SUMMER-14 EXAMINATION

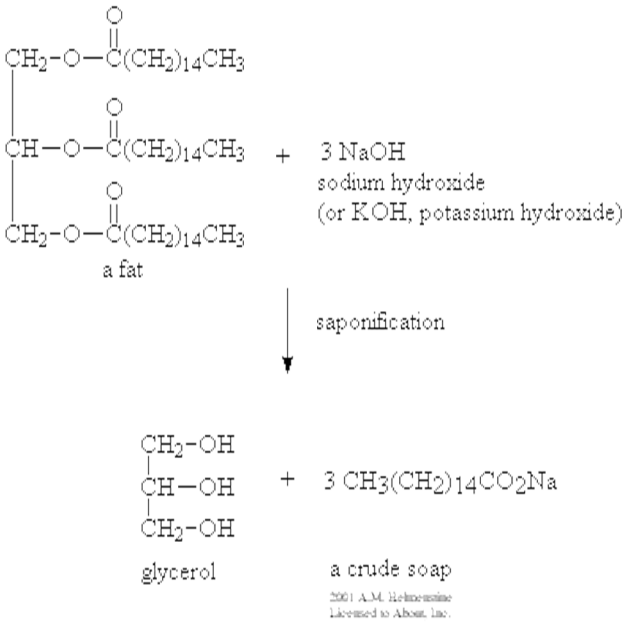
Model Answer

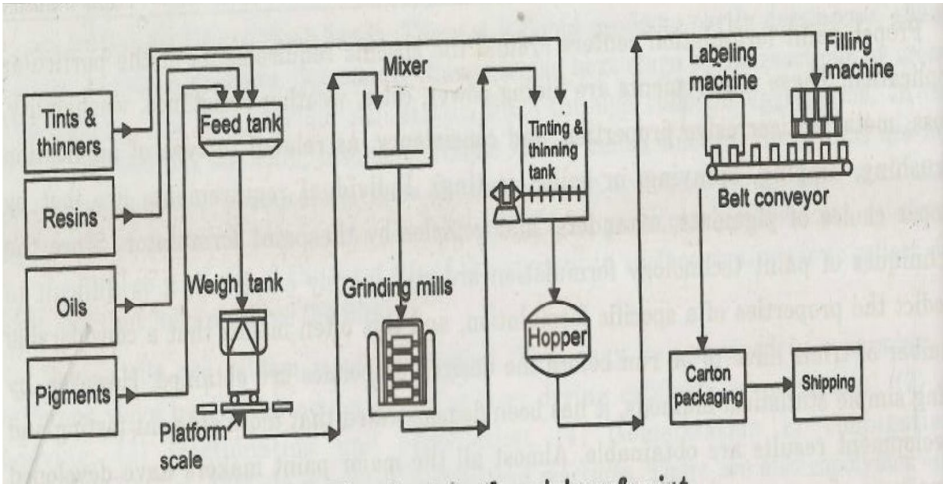
Important Instructions to examiners:

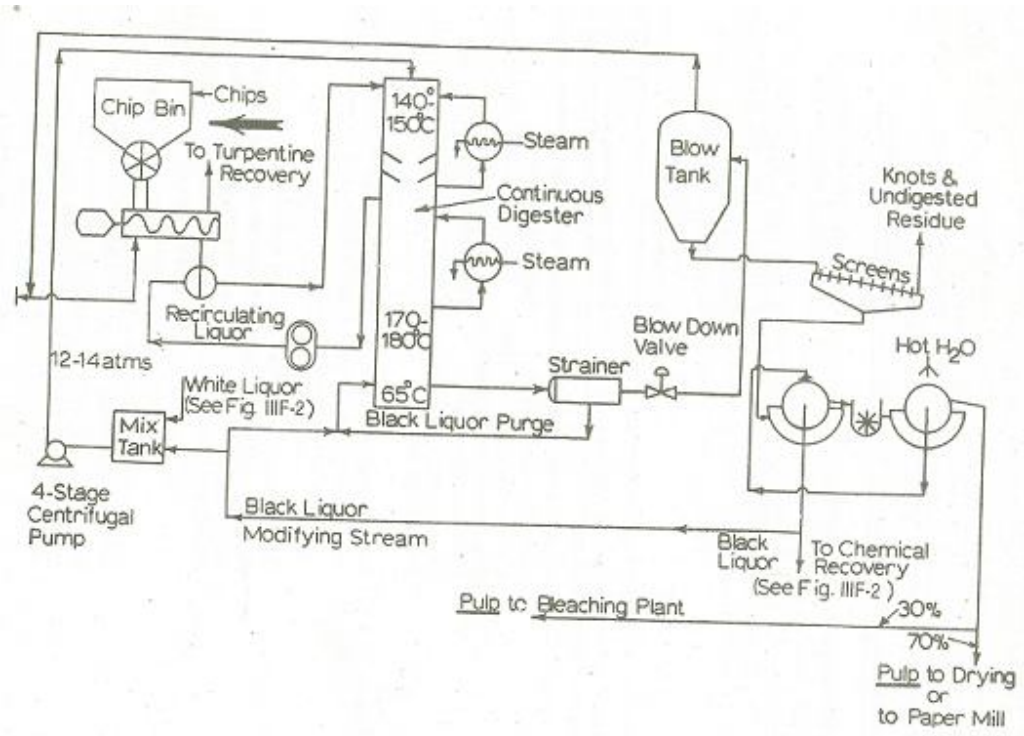
1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling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

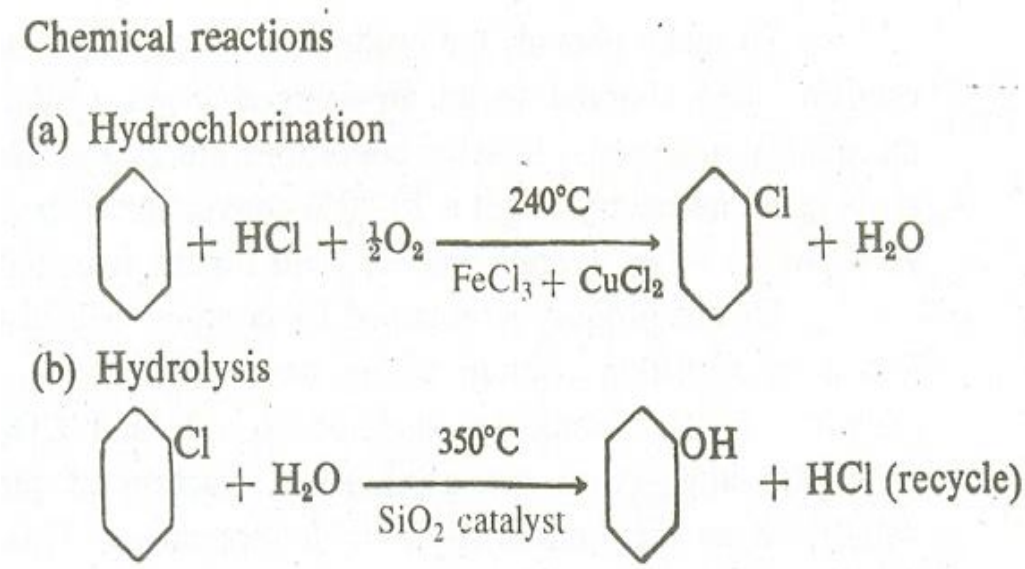
Q No.	Answer	marks	Total marks
1a-i	**Raw material for Pulp** • Babmoo • Agricultural residue • Bagasse, • Cereal straw • Reeds • Esparto grass • Jute • Flax • Sisal • Softwood (spruce, pine, fir, larch, aspen, eucalyptus)	Any four ½ mark each	2
1a-ii	**Acid Value** The acid number is defined as the number of milligram of KOH required to neutralize one gram of oil or fat.	2	2
1a-iii	**Denatured alcohol** Denatured alcohol is ethanol that has additives to make it poisonous, extremely bad tasting, foul smelling or nauseating, to discourage recreational consumption	2	2
1a-iv	**Enzymes used in manufacture of alcohol** • Invertase • Zymase	1+1	2
1a-v	**Solvent used for oil extraction** • Hexane	Any two (1 mark each)	2

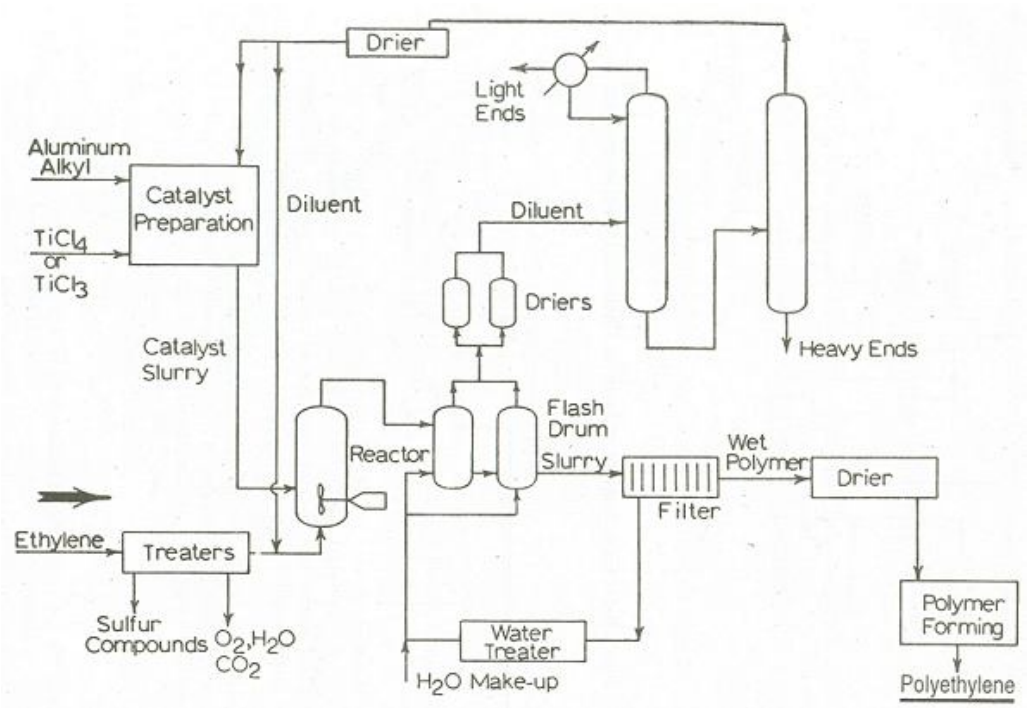
	• Petroleum ether • Benzene		
1a-vi	**Significance of Iodine Value** It give value of un saturation present in oil which can be useful for classification of oil.	2	2
1a-vii	**Use of Rayon** • making textiles, • making tyre cords • making carpets • surgical dressings	Any two (1 mark each)	2
1b-a	**Disadvantages of solution polymerization** • Auto acceleration will occur. • Possible problems with heat transfer during polymerization. • 100 % solution free polymer is difficult. • Additional cost of solvent	Any two (1 mark each)	4
1b-b	**Raw material of paint** **Pigments: -** It 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	4

1b-c	**Saponification** Saponification is a process that produces soap, usually from fats. It involves a reaction between a base, usually sodium hydroxide (caustic soda), and an ester group on a compound. Triglycerides are an example, which is an ester of a fatty acid. The triglycerides are hydrolyzed to form the sodium salt of a carboxylate. In addition to soap, such traditional saponification processes produce glycerol.  	2 2	4
2-a	**Acetic acid production can takes place by using quick Vinegar process or Acetaldehyde oxidation** **Quick vinegar process:-** In this process 10-13 % alcohol is subjected to bacterial oxidation to form acetic acid. In this process beechwood shaving are inoculated with a species of the genus acetobactor. The solution of alcohol mixed with nutrient for the growth of acetobactor is applied is applied in a trough at the top of chamber , and allowed to trickle down over the shaving . As the mixture passes through the shaving , the acetobactor oxidizes some of the alcohol to acetic acid. The mixture is collected	Any one process	4

	at the bottom . The mixture may be recirculated into the shaving for further oxidation until vinegar of desired strength is obtained. $C_2H_5OH + O_2 = CH_3COOH + H_2O$ **Acetic acid can be produced by catalytic oxidation of acetaldehyde.** $CH_3CHO + ½ O2 = CH_3COOH$ The continuous oxidation of acetaldehyde in liquid phase is generally carried out by using air or oxygen in the presence of magnous acetate. The reaction mixture containing acetaldehyde diluted with crude acid and magnous acetate solution is circulated upward through oxidation tower. Reaction condition is 55°C and 5 atm. The reaction mixture is drawn off from the top of oxidation tower and distilled continuously in three distillation columns. The crude acetic acid is fed to the top of distillation column and volatile components are withdrawn as overhead and residue containing magnous acetate is removed at the bottom.		
2-b	Manufacturing of paint  	2	4

	Manufacturing of paint is mechanical operation rather than chemical operation. All the raw material is weighted and send to the mixer. Where pigment and oils are mixed. To make homogenized paint it is send to grinding mill where particle of pigments are grinded. After production of final paints, thinner is added to make proper consistency of paints. Packaging is done in desired size containers.	2	
2-c	**Manufacturing of Pulp**  Preparation of wood pulp by sulfate process.	4	4

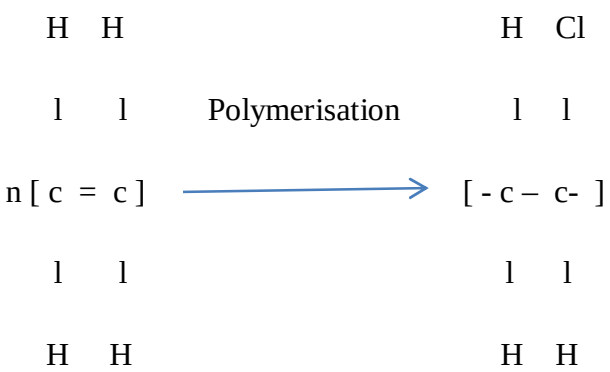
2-d	**Raschig process**  **Process:-** Purified benzene is fed to a heater , packed reactor containing ferric chloride and cupric chloride catalyst. Chlorination occurs at 220°C with short residence time to produce 10-20% conversion of benzene. Fractionation separates unreacted benzene from chlorobenazene and polychlorobenzene. The crude chlorobenzene is scrubbed with phenol; water washed and sends to second catalytic stage. Here it is hydrolysed in a tubular, high temperature furnace with catalyst. Phenol from hydrolyser is washed with water, extracted by benzene and finally purified by two stage distillation.	2 2	4

<table>
<tr>
<td>2-e</td>
<td>Ziegler process
 
</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>2-f</td>
<td>Difference between soap and detergent
<table>
<tr><th>Soap</th><th>Detergent</th></tr>
<tr><td>Soap is sodium salt of fatty acid</td><td>Detergents are salts of organic derivatives of sulfuric acid.</td></tr>
<tr><td>Not work satisfactorily in hard water.</td><td>Can work satisfactorily in hard water.</td></tr>
<tr><td>Yield alkaline solution</td><td>Yield neutral solution</td></tr>
<tr><td>Provide surface action</td><td>Force water to spread and penetrate</td></tr>
<tr><td>Raw material – oil (Fatty acid), caustic</td><td>Raw material – lauryl alcohol, sulphonic acid</td></tr>
</table></td>
<td>1 mark each for any four</td>
<td>4</td>
</tr>
</table>

3-a	**Manufacturing of Butanol** Propylene is compressed to 250 atm. & cobalt naphthenate added to give 0.5 to 1% co in solution. This stream is passed through a packed tower containing a porous carrier with 2% metallic cobalt. The reaction is highly exothermic & the temperature of 170^0C is controlled by recycle of a portion of the product stream after cooling. The liquid fraction is mixed with steam at 180^0C & a relative low pressure of 20 atm. This cobalt is dissolved in an acid wash & converted to the naphthenate for reused. The unconverted synthesis gas from the oxo converter is recompressed & recycled. The crude butyraledhyde can be fractionated for product sales. The resulting butanol are fed to a distillation section comprising several fractionating column in series. Light & heavy ends as by products are obtained in addition to the purified alcohol.	4	4
3-b	**Difference between Paint & Varnish.** 1. Paint is defined as a mechanical mixture consisting of pigments & extenders dispersed in a dry oil called vehicle. 1. Varnish is defined as a homogenous colloidal dispersal solution of natural or synthetic resin in oil or thinners or both. 2. Decorative & building paint, industrial & marine paints are two broad types of paint. 2. Oil varnishes & sprit varnishes are the types of varnishes. 3. Major unit operation in manufacture of paint – Grinding or milling. 3. Major unit operation in manufacture of Varnish – Cooking. 4. In oil based paint film former is oil. 4. In varnishes film former is natural or synthetic resins.	1each for any four points	4

	5. Clay, talc etc. pigment extenders are used in paints. 5. Extenders are not required for varnishes. 6. Major product uses (of paint) – General household & industrial application. 6. Major product uses (of varnish) – used in finishing furniture, exterior wood work, marine application, also in electrical impregnation.		
3-c	wood and other plant materials used to make pulp contain three main components cellulose fibres desired for paper making, lignin a three-dimensional polymer that binds the cellulose fibres together and hemicelluloses, shorter branched carbohydrate polymers. The aim of pulping is to break down the bulk structure of the fibre source, be it chips, stems or other plant parts, into the constituent fibres. Chemical pulping achieves this by degrading the lignin and hemicellulose into small, water-soluble molecules which can be washed away from the cellulose fibres without depolymerizing the cellulose fibres	4	4
3-d	**Various Methods for phenol manufacturing** 1. Cumene peroxidation – hydrolysis 2. Toluene two – stage oxidation. 3. Rasching : vapour phase hydrochlorination & hydrolysis. 4. Chlorobenzene - caustic hydrolysis. 5. Benzene sulfonate – caustic fusion. 6. Benzene – direct oxidation.	1each for any four methods	4
3-e	**Manufacturing Process of PVC** It is obtained by heating a water – emulsion of vinyl chloride in presence of a small amount of benzyl peroxide or hydrogen per oxide in an autoclave under	4	4

pressure.



Vinyl chloride Polyvinyl Chloride

Process Description

In emulsion Polymerisation, a typical formulation is 100 parts of water, 100 parts of Vinyl monomer, 1 part of catalyst persulfate & 1.5 parts of a detergent emulsifier. This is fed to a pressure reactor, either continuous or batch operating at 50 ^{0}c for period as long as 72 hours. The micellular polymer particles can be further stabilized by addition of more emulsifying agent & solid as vinyl latex. For solid polymer, mixture is either acid coagulated & dried or spray – dried directly.

<table>
<tr>
<td>3-f</td>
<td>
<table>
<tr><td></td><td>Thermo softening plastic</td><td>Thermosetting plastic</td></tr>
<tr><td>Formation</td><td>Formed by addition polymerization</td><td>Formed by condensation polymerization</td></tr>
<tr><td>structure</td><td>Linear long chain polymers with limited cross links</td><td>Three dimensional network structure joined by strong covalent bonds</td></tr>
<tr><td>Molecular weight</td><td>Polymers of small molecular weight</td><td>Polymers of large molecular weight.</td></tr>
<tr><td>Heating effect</td><td>Softened on heating & hence can be reused & reshaped</td><td>Do not softened on heating,hence cannot be used & reshaped.</td></tr>
</table>
</td>
<td>1 marks for each point</td>
<td>4</td>
</tr>
<tr>
<td>4-a</td>
<td>Polystyrene

Process description-

Polystyrene production is carried out by free radical initiation or by coordinated catalyst.Bulk suspension and emulsion polymerizations are in use.

In emulsion polymerization initiators are per-sulphates and emulsifiers are soap. Polymerisation is accomplished 3-5 m^3 enamelled reactors fitted with water jacket stirrer and reflux condenser.</td>
<td>4</td>
<td>4</td>
</tr>
</table>

	The monomer is Suspended in aqueous phase using a stabilizer, sodium sulphate is added to control pH A thorough agitation keeps the monomer suspended in medium.The aquous phase emulsified and mixed with monomer. The emulsion is sent into reactor which is kept & heated at60 ^{0}c. The polymerization is carried out in nitrogen atm. Catalyst is added into the reactor.The reaction takes placefor 3-6 hrs,after which sent into coagulator. The polymer formed the latex is separated by centrifugation. The polymer is washed & sent to drier.		
4-b	**Pigments** - It is a finely divided solid which form a paint when added to drying oils. Application 1. Pigments are used to give aesthetic appearance. 2. It is used to give a abrasion resistance,.	2 2	4
4-c	**Industrial spirit** By adding certain specified substances in alcohol, spirit is obtained. It has been rendered unfit for drinking. These spirits are denatured by adding wood naphtha only The substances added give the spirit an exceedingly disagreeable taste. This form of methylated spirit is mainly used for burning purposes.	4	4
4-d	**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 between140^{0}C-180^{o}C. From the second inlet ,pure hydrogen gas are well mixed with the oil. In the	4	4

	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.		
4-e	**Manufacturing of detergents**. Molten sodium is added slowly to coconut oil in an aliphatic solvent plus esterifying alcohol such as amyl alcohol. After certain time reaction is completed. The batch is pumped into a water tank where mixture settles into three layers, the top is the high molecular weight alcohols, the intermediate layer contains regenerated reducing alcohol, and the bottoms have caustic soda and glycerin for recovery. Lauryl alcohol is reacted with sulfuric acid to get sulfated fatty alcohol.	4	4
4-f	**Uses of polyester** • Textile • Fishing nets • Filter cloths • Conveyor belt	1 mark each	4
5-a	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.	4	8

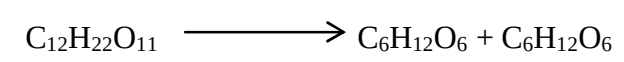
2. Yeast :

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.

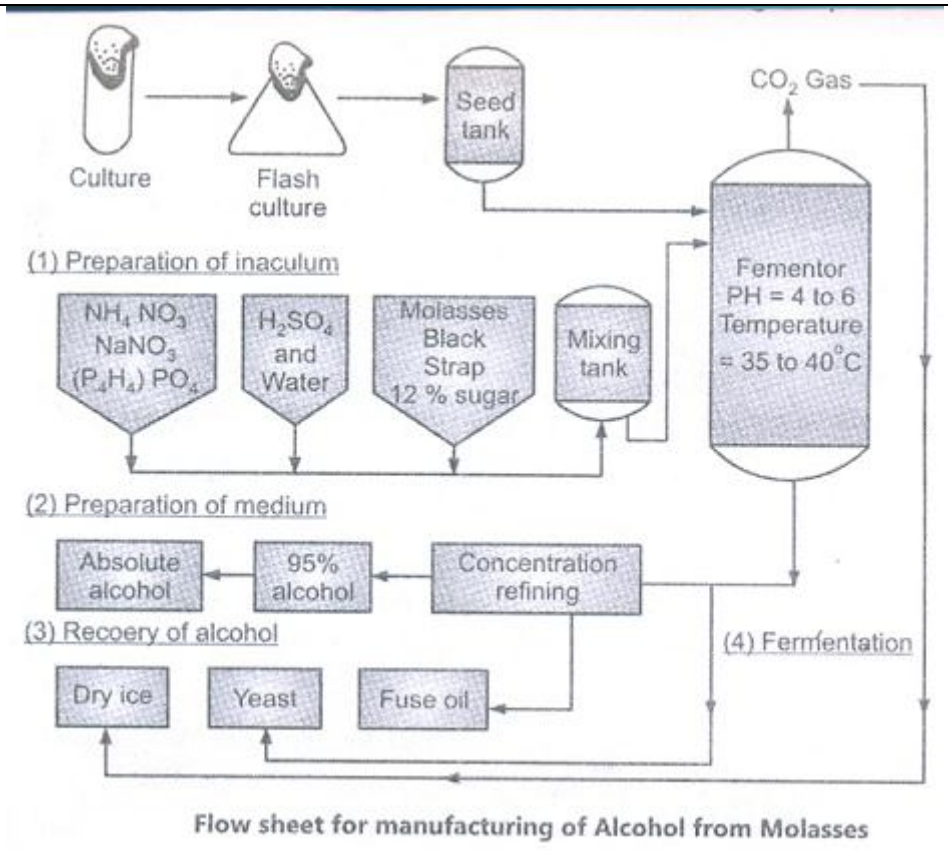


Sucrose Glucose Fructose

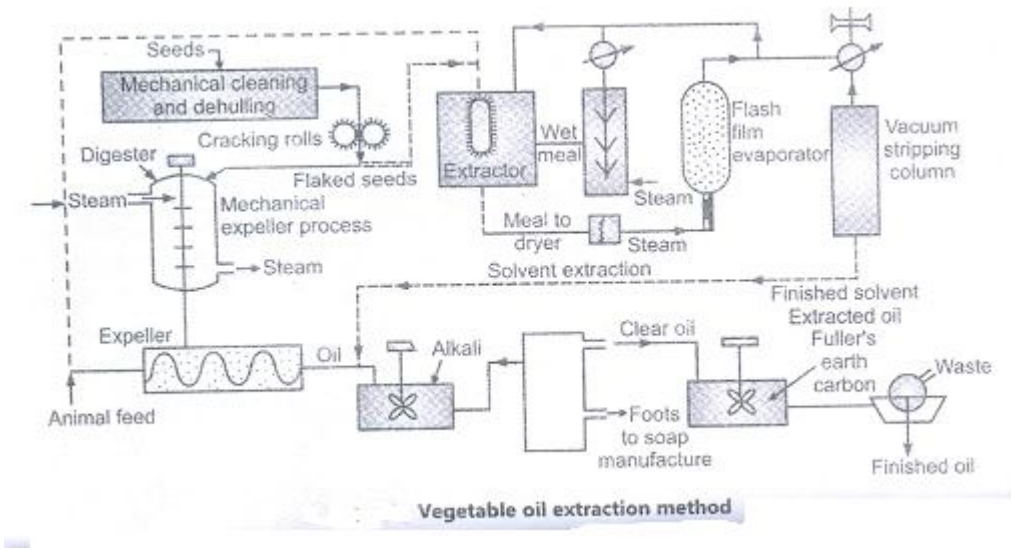
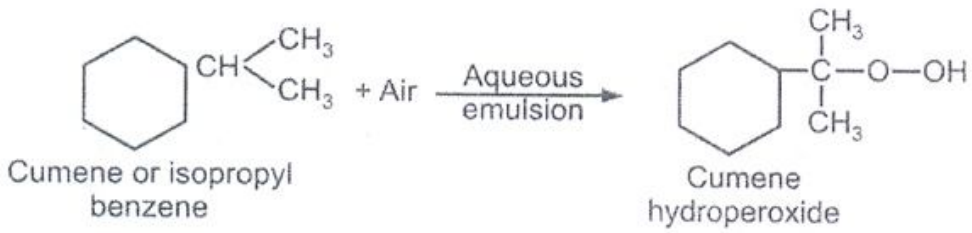
Glucose or Fructose Ethanol

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.

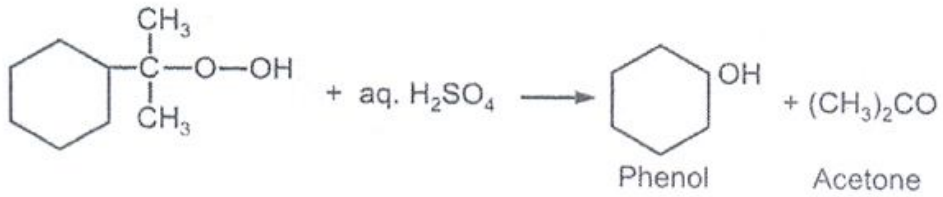
To prepare absolute ethanol, the 5% water is removed by forming a azeotropic mixture of benzene, water and ethanol which is then distilled with increasing temperature.

	 Flow sheet for manufacturing of Alcohol from Molasses	4	
5-b	**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 ^oF. 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	4	8

	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 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. **Refining** : The colour and flavor to fats of edible and non-edible oils is mainly due to presence of non-glyceride components. Free fatty acids, waves, coloured bodies, mucilaginous materials, gossypol compounds (found only in cottonseed oil) and phosphatides are responsible for the undesirable properties of fat or oil used for edible purposes and industrial applications. Most of those compounds are removed by treatment with aqueous solution of caustic soda at 40^{o} -85^{o}C . It reduces fatty acid contents to 0.01%. This process of refining is carried out in a tank called batch. The aquous emulsion of soaps formed from fatty acids along with the other impurities (soap-stock) settles to the bottom and is taken out. Then refined oil is washed with water to remove traces of alkali and soap stock. Oils which are refined with soda ash or ammonia generally require a treatment with caustic soda. After water-washing., the oil is dried by heating in a vaccum or by filtering through dry filter and material. This refined oil is used for industrial purposes or may be processed further to achieve food value.		

	 Vegetable oil extraction method	4	
5-c	**Raw materials** : i) Cumene ii) Air iii) Small quantities of sulfuric acid and emulsifying agents. **Chemical reactions :** **(a) Peroxidation :** 	4	8

(b) Hydrolysis :

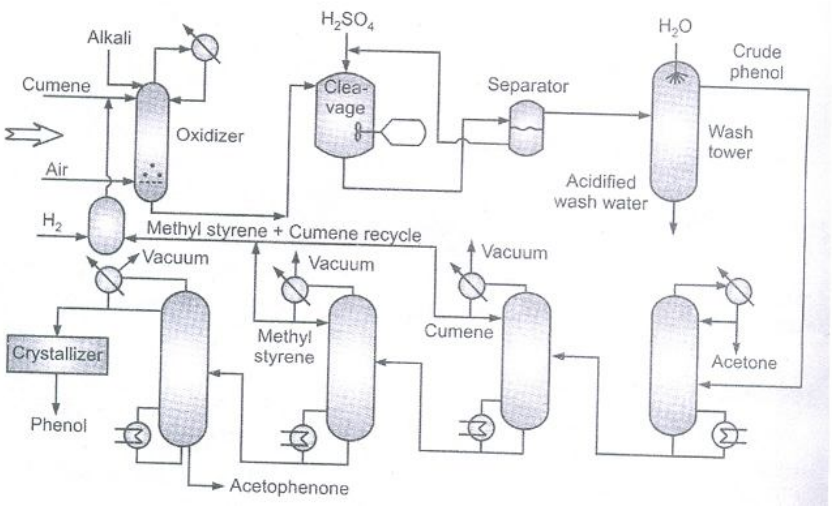


(c) Process description :

Cumene (isoproly benzene) made by alkylation of benzene with propylene is mixed with recycle Cumene (1:4 ratio) and sent to the hydrogenerator,. Unsaturated and a-methyl styrene are converted to saturated materials to avoid undersirable decomposition of the perioxide during the oxidation step. Hydrogen over nickel catalyst at 100^{o}C in a bath reactor is the usual process 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 hydrocarbons.

The Cumene peroxide thus formed is cleaved in an acidifier containing 10-25% H_2SO_4 .This is an agitated vessel at 55-65^{o}C. 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, and 1.2% a-methyl styrene and acetophenone. This mixture is separated in a series of four distillation steps, the last three of which are under vacuum. Phenol in the overhead of the last vacuum fractionator is purified by crystallization

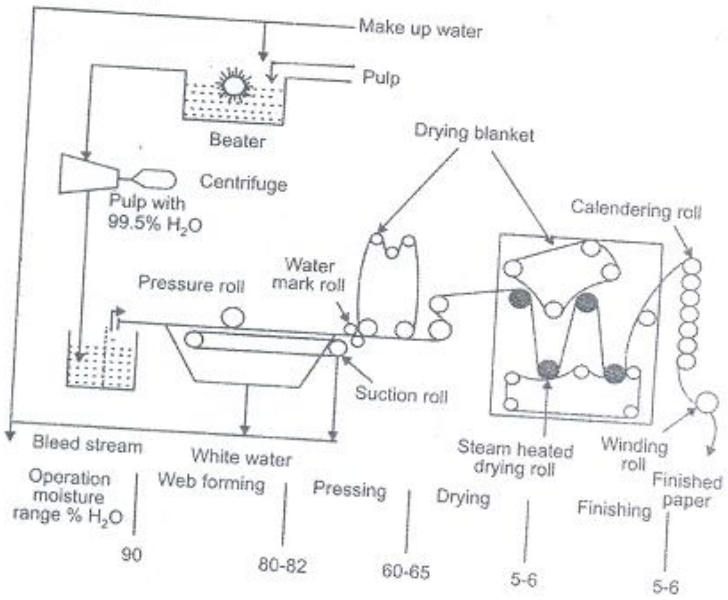
		4	
6-a	**FORMATION OF PAPER** Conversion of fibre suspension into paper sheet incorporates three principal steps. i) **Forming wet-web** : A wet sheet is formed by running 99.5% water-fibre slurry evenly into a moving endless belt of wire cloth at speed of 50 m/min for a fine paper to 500 m/min for newsprint. Water drain by gravity , apart is next removed by a pressure roll and then by suction roll. The screen also has a side wise shaking motion to give better interlocking of fibre on the mat. The water collected in this section of machine is called white water and is reused to obtain maximum recovery of fibre. ii) **Pressing the wet sheet** : The wet paper wheet containing about 80% water is fed via felt roll to the press section where water is removed by mild pressure to reduce content to 60-65% water. Bond or water mark, if needed is	4	8

formed on sheet during pressing.

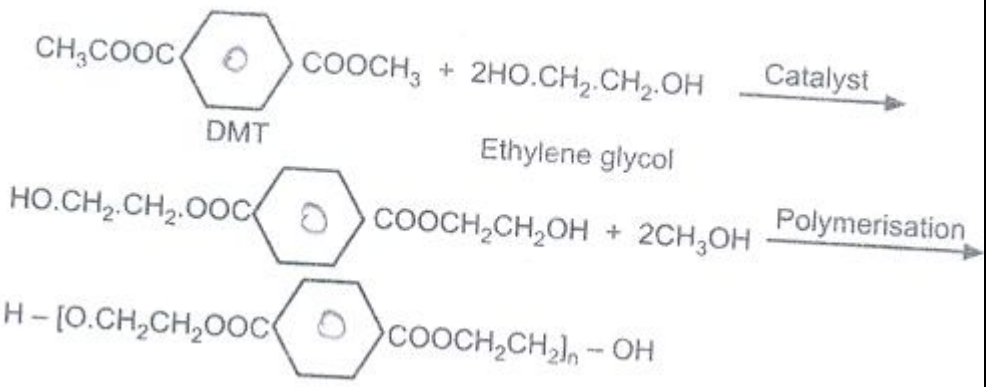
iii) **Drying of sheet** :

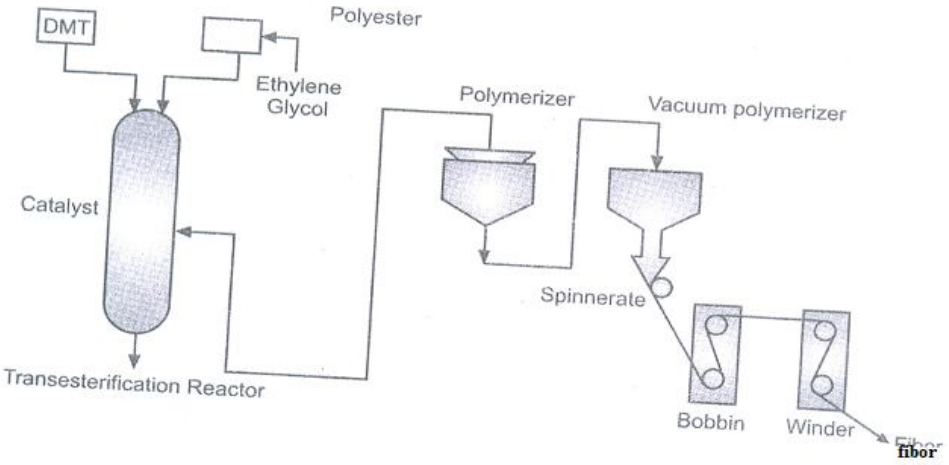
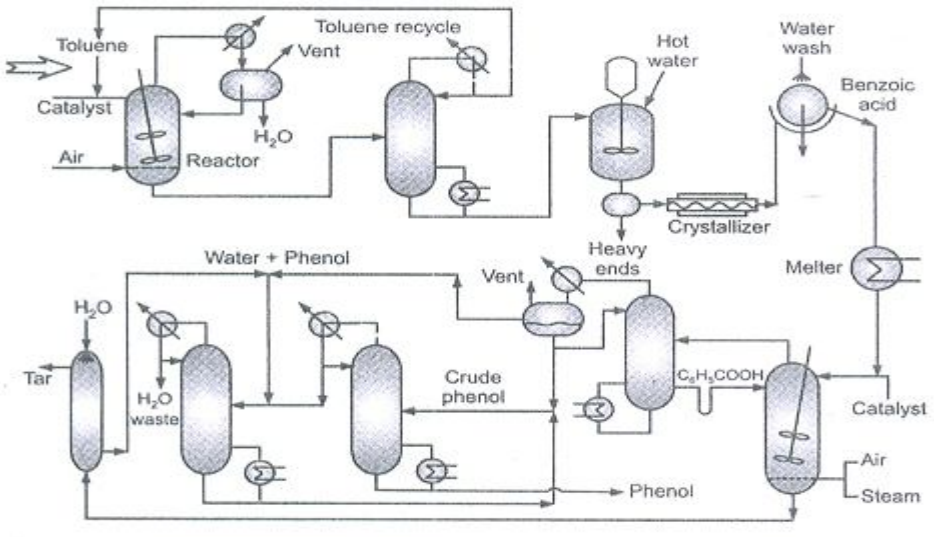
The sheet from the press section has sufficient strength to carry its own weight as it passed through smoothing rolls, then a series of steam heated metal cylinders where heat and moisture are transferred to a felting or canvas belt running on top of the paper. As the sheet leaves the east drying roll with 5-6% water, it passes through final series of pressure or calendaring rolls to produce a smooth well-finished paper. It is wound on large roll and transferred to finishing department where it may be cut, coated and packaged.

Flow Sheet :

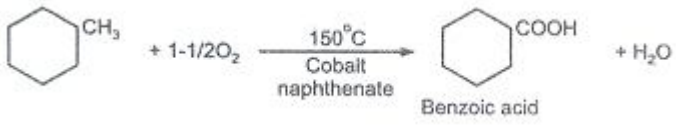


4

6-b	**RAW MATERIALS** (1) Dimethyl terephthalate. (2) Ethylene glycol. (3) Catalyst : Litharge or zinc salt, calcium , magnesium or alkali salt, etc. **REACTIONS :**  **PROCESS DESCRIPTION** : In production of polyester, one mole of DMT and two moles of ethylene glycol 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 0.0005 to 0.1%. The reaction start at 150^{o}C to 160^{o}C and methyl alcohol is distilled out until the reaction is complete. At the end of reaction, the temperature will raise up to 230 ^{o}C . The reaction product is a mixture of glycol terephithalate 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 ghlycol. Then the polymer is converted to fibre by spannerate and is converted to finished roll by using bobbin and winder.	4	8

		4	
6-c	**RAW MATERIALS** (1) toluene (2) Air (3) Small quantities of cobalt naphthenate and cupric benzoate catalyst.. **FLOW SHEET :**  Flow sheet for manufacturing of Phenol from Toluene oxidation **Chemical reaction :**	4	8

(a) Oxidation to benzoic acid :



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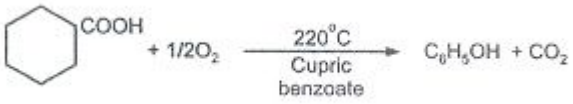
(b) Oxidation of benzoic acid to phenol :



PROCESS DESCRIPTION :

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 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 conventration, to the second stage oxidation tower.		