrations of 25% MTBE is recovered as the bottom product of the distillation unit. The methanol-rich C_4 distillate is sent to the methanol-recovery section. Water is used to extract excess methanol and recycle it back to process. The isobutene-depleted C_4 stream may be sent to a raffinate stripper or to a molsieve-based unit to remove other oxygenates such as DME, MTBE, methanol and tert-butanol.	2 2	4

	Very high isobutene conversion, in excess of 99%, can be achieved through a debutanizer column with structured packing containing additional catalyst. This reactive distillation technique is particularly suited when the raffinate-stream from the MTBE unit will be used to produce a high-purity butane-1 product. For a C_4 cut containing 22% isobutene, the isobutene conversion may exceed 98% at a selectivity for MTBE of 99.5%		
6-c	**Ignition Temperature**: A source of ignition, typically a spark and oxygen are required to ignite a gas, for ignition, the concentration of gas or vapour in air must be at a level such that the fuel and oxygen can react chemically,. Power of explosion depends on the fuel and its concentration in the atmosphere. "The ignition temperature is the llowest temperature at which flammable substance in an air-liquid mixture ignitges spontaneously and continues lto burn with any addition of heat."OR "The ignition temperature is the lowest temperature at which the vapour ignites spontaneously from the energy of the environment." Example : Ignition temperature of pentane = 1018^oF Ignition temperature of benzene = 1252^oF **Explosive limits :** It is the % of the compound in air between LEL and UEL. In this range explosion(ignition) take place. Example : Lower explosion limit of pentane = 1.4% Upper explosion limit of pentane = 7.8% Lower explosion limit of Benzene = 1.2% Upper explosion limit of Benzene = 7.8%	1 1 1 1	4

6-d	 **Udex process** : Reformate as a feed can be sent to extraction column, where in this column the reformate can be heated to about 140°C to 150°C in presence of lean solvent to get two phases , extraction and raffinate . Raffinate contains non aromatic compound and extract contains aromatic compound. Solvents can be used to extract the aromatic compound from reformate feed. In striping recovery of solvent take place.	2 2	4
6-e	**Chemical Reaction :** $CH_2Cl.CH_2Cl \xrightarrow{500°C,\ 4\ atms} CH_2{=}CHCl + HCl$ **Temperature :** 480-520°C **Catalyst :** Pumice or Charcol **Flow Sheet :**		4



Vinyl chloride via ethylene dichloride pyrolysis

2

Process Description :

Ethylene dichloride (EDC) vapours at 4 atms. are dried by silica gel and sent to a stainless steel tubular cracking furnace. This is externally flue gas fired and controlled at 480-520^{o}C. The contact surface catalyst within the tubes is pumice or charcoal. The conversion per pass is around 50% and the ultimate yield is 90 to 96%. Spray quenching with cold EDC prevents back reaction. Uncondensed gases are sent to a surface heat exchanger to remove the balance of the EDC and vinyl chloride.

The non-condensable containing HCl are either sent to the acetylene-HCl process in an adjacent process area or water scrubbed to recover HCl as muriatic acid.

2