SUMMER-22 EXAMINATION

Model Answer

Subject title: Petroleum and Petrochemical Technology Subject code 22611

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.
8)As per the policy decision of Maharashtra State Government, teaching in English/Marathi and Bilingual (English + Marathi) medium is introduced at first year of AICTE diploma Programme from academic year 2021-2022. Hence if the students in first year (first and second semesters) write answers in Marathi or bilingual language (English +Marathi), the Examiner shall consider the same and assess the answer based on matching of concepts with model answer.

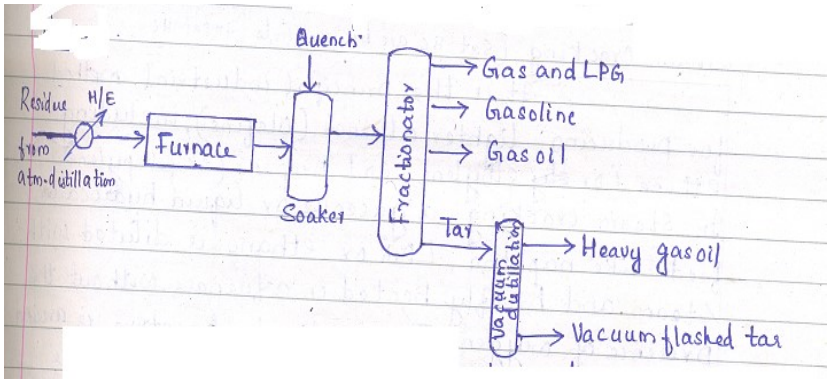
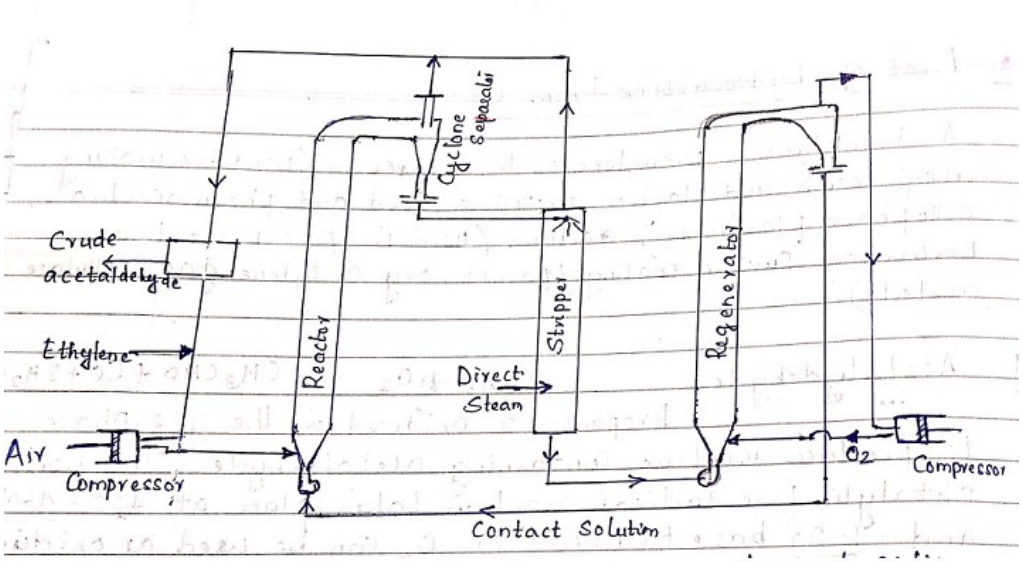
Q No.		Answer	Marking scheme
1		**Attempt any five**	**10**
1	a	**List of Indian Petroleum refinery(any four)** 1. Reliance petroleum Ltd at Jamnagar 2. Indian Oil Corporation Limited atKoyali in Gujarat 3. Manglore Refinery and Petrochemicals Ltd at Manglore in Karnataka 4. Chennai Petroleum Corporation Ltd at Manali 5. Indian Oil Corporation Limited at Mathura in Uttar Pradesh 6. Cochin Refineries Ltd. at Cochin , Kerala 7. Hindustan Petroleum Corporation Ltd. at Visakhapattanam in Andhra Pradesh 8. Bharat Petroleum Corporation Ltdat Mumbai. 9. Indian Oil Corporation Limited at Panipat in Haryana 10. Indian Oil Corporation Limited at Barauni in Bihar 11. Hindustan Petroleum Corporation Ltd at Mumbai	½ mark each
1	b	**Composition 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%	2

		The major compounds present in crude oil are: A. hydrocarbon i)Paraffins ii)Aromatics iii) Napthenesiv) dienes B. Non hydrocarbon i) S compounds ii)O_2 compounds iii)N_2 compounds C. Metallic compounds.	
1	c	**Flash Point** Flash pointis the lowest temperature at which the oil gives off enough vapors that ignite for a moment when a tiny flame is brought near it. **Fire point:** It is the minimum temperature at which oil will give enough vapors which will burn continuously for at least 5 seconds when a flame is brought near it.	1 1
1	d	**Cracking:** Cracking is the treatment by which heavy molecular weight hydrocarbons are broken up in to light hydrocarbon molecules by the application of heat and pressure , with or without the use of a catalyst to produce valuable products such as gasoline, fuel oil and gas oil.	2
1	e	**Hyrogenation:** It is the type of chemical reaction which takes place with the addition of hydrogen.	2
1	f	**Chemicals derived from C3 Hydrocarbon(any four)** Acetaldehyde, propylene oxide, glycerin, acetone, Propane, Isopropanol,	½ marks each

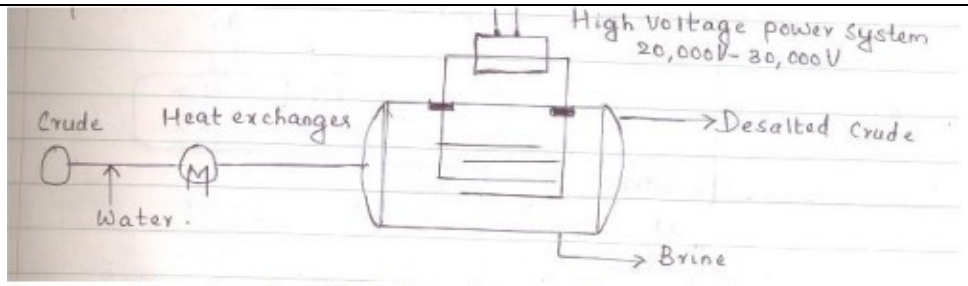
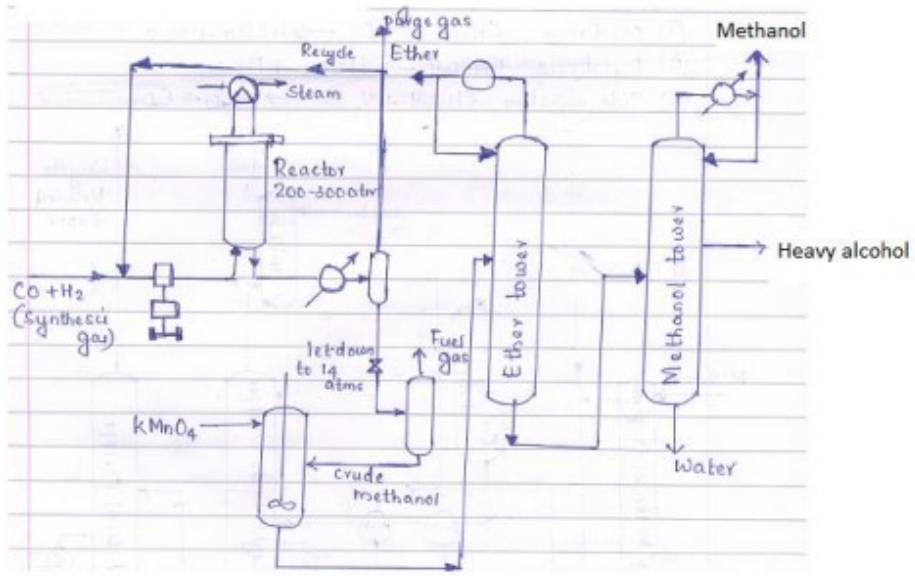
		Acetone, Cumene	
1	g	**Uses of** **i. Benzene(any two)** In the production of phenol, styrene, aniline, sulfonated detergents, chlorobenzene, Maleic anhydride **ii. Butadiene (any two)** In the manufacture of synthetic rubber, as a chemical intermediate,in the manufacture of cycloalkanes and cycloalkenes.	½ mark each ½ mark each
2		**Attempt any three**	**12**
2	a	**Explanation of crude oil reserves available in India** Reserves are known quantities of crude petroleum usually expressed in barrels, which are available for further processing. India had estimated crude oil reserves of 500 million tonnes (MT), ranking 24th in the world and accounting for about 0.3% of the world's total oil reserves. The reserves of India are going day by day due to the improved technological skills and massive investments. The largest reserves are found in the Western Offshore (37%) and Assam (27%). Reserves are also found in Arunachal Pradesh, Andhra Pradesh, Gujarat, Nagaland, Rajasthan, Tamilnadu, and Tripura.	4
2	b	**Fractions obtained in crude oil with their boiling range**	2marks for listing the fractions and 2 marks for writing the boiling range

Fractions	**Boiling point range**
1. Uncondensed gases	< 30°C
2. Petroleum ether	30-70°C
3.Gasoline or petrol or motor spirit	40-120°C

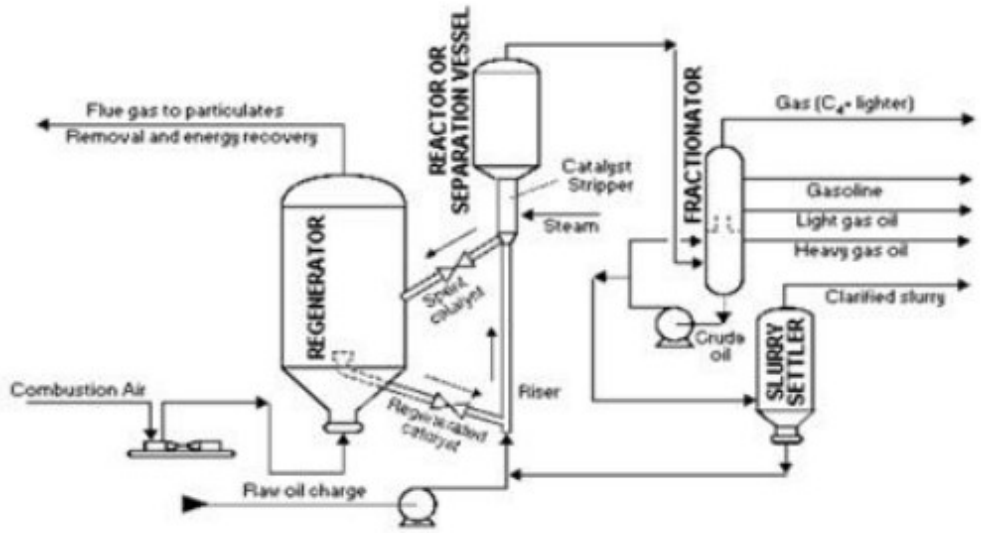
			4. Naphtha — 120-180°C 5. Kerosene oil — 180-250°C 6. Diesel oil — 250-320°C 7.Heavy oil — 320-400°C On vacuum distillation of heavy oil gives a. lubricating oil b. petroleum jelly c. greases d. paraffin wax etc. 8.Residue — > 400°C		
2	c	**Visbreaking:** It is a mild form of thermal cracking which cracks large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons (LPG and gasoline) Residue from the atmospheric distillation tower is heated in a heat exchanger to 250°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		2

		and the distillate recycled 	2
2	d	**Manufacture of acetaldehyde with flow sheet**  $C_2H_4+1/2O_2 \rightarrow CH_3CHO$ **Description**: The process is operated at pressure below 50 atm& temp of 50 to 100^0C.Typical reaction times range from 6 to 40 min. Air and ethylene is passed through a tower reactor along with catalyst solution. Catalyst solution containing acetaldehyde is separated in a stripper. The crude acetaldehyde is distilled twice. In the first stage, low boiling substances like chloromethane,	2 2 2

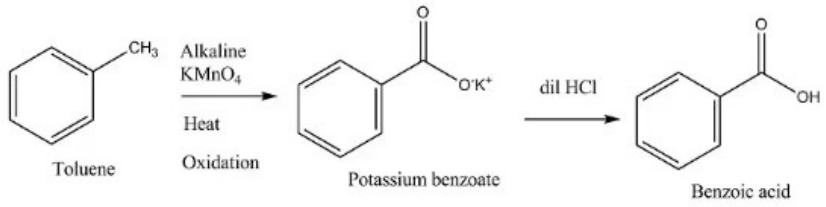
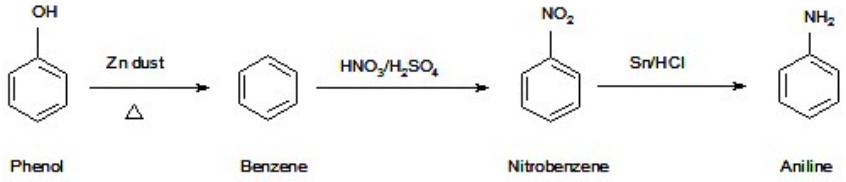
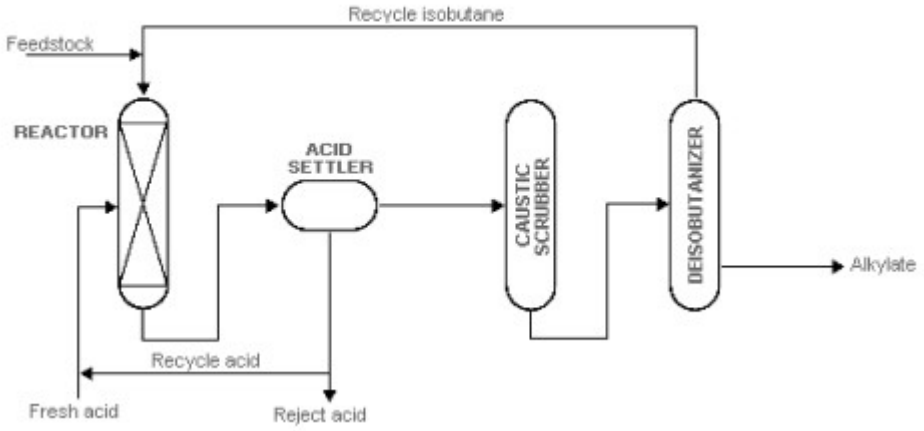
		chloromethaneetcare separated. In the second stage, water and high boiling biproducts like acetic acid are removed and acetaldehyde is obtained in pure form from overhead. **OR** Reaction: $C_3H_8 + 1.5\ O_2 \rightarrow CH_3CHO + CO + 2H_2O$ Propane is oxidized in the gas phase to produce mixture containing acetaldehyde. The non-catalytic free radical reaction takes place at 425-460^oC and 7-20 bar. Either air or oxygen can be used as the oxidizing agent. About 15-20% of hydrocarbon is completely oxidized. The remaining complex reaction mixture contains besides acetaldehyde formaldehyde, methanol, acetic acid, n-propanol and numerous other oxidation products. (Since it is uneconomical to separate acetaldehyde from other oxidation products, it is no longer practiced)	
3		**Attempt any three**	**12**
3	a	**Desalting of crude:** Electric desalting: The feedstock crude is heated between 1500 & 3500 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.	2

		 **(Due consideration should be given for any other method)**	2
3	b	**Methanol** **Flow sheet**  **Description:** Reaction: $CO + 2\ H_2 \rightarrow CH_3OH$ $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$ $CO_2 + H_2 \rightarrow CO + H_2O$ Hydrogen and carbon monoxide in a mole ration of 2.25, is compressed to	2

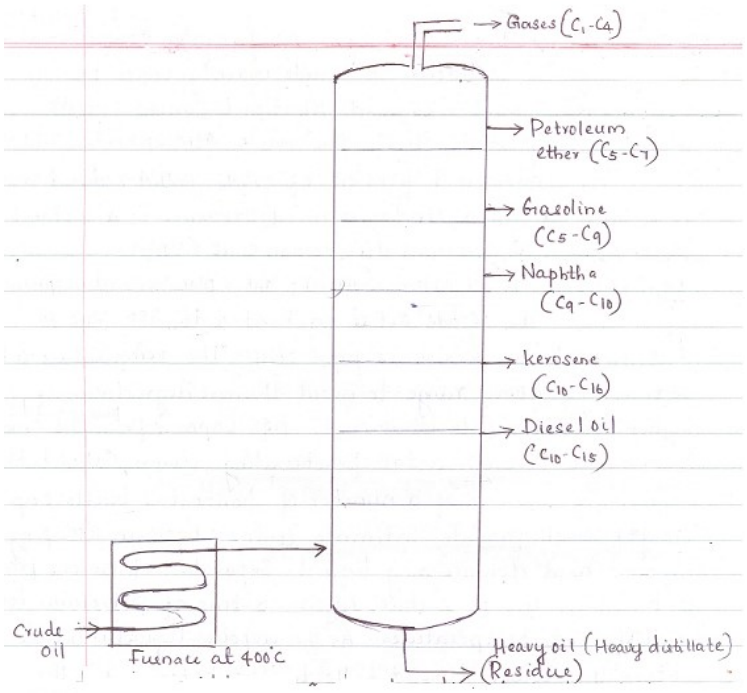
		3000-5000 psi, mixed with recycle gas and fed to high pressure convertor. Internal preheat is usually employed. The reactor is copper lined steel and contains a mixed catalytic of zinc, chromium, manganese or aluminum oxides. The temperature is maintained at 300-375 ^{0}C by proper space velocity and heat exchange design. The exit gases are cooled by heat exchange with reactants, then with water. The methanol condenses under full operating pressure to maximize yields. The liquid methanol is depressurized, purified by permanganate to remove traces of ketone, aldehydes, and other impurities and then send to striper to remove light ends such as dimethyl ether and other to fractionator to separate the methanol from higher molecular compounds	2
3	c	**Fluidized bed catalytic cracking** A typical FCC process involves mixing of a preheated hydrocarbon charge with hot, regenerated catalyst .The charge is combined with a recycle stream within the riser, vaporized & 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 vapors 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.	4

			
3	d	**Oil removal from waste water in oil refinery** Primary treatment consists of oil removal in two stages by physical methods. The first stage of oil removal is done in small ponds 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.  *API Separators:* API or American Petroleum Institute Separators are normally the first and most important step in a refineries wastewater treatment. It uses the differences in oil and water's specific gravity to filter out the majority of	4

		free oil within the mixture. The lighter oils will remain at the top of the liquid and can be skimmed off, while the heavier oil will settle to the bottom. The above figure shows a detail drawing of a typical API separator. A conventional oil-water separator contains a conveyor to assist in the separation of the heavier oils and grease, a scraper/skimmer and a baffle. ***(Due consideration should be given for any other method of oil removal)***	
4		**Attempt any three**	**12**
4	a	**Properties of** **(i) Natural Gas (any two):** I. The state of matter of this gas is gaseous. II. It doesn't have any color and is a tasteless gas. III. It is free of any kind of toxic, there is no smoke on burning and it has high calorific value. IV. The gas is odorless. V. It is a combustible gas and a fossil fuel. **(ii) Gasoline (any two):** I. This is a volatile fraction and is known as motor spirit. II. The boiling range from 37^0C to 180^0C III. The specific gravity of gasoline ranges from 0.71 to 0.77 IV. Quality gasoline should be stable for six months if stored properly, but as gasoline is a mixture rather than a single compound, it will break down slowly over time due to the separation of the components	1 mark each 1 mark each

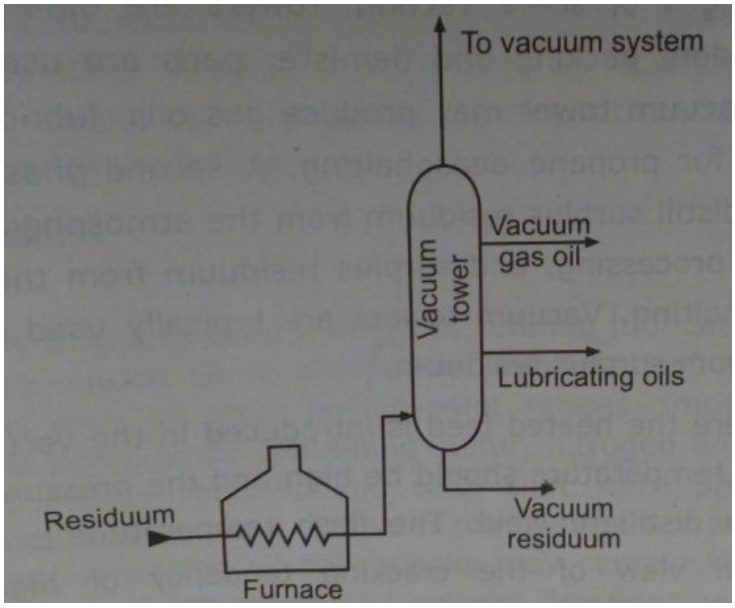
4	b	Chemical reactions involved in the manufacture of **(i) Benzoic acid from toluene**  **Aniline from phenol**  	2 2
4	c	**Sulphuric acid alkylation process**  In cascade type sulfuric acid (H_2SO_4) alkylation units, the feedstock (propylene, butylenes and fresh isobutane) enters the reactor and contacts the concentrated sulfuric acid catalyst (in concentrations of 85% to 95% for good operation and to minimize corrosion). The reactor is divided into zones, with	4

		olefins fed through distributors to each zone, and the sulfuric acid and isobutanes flowing over baffles from zone to zone. The reactor effluent is separated into hydrocarbon and acid phases in a settler, and the acid is returned to the reactor. The hydrocarbon phase is hot-water washed with caustic for pH control before being successively depropanized, deisobutanized, and debutanized. The alkylate obtained from the deisobutanizer can then go directly to motor-fuel blending or be rerun to produce aviation-grade blending stock. The isobutane is recycled to the feed.	
4	d	**Definition:** (i) **Cloud point:**When oil is cooled slowly, the temperature at which it becomes cloudy is called as cloud point. (ii) **Pour point**: The temperature at which oil stops flowing or getting poured is called pour point of oil. (iii)**Drop Point**: The droping point is the temperature at which the grease passes from a semisolid to a liquid state under the conditions of test. (iv)**Smoke point**: The smoke point, also referred to as the burning point, is the temperature at which an oil or fat begins to produce a continuous bluish smoke that becomes clearly visible, dependent upon specific and defined conditions.	1 1 1 1
4	e	**Chemicals derived from aromatics:** 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	½ mark each for any two 1.5 each

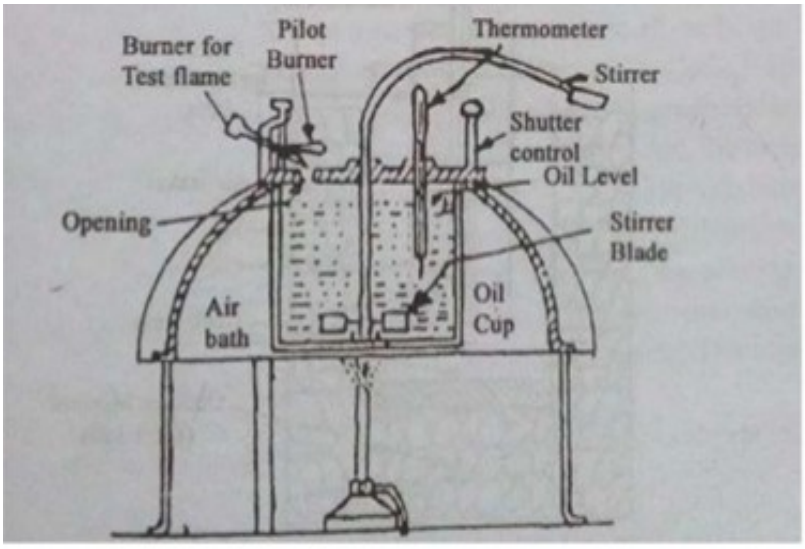
		as plasticizer, solvents for paint, rubber etc (any two) **Uses of xylene:** Used in refinery streams for gasoline blending or further separated by isomers for chemical applications. Solvent for alkyd resins, in the production of phthalic anhydride, dimethyl terephthalate (any two)	
5		**Attempt any two**	**12**
5	a	**Atmospheric Distillation-**  At the refinery, desalted crude feedstock is preheated. 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 pressure slightly above atmospheric pressure & temperature ranging from 340 to 370 ^{0}c. Heavy fuel oil or asphalt residue is taken from bottom. At successively higher points on	3

the tower, the various products such as lubricating oil, kerosene, gasoline &uncondensed gases are drawn off. The fractionating tower a steel cylinder about 120 feet high, contains horizontal steel trays for separating & collecting liquids. At each tray vapors from below enter perforations and bubble caps. They permit the vapors to bubble through the liquid on the tray causing some condensation at the temperature of that tray. An overflow pipe drains the condensed liquid from each tray back to the tray below, where the higher temperature causes re-evaporation. Products ranging from uncondensed fixed gases at the top to heavy fuel oils at the bottom can be taken continuously from a fractionating tower.

Vacuum distillation:

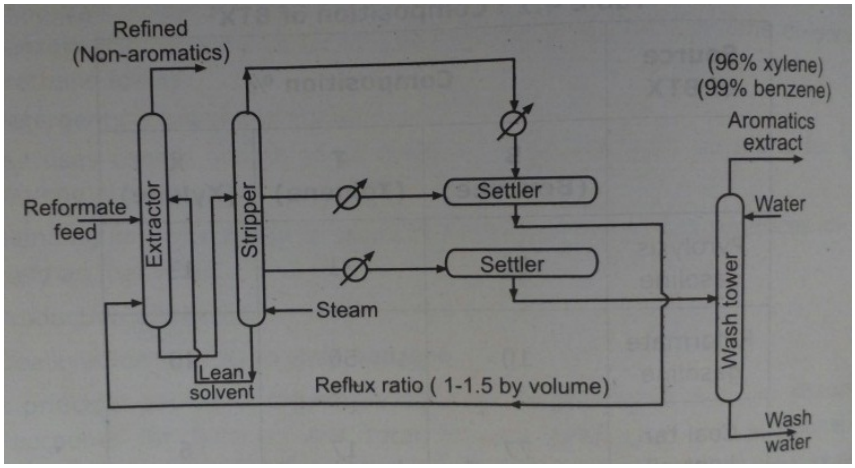


Heavier fractions from atmospheric distillation unit that cannot be distilled without cracking under its pressure & temperatureconditions are vacuum distilled. Vacuum distillation is simply distillation of petroleum fractions at

		very low pressure to increase volatilization & separation. In most system vacuum inside the fractionators is maintained with steam ejector & vacuum pumps, barometric condensers or surface condensers. The injection of superheated steam at the base of vacuum fractionators further reduces the partial pressure of hydrocarbons in the tower, facilitating vaporization & separation. The principle of vacuum distillation resembles those of fractional distillation except that larger diameter columns are used to maintain comparable vapor velocities at the reduced pressure. This vacuum distillation process has become an important chain in maximizing the upgrading of crude oil. The residue from vacuum distillation can be used as feedstock for further upgrading, as bitumen feedstock or as fuel component.	3
5	b	**Pensky martens apparatus** **Diagram**  Clean the cup & fill it with given sample of oil up to the filling mark. Cover the cup with lid. Thermometer is inserted and it should not be touch the metallic cup. Heat the oil by means of electric heater or burner so that the	3

		sample of oil gives out vapour at the rate of 5-6 ^{0}C per minute. Stir the samples at one or two revolutions per seconds. When the oil gives out vapours, introduce the test flame above lid, wait for flash. Introducing test flame should be continued at regular intervals until the first flash is observed with peak flickering sound. The temperature corresponding to the flickering sound is noticed & it is the flash point temperature. Continue the process of heating & introducing the test flame until the oil will begin to burn continuously (for 5 seconds) and observe the temperature. This is the fire point temperature of oil.	3
5	c	**Uses of** **(i) Formaldehyde(any two)** i)It is used in pressed-wood products, such as particleboard, plywood. ii) glues and adhesives iii) Used as an antiseptic in medicine. iv) disinfectant in funeral home **(ii) Ethylene oxide(any two)** i)It is used as a chemical intermediate in the manufacture of ethylene glycol. ii) Used in textiles, detergents, polyurethane foam, antifreeze, solvents, medicinal, adhesives.	1.5 mark each 1.5mark each
6		**Attempt any TWO of the following**	**12**
6	a	**Production of BTX:** **Udex Process-** Reformate as a feed can be send to the extraction column where reformate is heated to about 140-150^{0}c in presence of lean solvent. During extraction we get two phases extract phase &raffinate phase. Extract phase contains aromatic compounds &raffinate phase contains non aromatic compounds. Solvent is	3

used to extract aromatic compounds from reformate feed & then it sends to the stripper. In stripping column, recovery of solvent takes place which is removed from bottom side, aromatic extract can be exit from top side. Aromatic extract phase is cooled & then sent to settler. Two settlers can be used, part of one settler is feed back again to extraction column as a reflux. Now the remaining part of aromatic extract phase is fed to wash tower, for washing with water. Higher % of concentrated aromatic extract component can be withdrawn from top as a product,whereas water with impurity can be obtained from bottom side.



Separation of BTX into Benzene, Toluene, xylene:

The aromatic mixture from Udex process containing BTX is fractionated in column 1,2,3. The separation is according to relative volatility. This mixture is preheated to about 230-270^{0}C.Then it is send to clay tower. Bottom effluent send to the series of three fractionating column where benzene toluene can be obtained as pure components by fractionation.C_8 aromatics consists of ethyl benzene, o,m,p-xylenes and are taken out as overhead product of column 3.

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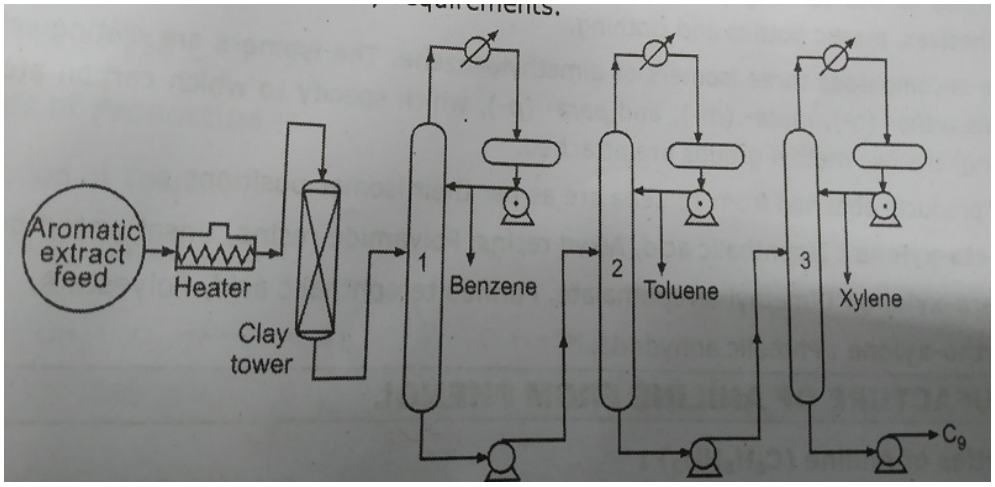
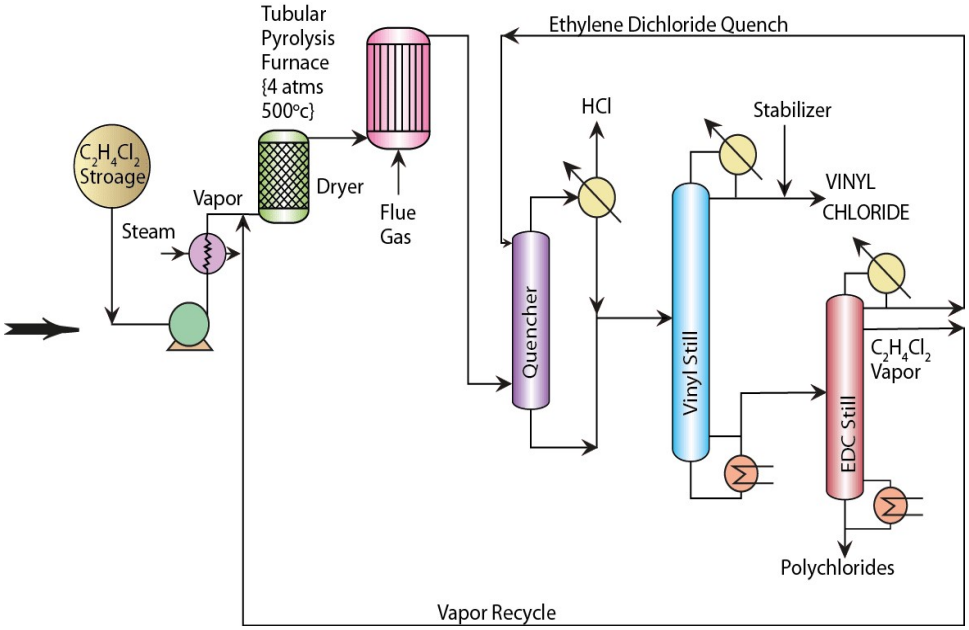
		The heavier fraction C_9 is obtained as bottom product. Further purification of benzene & toluene can be done by selective treatment depending upon purity requirements.  	
6	b	**Manufacture of Vinyl chloride** **Explanation:** Chemical Reaction: $CH_2Cl.CH_2Cl \rightarrow CH_2=CHCl + HCl$ Temp- 500^0c Pressure- 4 atms. Ethylene dichloride vapours at 4 atmospheres are dried by silica gel & sent to a stainless steel tubular cracking furnace. This is externally flue gas fired and controlled at 480-520^0C.The contact surface catalyst within the tubes is pumice or charcoal. The conversion per pass is around 50 % & the ultimate yield is 90-96%. Spray quenching with cold ethylene dichloride prevents back reaction. Uncondensed gases are sent to a surface heat exchanger to remove	3

		the balance of EDC and vinyl chloride. **Flow sheet**  	3
6	c	**Definition:** **(i) Octane Number:** The octane number is the percentage by volume of isooctane in the iso-octane –heptane mixture that matches the fuel being tested in a standard test engine. **Significance:** It is a standard measure of the performance of a motor or aviation fuel. The higher the octane number the more compression the fuel can withstand before igniting. It is also called as Antiknock rating measure of the ability of a fuel to resist knocking when ignited in a mixture with air in the cylinder of an internal combustion engine. It is determined by comparing under standard conditions, the knock intensity of the fuel with that of blends of two reference fuels.	1 1

		Isooctane which resist knocking and heptane which knocks readily. ii) **Cetane number:** Cetanenumber is defined as the percentage volume of n-cetane in a mixture of n-cetane and heptamethylnonane, which gives the same ignition delay as the fuel under consideration. **Significance :** Cetane Number is a measure of fuels ignition delay, the time period between the start of the injection and the first identifiable pressure increase during combustion of the fuel. In a diesel engine higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. The higher the cetanenumber, the more easily the fuel wills combust in a compression setting. A higher cetane fuel usually causes an engine to run smoothly and quietly. iii) **Aniline point :** The aniline point of oil is defined as the minimum temperature at which equal volumes of aniline & the oil are miscible.i.e. form a single phase upon mixing. **Significance:** Aniline point gives an approximation for the content of aromatic compounds in the oil, since the miscibility of aniline which is also an aromatic compound suggest the presence of similar compounds in the oil. It gives an indication of the aromatic hydrocarbon content in a hydrocarbon mixture and can also be an indicator of the ignition point of a diesel fraction.	1 1 1 1