Summer-17 EXAMINATION

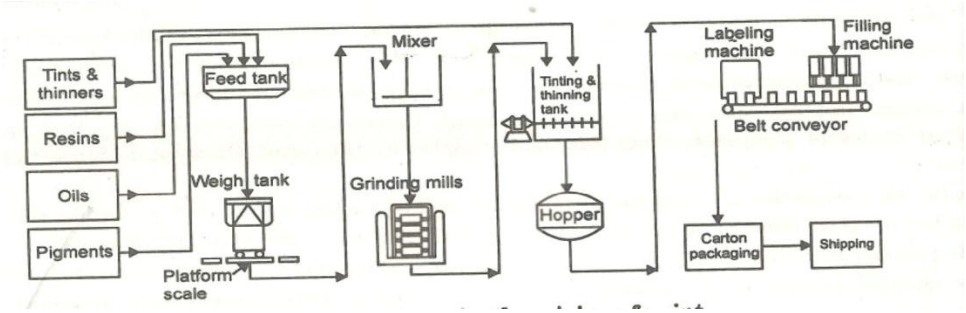
Model Answer

Subject Title: Chemical Process Technology Subject code: 17427

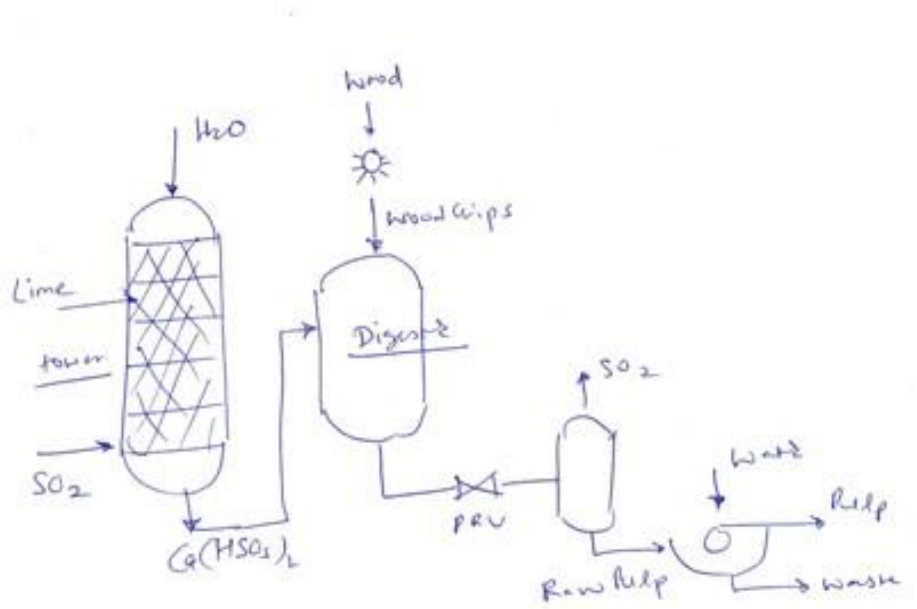
Important Instructions to examiners:

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 one quivalent concept.

Q No.	Answer	Marks
1a	**Attempt any six**	12
i)	**Saponification value** It is the no. of milligrams of KOH required to saponify one gram of an oil or fat	2
ii)	**Pulp** is a lignocellulosic fibrous material prepared by chemically or mechanically separating cellulose fibers from wood, fiber crops or waste paper. Methods: Mechanical, Semi chemical, chemical (Sulphate and sulphite)	1 1
iii)	**Fermentation:-** Fermentation is a metabolic process that converts sugar to acids, gases and/or alcohol. It occurs in yeast and bacteria, but also in oxygen-starved muscle cells (see "Lactic acid fermentation" below). Fermentation takes place in the absence of oxygen, when the electron transport chain is unusable. **Fermentation is used for the production of** Alcohol Medicine Food processing Industrial solvents	1 1 mark each for any two
iv)	Uses of Acetic Acid For the production 1. Vinyl acetate monomer 2. Ester 3. Acetic anhydride 4. As a solvent	1 mark each for any two uses

	5. Medical 6. Food (vinegar)	
v)	**Polymerization process** Addition polymerization Condensation polymerization Emulsion Polymerization	1 mark each for any two
vi)	**Acid Value significance** It gives information about age of oil sample, also it signifies due to attack of atmospheric oxygen, hot moist air or microorganisms how much generation of free fatty acid has taken place leading to rancidity	2
vii)	**Iodine value** Iodine value is the no. Of grams of iodine absorbed by 100 grams of oil or fat for its complete saturation.	2
1B	**Attempt any two**	**8**
i)	**Block diagram of paint production** 	4
ii)	**Comparison between soap and detergents. (any four)** **Soaps** / **Detergents** 1. Are sodium salts of long chain carboxylic / Are sodium salts of long chain benzene sulphonic acids or alkyl 2. Obtain by natural resources from plants and animals (fats, oils) / Synthetic materials, hydrocarbon of petroleum or coal	1 mark each for any four

	3. Calcium and magnesium salts are insoluble in water 4. Produces scum in hard water which affects it's cleaning 5. Biodegradable	Calcium and magnesium salts are soluble in water Hard water does not affect it's cleaning action Not too biodegradable
iii)	**Uses of Polystyrene** disposable plastic cutlery and dinnerware, CD "jewel" cases, smoke detector housings, license plate frames, plastic model assembly kits, Polystyrene foams, disposable razers	1 mark each for any four
2	**Attempt any four**	**16**
i)	**Uses of ethyl alcohol** Following are the uses of ethyl alcohol i) In manufacturing of alcoholic beverages, ii) As a solvent for paints and varnishes, iii) in drug preparation, iv) In manufacture of chloroform, acetaldehyde, chloral, ether, etc. and synthetic rubber v) As anti freeze in automobile radiators	1 mark each for any four
ii)	**Constituents of paint** **Pigments: -** It is finely divided solids generally made up metal oxides .It is used to give colour to paint. **Drying oil: -** These are unsaturated oils. It is used to form protective film and give gloss. **Thinners or solvent: -** It is alcohols or turpentine. is used to dissolve polymers in paint and to disperse pigments (emulsion formation).It adjust viscosity, form thin film. **Plasticizer: -** These are polymers. Used to impart elasticity to paint.	1 mark each
iii)	**Sulphite Process for Pulp**	4

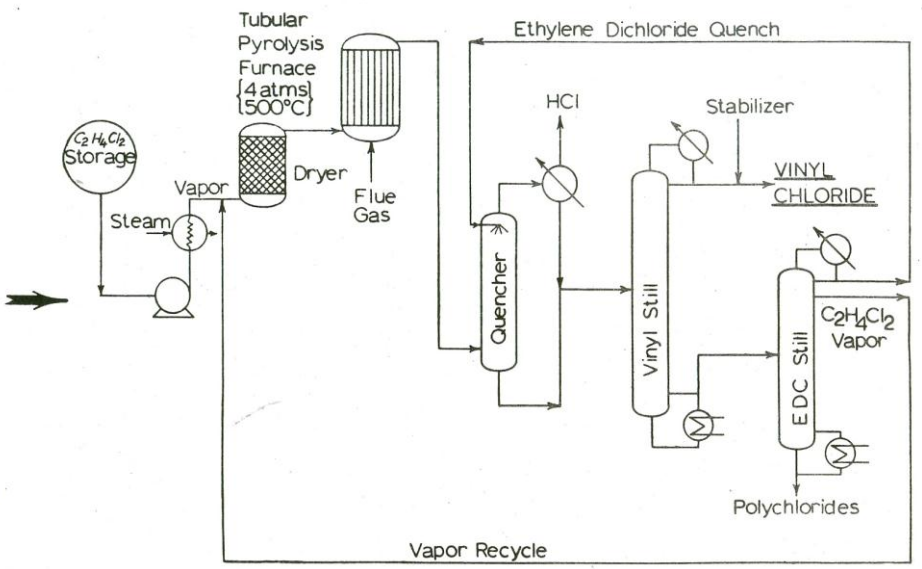
		
iv)	**Phenol by toluene oxidation process** A two-stage air oxidation process is used. In the first stage, fresh plus recycle toluene are mixed with a small quantity of cobalt naphthenate catalyst and charged to the reactor which is a liquid-filled tower through which air is sparged. Cooling tubes are provided to remove the exothermic heat of reaction. The reactor is run at 150^{o}C and 3 atms. Excess air is used, but toluene conversion is limited to 40% to avoid excessive side reactions, These give by-products such as benzaldehyde, benzyl alcohol, benzyl benzoate, CO and CO_2.With conversion of toluene at 40% the ultimate yield of benzoic acid is about 90%. Off-gases from the reactor are vented through a water-cooled condenser to remove water and to allow return of toluene. Liquid from the reactor	4

continuously passes to a distillation column which strips the toluene and other volatile by-products from the acid fraction in the bottoms. Purified benzoic acid is separated by extracting the bottoms with hot water, then crystallizing and filtering the crude benzoic acid. The latter can be recrystallized to meet USP specifications as a market outlet for benzoic acid.

To make phenol, the crude acid is melted, mixed with cupric benzoate catalyst, then charged to an air-sparged tower containing cooling tubes and mechanical agitation,. Reactor conditions are 220^{o}C and 13-17 atms. Excess air is again necessary to get a 70-80% conversion of benzoic acid with a yield of 90% phenol. The overall process yield for the two steps is about 80%.

Phenol product is obtained by continuously distilling the reactor liquor into a fractionating column where unreacted benzoic acid is returned to the reactor. Non-condensable such as N2 O2 and CO2 are vented through a condenser along with the condensable fraction phenol-water. Phenol is withdrawn as the bottom layer in a separator. This crude phenol is again fractionated with purified phenol coming off as bottoms and the overhead phenol-water azeotrope sent to another column for splitting.

The heavy ends in the benzoic acid oxidation tower are water-extracted to recover phenol and benzoic acid which are then recycled, after concentration, to the second stage oxidation tower.

v)	**Flow sheet for vinyl chloride**  	4
vi)	**Difference between hot and cold process for soap** **Hot process** / **Cold process** High purity of soap is obtained. / Low purity of soap is obtained. Byproduct glycerol is separated. / Glycerol is mixed in soap Reaction temperature is high / Reaction temperature is low Maximum yield is possible. / Lesser yield is obtained.	1 mark for each
3	**Attempt any four**	**16**
i)	Manufacture of Alcohol from Molasses : **i) Raw materials :** **1. Molasses (Black strap) :** Molasses is considered as the mother liquor left after the removal of sugar crystals. Hence, it is a by-product of the sugar industry. It contains about 55% sugar (2/3 sucrose and 1/3 invert sugar.	2

2. Yeast :

i. Selected strains of saccharomyces cerevisiae :are commonly employed for fermentation. It produces a large amount of alcohol. Yeast is a source of different enzymes.

ii. Preparation of inoculum : From the selected strains of yeast, the inoculum is prepared. The starter containing yeast is in its log phase. The yeast developed in a seed tank should be pure and free from contamination and mutation.

iii. Preparation of medium : The molasses is difuted with water to 10 to 18%. These molasses can be used directly as fermentation medium. Nutrients such as ammonium sulphates or ammonium phosphate may be added to improve the quality of fermentation. The pH value of the medium is adjusted to 4 or 5 by adding sulphuric or lactic acid. Lactic acid is particularly beneficial as it inhabits the growth of butyric acid bacteria. pH below 5 inhibits lactic acid bacteria. Other possible microbial contaminants are inhibited by high sugar and alcohol concentration and the anaerobic condition of the fermentation. /as a result of these considerations, the molasses medium is not sterilized.

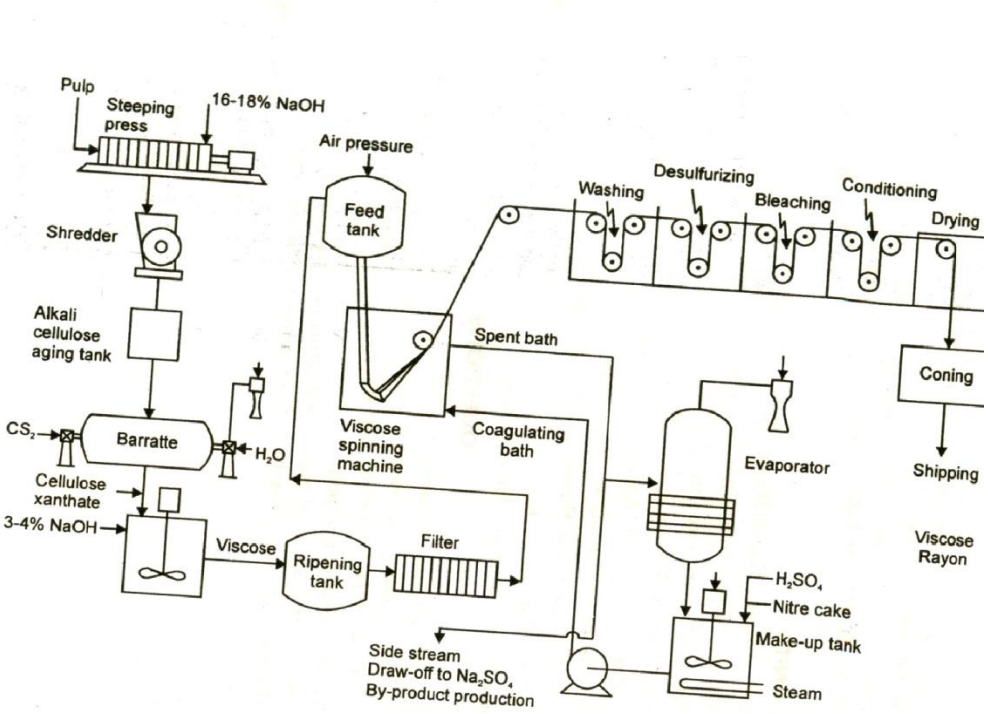
iv. **Fermentation** : Alcoholic fermentation is an example of anaerobic fermentation. Fermentation has therefore to be carried out in the absence of oxygen. In alcoholic fermentation, the carbon dioxide produced pushes out air and automatically creates an anaerobic atmosphere. The fermentation reaction being exothermic, the fermenter get heated and no temperature control is needed. The fermentation is carried out for 50 hours at 30 to 40^{o}C in fermenter, after mixing yeast starter and medium.

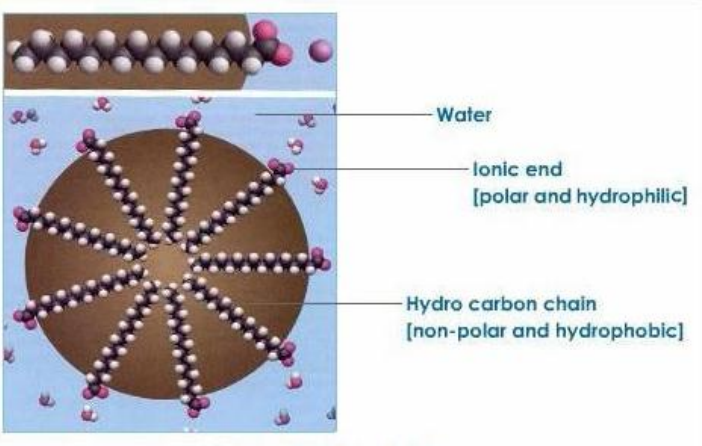
“invertase

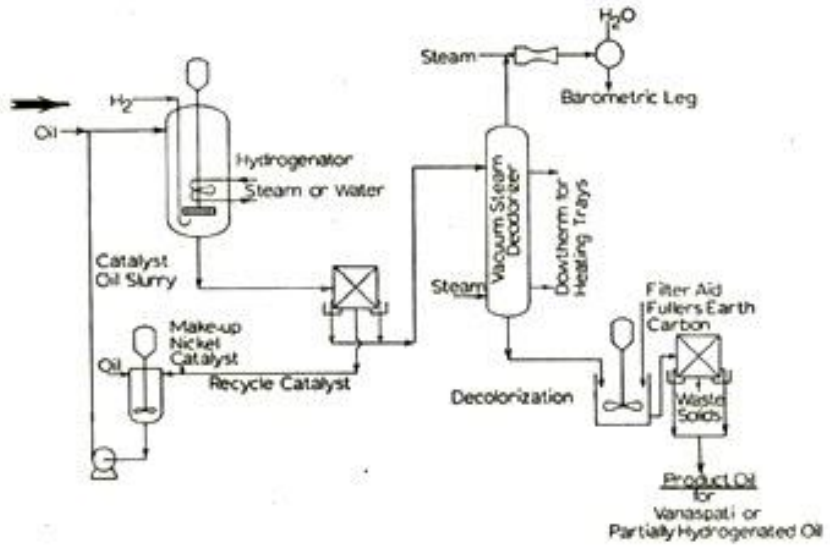
	$C_{12}H_{22}O_{11}$ = $C_6H_{12}O_6 + C_6H_{12}O_6$ Yeast Sucrose Glucose Fructose zymase $C_6H_{12}O_6$ = $2C_2H_5OH+2CO_2$ Yeast Glucose or Ethanol Fructose v. **Recovery** : The fermented mesh (beer) is distilled to obtain pure ethyl alcohol. The fractions containing 60% alcohol are known as high wine. These fractions are then distilled to get 95% alcohol (raw spirit). Because of the lability of alcohol to form an azeotropic mixture containing 5% water ever after successive distillation only 95% alcohol is obtained. To prepare absolute ethanol, the 5% water is removed by forming aazeotropic mixture of benzene, water and ethanol which is then distilled with increasing temperature.	2
ii)	**Difference between varnish and lacquer** **Varnish** | **Lacquer** Varnish is a homogenous colloidal dispersion solution of resin in oils or thinner or both. | Lacquers are dispersion of cellulose or other cellulose derivatives, resins and plasticizers in solvents Solvent used-Oil | Solvent used – Ether, alcohol, ketones	2 mark each for any two

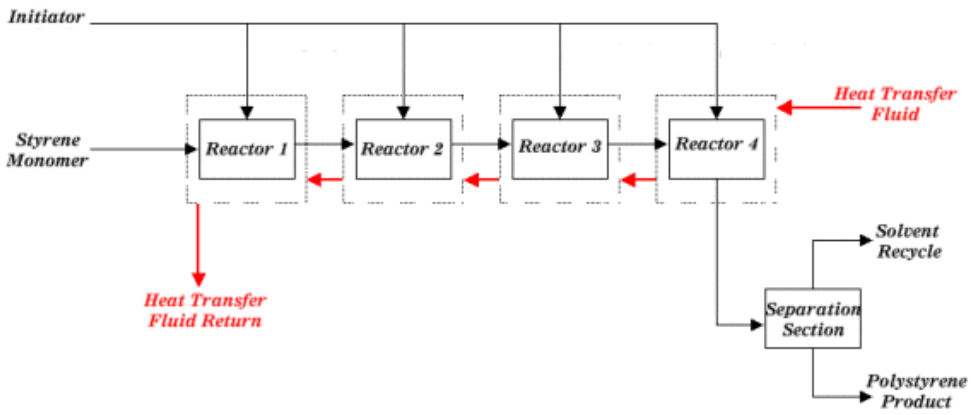
		Manufacturing- Cooking	Manufacturing - Mixing
		Mode of drying – Oxidation or polymerisation	Mode of drying - Evaporation
iii)	**Raw material for Pulp** • Babmoo • Agricultural residue • Bagasse, • Cereal straw • Reeds • Esparto grass • Jute • Flax • Sisal • Softwood (spruce, pine, fir, larch, aspen, eucalyptus) **Additives for improving quality of Paper** China clay Alkyl ketene dimer Epichloriohydrine Malamine Carboxymethyl cellulose Calcium carbonate		2 1 mark each for any two
iv)	**Low Pressure Process** This process was originally developed in Germany for preparing high density polyethylene (HDPE). The catalyst used in this process consists of aluminium triethyl activated with heavy metal derivatives such as $TiCl_4$.		4

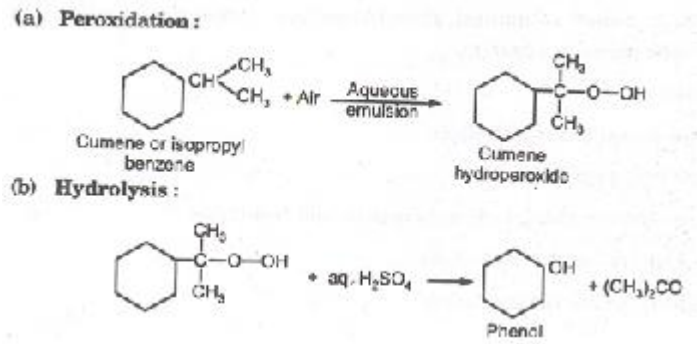
	OR **Low Pressure Ziegler Process to produce polyethylene** At the very onset, through the process of desulphurization and removal of light ends, high purity ethylene is prepared. The ethylene is further treated to remove traces of oxygen and its compounds which can possibly deactivate the catalyst. The ethylene is first pumped into a reactor where it is mixed with catalyst diluents stream. The optimum temperature and pressure maintained should be 70°C and 7 atms gage. The effluent stream then follows across a series of flash drums inorder to remove the solvent from the catalyst. The residual catalyst at this point is removed by adding water. The flashed solvent is thereafter recycled to the catalyst make –up unit after appropriate drying and redistillation. The slurry which results is then centrifuged to remove the water, and the water is treated to remove the catalyst before recycle. The final products of polyethylene solids are then dried, extruded and given the required final forms.	4
v)	**Phenol from benzene** **Raw material** Benzene, hydrochloric acid , air, water **Reaction** $C_6H_6 + HCl + ½ O_2 \rightarrow C_6H_5Cl + H_2O$ $C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$ (Or any other process where benzene is used as raw material)	2 2

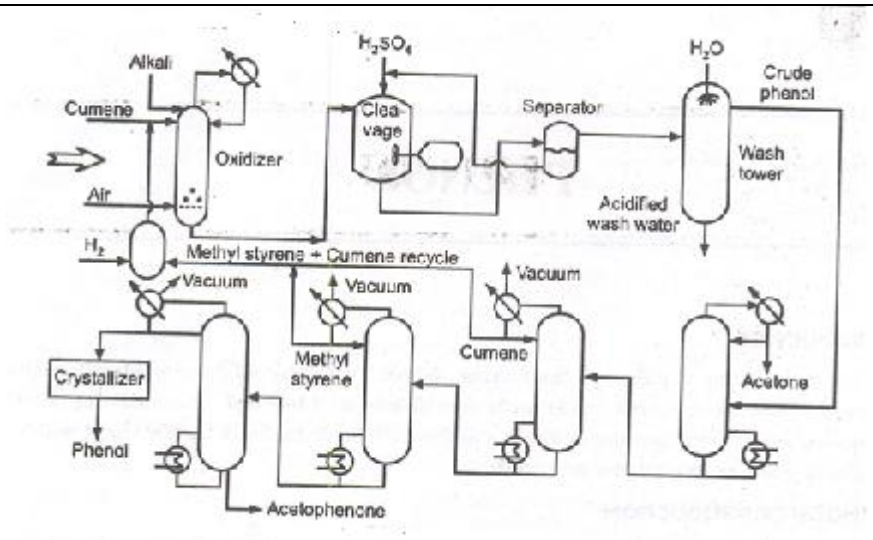
vi)	**Rayon manufacturing flowsheet** 	4
4	**Attempt any four**	**16**
i)	**Cleansing action of soap** The dirt on skin or cloth sticks due to greasy matter. When rubbed with soap solution, it is easily washed away. Soap molecule has a polar end (-COO-Na+) and a non polar end (a long carbon chain of 12 to 18 carbons). The polar end is water soluble while the non polar end is oil soluble. Normally oil droplets in contact with water tend to coalesce to form oil layer and aqueous layer. The non polar ends of soap molecules dissolve in the oil droplet leaving the carboxyl ate ends projecting into the surrounding water. Due to the presence of negatively charged carboxylic groups, each of the oil droplets surrounded by an ionic atmosphere. Oil droplets do not coalesce due	3

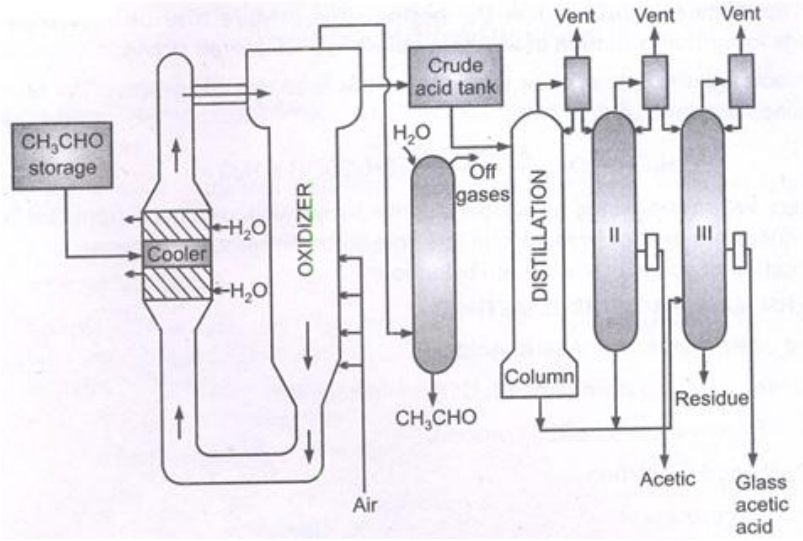
	to the repulsion between similar charges thus stable emulsion of oil in water is formed. In this way soap cleans by emulsifying the fat or grease containing dirt.  	1
ii)	**Hydrogenation of Oil** The dry pure oil and nickel catalyst is taken in an iron cylinder. The cylinder has two inlets & outlets. One inlet is used for the introduction of oil & the other to introduce dry hydrogen. Unused hydrogen is removed through the upper outlet, while lower outlet is used to take the hydrogenated oil. The cylinder is provided with stirrer inside it. The temp. is regulated between1400C-180oC. From the second inlet, pure hydrogen gas is well mixed with the oil. In the cylinder oil &dry hydrogen gas are well mixed with mechanical stirrer. After certain time a sample of hydrogenated oil is taken through outlet is situated at the bottom of the cylinder. The iodine value of the hydrogenated oil is determined. If it is 60, the process of hydrogenation is stopped. And all the hydrogenated oil is taken out It is passed through cooler then filter pressed to remove nickel particles.	2

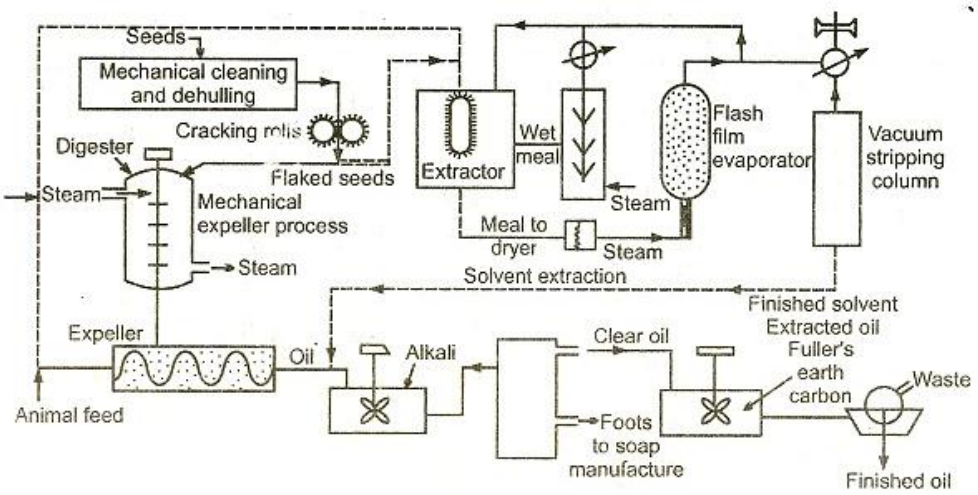
		2
iii)	**Oxo Process** Propylene is compressed to 250 atms and cobalt napthenate added to give 0.5-1 % Co in solution. This stream is passed co currently through packed tower containing porous carrier with 2% metallic cobalt deposited. The reaction is highly exothermic & temp. of 170 deg.C is controlled by recycle of a portion of the product streams after cooling. The liquid fraction is mixed with steam at 180 deg.C & low pressure of 20atm.to decompose the Co carbonyl & naphthenate ,depositing the Co on porous carrier as the oxide. These CO is dissolved periodically in an acid wash & converted to the naphthenate for reuse. The unconverted synthesis gas from the oxo converter is recompressed & recycled. The crude butyraldehyde can be fractionated for product sale or continuously hydrogenated using fixed bed Ni catalyst,100 atm,H2 press.,&150 deg.C. The resulting butanols are fed to distillation section comprising several fractionating columns in series. Light & heavy ends as by-product obtained in addition to the purified alcohol.	4

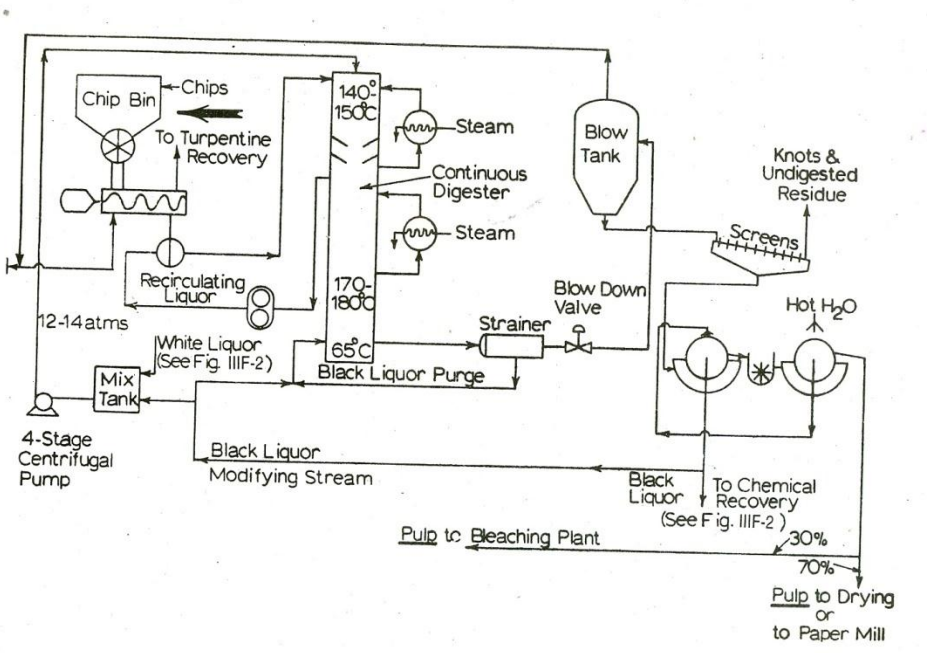
iv)	**Pigments** White : Titanium oxide or zinc oxide Black : Carbon black Blue : Ultramarine (sulfur-containing sodio-silicate) Red: Cadmium red(Cadmium selenide)	1 mark each
v)	**Types of polymers** On the basis of manufacturing 1) Addition polymer eg. Polyethylene, polystyrene 2) Condensation polymer eg. Phenol formaldehyde On the basis of characteristics 1) Elastomers e.g synthetic rubber 2) Themosets e. g phenol formaldehyde, melamine formaldehyde, urea formaldehyde, epoxies 3) Thermoplastic e.g polyethylene, poly(vinyl chloride), polystyrene, nylon, cellulose acetate, acetal, polycarbonate, poly(methyl methacrylate), and polypropylene	2 2
vi)	**PFD Polystyrene**  	4

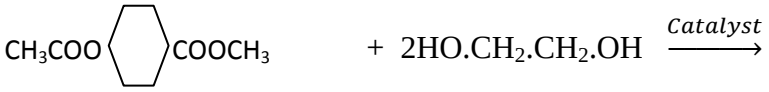
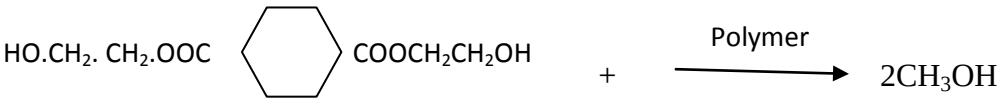
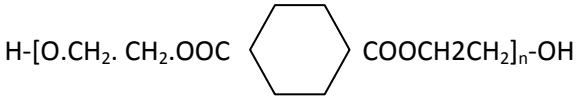
5	**Attempt any two**	
i)	**Manufacturing of Phenol from Cumene**  Process description: Cumene is mixed with recycle cumene & send to the hydrogenerator. Unsaturated compounds are converted to saturated materials to avoid undesirable decomposition of the peroxide during the oxidation step.H2 over nickel catalyst at 1000c in a batch reactor is used for purification. Oxidation is carried out in the presence of air in an aqueous emulsion stabilized by an alkali such as sodium carbonate in the 8.5-10.5 pH range. Vent gases are passed through a condenser to recover hydrocarbon. The cumene peroxide thus formed is cleaved in an acidifier containing 10-25% H_2SO_4 . This is an agitated vessel at 55-650C . The reaction products are separated into an aqueous acid layer for recycle to the cleavage vessel and an oil layer containing 76 wt % cumene,14% phenol,8% acetone % 1-2% α- methyl styrene & acetophenone. This mix is separated in a series of four distillation steps, that last three of which are under vacuum. Phenol is the overhead of the last vacuum fractionator.	2 2

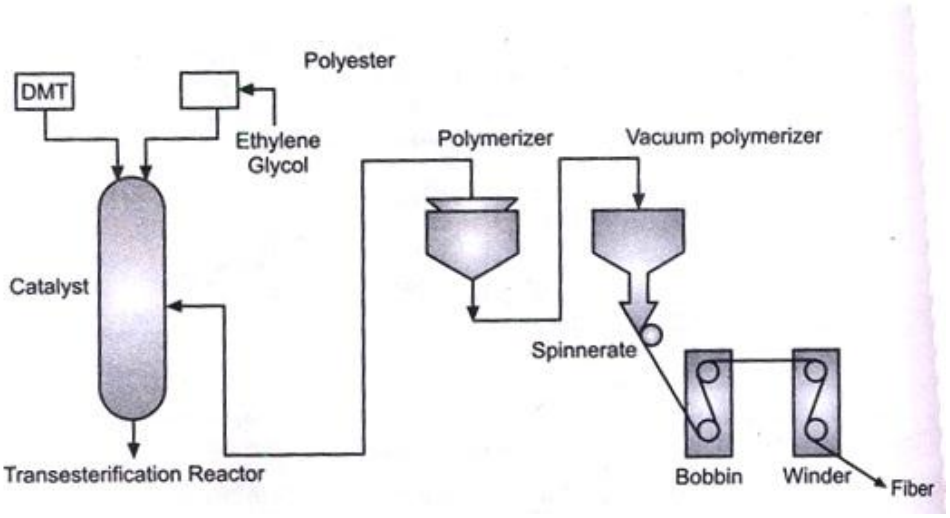
		4
ii)	**Manufacturing process of acetic acid from acetaldehyde** The continuous oxidation of CH_3CHO in liq. phase is carried out by using air or O_2 in presence of manganous acetate. The reaction mix cantaining CH3CHO diluted with crude acid & manganous acetate solution is circulated upward through oxidation tower. Reaction condition when air is used 55^oC-65^oC & 5 atm. Press and when O_2 used then temp 700c-800c and press sufficient to keep the acetaldehyde in liq.state. The reaction mix is drawn off from top of oxidation tower and distilled continuously in three distillation columns. The crude acetic acid is fed to the top of distillation column and other volatile components are withdrawn as overhead and residue containing manganous acetate is removed at the bottom. **Reaction** $CH_3CHO + ½\ O2 = CH_3COOH$	3 1

		4
iii)	**Solvent extraction** : Cakes obtained by pressing operations contain 5 – 10% oils. Further oil is extracted by heating the cake with volatile hydrocarbon like benzene. Petroleum ether, carbon disulphide or carbon tetrachloride are used for the extraction. The common solvent for edible oils is hexane or hexane type naphtha boiling in the range of 146 – 156 ^{o}F. In large-scale operations, solvent extraction is a more economical means of oil recovery than pressing by mechanical means. The use of chlorinated solvents mainly to decrease the explosion and fire hazard did not prove much satisfactory. The solvent used should not make the oil toxic for the application. Finally, organic solvent used for the extraction of oil is removed completely by distillation from the miscella (solvent and oil) to avoid objectionable odour to the oil. The resulting oil is then ready for use. The extent of processing applied to oil or fat depends on their source, quality	4

	and ultimate use. Most of the fats are used for edible purposes with clarification by filter. Many cold pressed and virgin oils are used as food, directly. Peanut, coconut oils can be used directly without further processing. The growing demand for bland testing and stable salad oils and shortening led to extensive processing techniques. In less industrialized countries, processing is limited because of the lack of facilities and added costs.  	4
6	**Attempt any two**	**16**
i)	**Manufacturing of paper from kraft process** The wooden chips are metered via star valve to a deaerator preheater . After several minutes, the chips are discharged through a rotating tapered plug into the lift line where recirculating digestion liquor at 12 atms. Transfers chips to the upper soaking zone of the 25-30m tall digester tower. Chips flow down past a series of circumferential screen plates. Cooking liquor is withdrawn as side streams and circulated through external heat exchangers to reheat and control the digestion temp. within the tower. The digestion time and temp. is adjusted so that max lignin removal is	3

	accomplished with a minimum cellulose hydrolysis and consequent loss of bulk yield. The digested chips are cooled at the base of tower by injection of cold black liquor. This is to avoid mechanical weakening of fibers from steam explosion of hot liquor when passed through a blow down valve. The pulp liquor slurry is passed through the valve to a blow tank where residual heat is recovered in the form of steam. which passes overhead with turpentine vap. To the chip preheater. The pulp is filtered to separate black liquor and screened to remove wood knots and other undigested residue.	3
		2
	Paper from pulp 1)Preparation of fibre suspensions- Pulp is water slurried to 50-75% fibre content by mechanical disintegrations of various designs 2)Formation of paper i) Forming wet web: A wet sheet is formed by running 99.5% water fibre	

	slurry. ii) Pressing the wet sheet: Water from wet sheet is removed by mild pressure to reduce content to 60-65% water. iii) Drying of sheet: A sheet from press section is passed through drying roll and then calendaring rolls to produce smooth well finished paper. Followings are various zones with moisture content i) Web forming-80-82% ii)Pressing- 60-65% iii) drying-5-6% iv) Finishing 5-6%	
ii)	**manufacturing process of polyester from DMT** **Raw Materials:** DMT, Ethylene glycol. **Chemical Reactions:**  DMT   **Process Description:** In production of polyester one mole of DMT and two moles of ethylene glycol	1 2 2

	in presence of catalyst like litharge or zinc, calcium, magnesium salt or alkali salt are taken and fed to trans-esterification reactor. The catalyst concentration may vary from 0.005 to 0.1 %. The reaction starts at 150 deg C to 160 deg C and methyl alcohol is distilled out until the reaction is complete. At the end of reaction the temperature will raise up to 230 deg C. the reaction product is mixture of glycol terepthalate and low polymer. In second stage the temperature is raised further and reaction takes place between hydroxyl end group to produce polymer and glycol vacuum applied slowly and temperature raised to remove glycol. Then the polymer is converted to fiber by spannerate and is converted to finished roll by bobbin and winder.  	3
iii)	**Phenol by benzene sulphonate process** **Reactions :** a) Sulphonation : $C_6H_6 + H_2SO_4 \rightarrow C_6H_5\text{-}SO_3H + H_2O$ b) Neutralization : $2C_6H_5\text{-}SO_3H + Na_2SO_3 \rightarrow 2C_6H_5\text{-}SO_3Na + SO_2 + Na_2SO_4$	2

c) Fusion :

C_6H_5-SO_3Na + NaOH $\rightarrow$ C_6H_5-ONa + SO_2

d) Acidification :

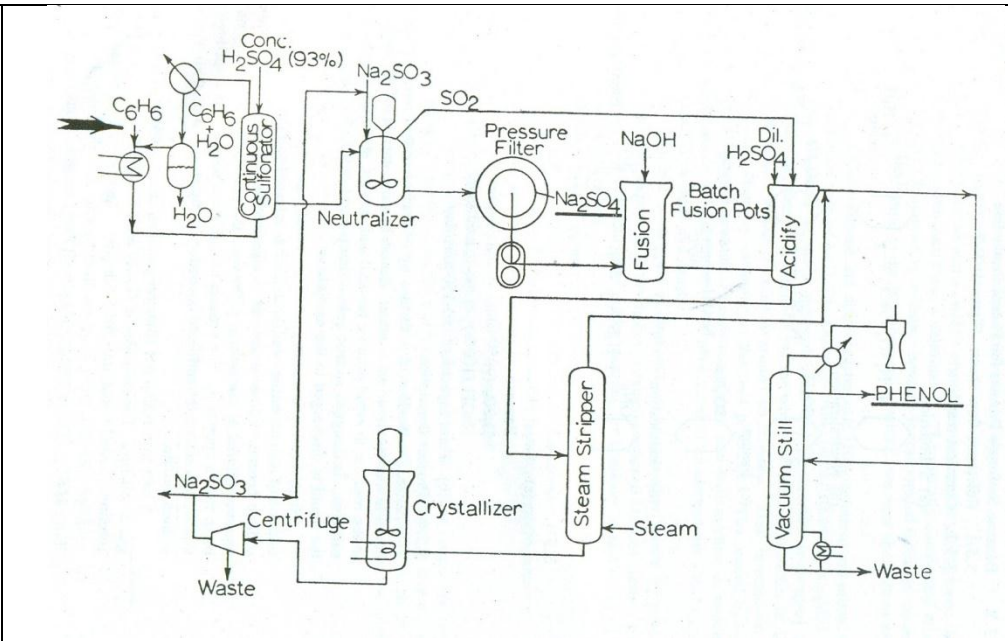
C_6H_5-ONa + H_2SO_4 + SO_2 $\rightarrow$ C_6H_5-OH + Na_2SO_3 + Na_2SO_4

Process description :

Benzene sulphonic acid is formed by contact of benzene vap. With H_2SO_4 liquid in a counter current reactor. Excess benzene carries off the water form in the reaction to avoid the diluting the acid and slowing down the sulphonation. The sulphonator is designed so that only a few percent of free H_2SO_4 remains before the liquid is discharged to the neutralizer . 2

Neutralisation is accomplished by rapidely adding the reactor liquor to a solution of sodium sulfite . Sulphur dioxide is released and the pot residue contains sodium benzene sulphonate in a solution and precipitated Na_2SO_4 . This mixture is pressure filtered at the B.P with the clear solution moving onto the batch fusion operation. In a process modification some plant centrifuge the hot liquor concentrate the sulfonate liquor further by evaporation then removed more sodium sulfate .

A cast iron fusion pot containing molten caustic is kept at 300^0c by the direct gas or oil fire. The sulfonate is slowly added at the bottom of the pot and the reaction allowed to continue for 5-6 hrs. The melt is then diluted with water ,acidified with SO_2 from the neutralization step and the final PH adjusted with H_2SO_4 . The released crude phenol floats on an aq. Solution containing sodium sulphate, sodium sulfite and small percentage of phenol.

	 Conc. H_2SO_4 (93%) Na_2SO_3 SO_2 C_6H_6 C_6H_6 H_2O Continuous Sulfonator H_2O Neutralizer Pressure Filter NaOH Dil. H_2SO_4 Na_2SO_4 Fusion Batch Fusion Pots Acidify PHENOL Steam Stripper Vacuum Still Na_2SO_3 Centrifuge Crystallizer Steam Waste Waste	4