



**NATIONAL OPEN UNIVERSITY OF NIGERIA**

**DEPARTMENT OF PURE AND APPLIED SCIENCE  
FACULTY OF SCIENCES**

**COURSE CODE: CHM415**

**COURSE TITLE: INDUSTRIAL CHEMICAL TECHNOLOGY II**

**CHM415**  
**INDUSTRIAL CHEMICAL TECHNOLOGY II**

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## **INTRODUCTION**

Industrial chemistry deals with the chemical unit operation and process in manufacturing industry. Chemical process technology has a variety of branches that tilted to development. Processes such as distillation, heat transfer, fluid flow, mass transfer etc, In the stage of product and process development several discipline were integrated including kinetics and catalysis, reactor technology, unit operation, process technology, process control etc. The chemical industry involves creation of wealth/value adding by converting raw materials like salt, oil and limestone to consumable products. Manufacturing of soap, wine, glass etc, originally practiced in small scale unit has now blossomed into large scale because of continuous process mentioned above in chemical and other physical processing of industrial chemicals, raw materials, feedstock, food and biological products, simple flow diagram may suffice.

### **Raw Material**

**Fig 1: Flow diagram for a simple chemical process**

### **COURSE DESCRIPTION**

Industrial chemical technology 11 is a two (2) credit hours course with introductory industrial chemical technology 1 as a prerequisite. It is a course that integrates the discipline of chemical engineers; chemists, biologist and physicists. The course deals mainly with the transfer and change of materials mainly by physical or chemical means or with a combination of the two. The course will lead the student into developing a vision on chemical processes at micro scale level biology, chemistry, physics), the meso scale (reactor, separation units), and the macro scale (the process). Processes involved in conversion of raw materials to finished product are involved, key processes involved in biomass conversion, alternative feedstock, fine chemicals and biotechnological processes, simple chemical process to bulk chemical production including chemical routes and flow diagrams and environmental pollution are covered. Students who have participated in students industrial work experience scheme (SIWES) must have carried out or have come in contact with some techniques and processes without knowing it. This course will definitely fill such gap.

### **WHAT YOU WILL LEARN IN THIS COURSE**

The course will expose the students to inorganic and organic chemical synthesis and you will learn the synthetic process of converting raw materials to finished products. Technical and economic principles governing the process, chemical process, equations, flow diagrams, formulas, side products and environmental pollution will be explained vividly.

### **COURSE AIMS.**

The course aims to explain the basic chemical processes and principles enumerated in introductory industrial chemical process 1 and further into diverse parts of chemical industry, scale of operation and characteristics. In addition, students will learn modern production techniques and different industrial organic materials, principles behind each and every process and product routes

### **COURSE OBJECTIVES**

At the end of the course, the student should be able to:

- Understand synthesis and water gas generation by reaction of hydrogen and carbon monoxide
- Hydrogen, sources, properties and applications, different raw materials and industrial production of organic material from local sources

- Different conversion routes of raw materials to finished products.
- Principles governing processes, product routes and flow diagrams
- Production methods of some elected products such as fats and oils, detergents, sugar, cement, ceramics, wood, paper and pulp etc.

### **GOING THROUGH THE COURSE**

The course is in three modules which are subdivided into 8 units. The students are expected to carry out detailed study of each unit, participate in tutorial classes and be involved in group discussion with fellow students.

### **COURSE MATERIALS**

The following materials will be made available to the student:

1. Course guide
2. Study units

### **STUDY UNITS**

The three course modules and 8 study units contained in this course are shown below:

#### **Module 1**

- Unit 1 Hydrogen and carbon monoxide – synthesis gas, oxo process  
Unit 2 Water gas, sources of hydrogen and its application

#### **Module 2**

- Unit 1 Industrial organic materials and raw materials  
Unit 2 Technical and economic principles of processes and products routes, flow diagrams

#### **Module 3**

- Unit 1 Selected oil and fats  
Unit 2 Soaps and detergents, sugar, varnishes, glass, cement and ceramics  
Unit 3 Plastics, wood pulp and paper  
Unit 4 Environmental pollution

Having understanding of production techniques, its properties, sources and reactions is fundamental to the knowledge of processes involved in production of products (eg ammonia, urea) using available feedstock.



In module 1, the reactions of hydrogen and carbon monoxide forming synthesis gas and in production of other products will be explored

Reactions of hydrogen and carbon monoxide to form synthesis gas normally utilized as fuel gas which is closely followed by water gas is elucidated. Their uses in industrial synthesis of organic chemicals glass making and in other high temperature reactions are explained. Hydro formylation, known as oxo synthesis or oxoprocess used for the production of aldehydes from alkenes are well treated.

In Module 2, Industrial organic chemicals such as solvent mostly derived from petroleum (oil) or natural gas will be explained. The student will be taught that crude oil and natural gas are the primary raw materials for the production of most bulk organic chemicals. Conversion of raw materials to base chemicals is the first stage, followed by intermediates before final products in the structure of chemical industry. Raw materials can be divided into inorganic and organic materials. Inorganic raw materials include water, air and minerals. Oil, coal, natural gas, fossils and biomass are termed organic raw materials. Several intermediates can be produced from base chemicals. The use of flow diagrams to depict direction of reactions, starting with reactants to product; it is used to represent dynamic relationship in a system and can be synonymous with flow chart; many examples will be encountered in the course of this lecture.

Module 3 explains the basic production techniques and chemical processes involved in the manufacture of selected oils and fats, soaps and detergents, sugar, ceramics, glass, cement, varnishes, plastics, wood pulp and paper, their starting raw materials (feedstock), reaction intermediates and final products are well explained. Processes, techniques and reaction equations (where applicable) are also well treated. The viability of product manufacturing process is dependent on the raw material availability and type, classes of products to be produced, reaction equation and steps of production processes are well covered, product properties and uses are also included

### **TEXT BOOKS AND REFERENCES**

There are numerous books, monographs, encyclopedia and other materials that treat industrial chemical technology processes. Some are general while some are specific. Online materials

can be consulted for useful information but the learners are advised to apply caution in surfing internet. The following books are recommended:

1. Mouljn JA, Makkee M, Diepen AEV (2013) Chemical Process Technology. 2<sup>nd</sup> edition, Wiley Publishers UK
2. Alan H (1996) An introductory to industrial chemistry, 3<sup>rd</sup> edition. Blackie Publishers, London
3. Ababio OY (2013) New school chemistry for senior secondary schools. 6<sup>th</sup> edition. African Publishers Onitsha, Nigeria
4. Douglas J. M (1988) Conceptual design of chemical processes McGraw- Hill, New York.
5. Kirk Othmer Encyclopedia of Chemical Technology (1999-2011), online edition. John Wiley and Sons Hoboken Doi: 10.1002/0471238961.
6. Geankoplis C.J (1993) Transport processes and unit operations 3<sup>rd</sup> edition, Prentice Hall International Edition 408-412

## **ASSESSMENT**

There are two aspects to this course:

The tutor-marked assignment (TMA) and end of course examination

The TMAs shall constitute the continuous assessment component of the course. The tutor will mark them and they will account for 30% of the entire score. Each student will be expected to participate in four TMAs before the end of course examination. The course end examination will constitute 70% of the total course score.

## **SUMMARY**

CHM 415: Industrial chemistry technology II introduces hydrogen and monoxide as precursors of synthesis and water gas and their utilization as fuel gas. This explains Industrial organic materials, raw materials, production methods involved in the production of oils and fats, soaps and detergents, sugar, cement, ceramics varnishes, plastics, wood pulp and paper are well explained. Technological and economic principles of cost, energy input cost, royalty/license payments, including labour and depreciation are also treated. Uses of flow diagrams (flow chart) to depict reaction direction were covered.

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## MODULE 1

UNIT 1	Hydrogen and Carbon monoxide Synthesis Gas, Oxo-process
UNIT 2	Water Gas, Sources of Hydrogen its Application

## **UNIT 1      HYDROGEN AND CARBON MONOXIDE SYNTHESIS GAS, OXO- PROCESS**

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### **1.0 INTRODUCTION**

Synthesis gas (or syngas) is a general term used to designate mixtures of hydrogen and carbon monoxide in various ratios. These mixtures are used as such and are also sources of pure hydrogen and pure carbon monoxide. Various mixtures include the following: H<sub>2</sub> only,

3H<sub>2</sub>: 1 N<sub>2</sub>, 2H<sub>2</sub>: 1 CO, H<sub>2</sub>: CO and CO only. From the examples, it can be noted that the term “syngas” is used more generally than stated above: the N<sub>2</sub>/H<sub>2</sub> mixture for the production of ammonia is also referred to as syngas.

Syngas may be produced from a variety of raw materials ranging from natural gas to coal. The choice for a particular raw material depends on the cost and availability of the feed stock, and on the downstream use of the syngas. Syngas is generally produced by one of three processes, which are distinguished based on the feedstock used.

1. Steam reforming of natural gas or light hydrocarbons, optionally in the presence of oxygen or carbon dioxide.
2. Partial oxidation of (heavy) hydrocarbons with steam and oxygen.
3. Partial oxidation of coal (gasification) with steam and oxygen.

The name of the processes may be somewhat confusing. The term steam reforming is used to describe the reaction of hydrocarbons with steam in the presence of catalyst. In the gas industry, reforming is commonly used for conversion of hydrocarbon by reacting it with oxygen containing molecules, usually H<sub>2</sub>O, CO<sub>2</sub>, and/or oxygen. A combination of steam reforming and partial oxidation in which endothermic and exothermic reactions are coupled, is often referred to as auto-thermal reforming. Partial oxidation also called steam/oxygen reforming is the non-catalytic reaction of hydrocarbons with oxygen and usually also steam. This process may be carried out in an auto-thermal or allothermal way. If catalyst is involved, the process is often referred to as Catalytic partial oxidation of coal or petroleum coke (Petcoke).

## 2.0 OBJECTIVES

At the end of the unit, students should be able to;

1. Explain hydrogen and carbon monoxide.
2. Describe synthesis gas and oxo-process.
3. Understand different sources of synthesis gas.
4. Discuss thermodynamic reactions in the production of synthesis gas.
5. Explain different processes for hydroformylation of propene and other alkenes.

## 3.0 MAIN CONTENT

### 3.1 HYDROGEN

Hydrogen is a chemical element with symbol H and atomic number 1. With a standard atomic weight of 1.008, hydrogen is the lightest element on the periodic table. Its monoatomic form (H) is the most abundant chemical substance in the universe constituting roughly 75 % of baryonic matter (Protons and Neutrons). At standard temperature and pressure, hydrogen is a colourless, odourless, tasteless, non-toxic, non-metallic, highly combustible diatomic gas with molecular formula  $H_2$ . Since hydrogen readily forms covalent compounds with most non-metallic elements, most of the hydrogen on earth exists in molecular forms such as water or organic compounds. Hydrogen plays a particularly important role in acid-base reactions because most acid-base reactions involve the exchange of protons between soluble molecules. In ionic compounds, hydrogen can take the form of negative charge (i.e. anion) when it is known as a hydride, or as a positively charged (cation) species denoted by the symbol  $H^+$ .

### 3.2 CARBON MONOXIDE

Carbon Monoxide (CO) is colourless, odourless and tasteless gas that is slightly less dense than air. It is toxic to haemoglobin animals (both invertebrate and vertebrate, including humans) when encountered in concentrations above 35ppm, although it is also produced in normal animal metabolism in low quantities and is thought to have some normal biological functions. In the atmosphere, it is spatially variable and short lived, having a role in the formation of ground-level ozone. Carbon monoxide consists of one carbon atom and one oxygen atom, connected by a triple bond that consists of two covalent bonds as well as one dative covalent bond. It is the simplest oxocarbon and is isoelectric with the cyanide anion, the nitrosomium cation and molecular nitrogen. In coordination complexes the carbon monoxide ligand is called carbonyl.

### 3.3 SYNTHESIS GAS

Most syngas today is produced by steam reforming of natural gas or light hydrocarbons. For light feedstocks, partial oxidation is usually not an economic option, because of the high investment costs as a result of the required cryogenic air separation. Partial oxidation processes, however are employed where feeds suitable for steam reforming are not available or in special situations where local conditions exist to provide favourable economies. Coal gasification is an important source of chemicals via syngas production in countries with abundant coal resources.

The general flow scheme of the main processes for syngas production is shown in Fig 2:

## Fig 2: General Process Flow Diagram for the Production of Syngas

Processes for the production of syngas based on coal and heavy oil fractions require removal of sulphur compounds mainly H<sub>2</sub>S from the syngas. Feed purification is not possible with these raw materials, although attempts have been made using biotechnological approaches.

Depending on its production process and its downstream use, the raw syngas may be treated in several ways. Syngas conditioning includes such processing steps as the water-gas shift reaction, carbon dioxide removal, methanation and so on to achieve the right composition.

### 3.4 SYNTHESIS GAS FROM NATURAL GAS

Reactions and Thermodynamics

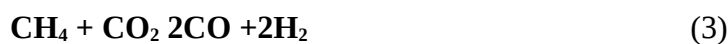
Although natural gas does not solely consist of methane, for simplicity it is assumed this is the case. When converting methane in the presence of steam the most important reactions are the steam reforming reaction.



and the water-gas shift reaction



Some processes, such as the reduction of iron ore and the hydroformylation reaction require syngas with a high carbon monoxide content which might be produced from methane and carbon dioxide in a reaction known as CO<sub>2</sub> reforming



Reaction (3) is also referred to as “dry reforming” obviously because of the absence of steam. The main reactions may be accompanied by coke formation, which leads to deactivation of the catalyst. Coke may be formed by decomposition of methane.



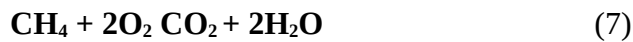
Or by disproportionation of carbon monoxide through a reaction known as Boudouard reaction



In the presence of oxygen, methane undergoes partial oxidation to produce carbon monoxide and hydrogen.



Side reactions such as the complete oxidation of methane to carbon dioxide and H<sub>2</sub>O



And the oxidation of the former carbon monoxide and hydrogen may also occur.



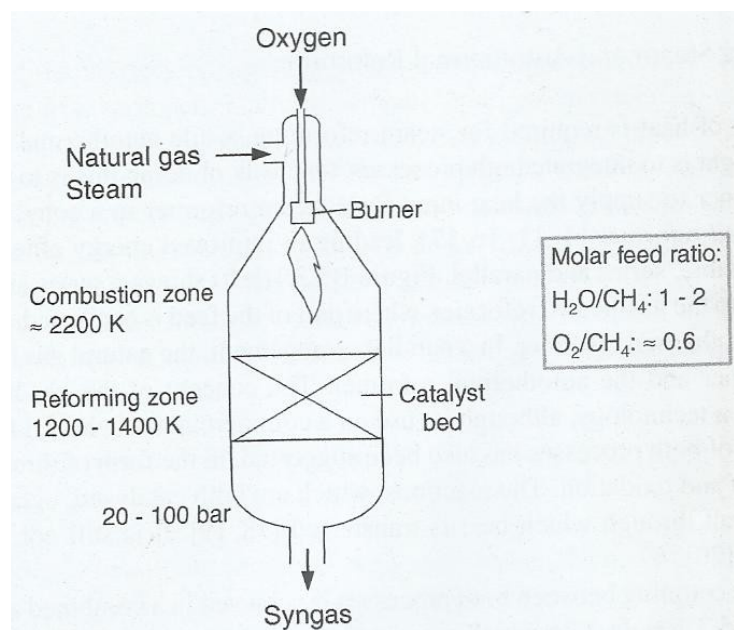
The reaction of methane with steam, reaction (1) is highly endothermic while the reactions with oxygen reaction (6 and 7) are moderately to extremely exothermic. Operation can hence be allothermal (steam and little or no oxygen added, required heat generated outside the reactor) depending on steam/oxygen ratio. The hydrogen and carbon monoxide contents of the equilibrium gas increase with temperature which is explained by the fact that the reforming reactions (1) and (3) are endothermic. The carbon dioxide content goes through a maximum. This can be explained as follows: carbon dioxide is formed in exothermic reactions only, while it is a reactant in the endothermic reactions. Hence, at low temperature, carbon dioxide is formed, while with increasing temperature the endothermic reactions in which carbon dioxide is converted (reaction 3) becomes more important. Both steam reforming and partial oxidation of methane are hindered at elevated pressure because the number of molecules increases due to these reactions.

### 3.5 STEAM REFORMING PROCESS

Even though steam reforming is carried out at high temperature (>1000 K), a catalyst is still required to accelerate the reaction. The reason for this is the very high stability of methane. The catalyst is contained in tubes which are placed inside a furnace that is heated by combustion of fuel. The steam reformer (Fig 3) consists of two sections. In the convection







**Fig.4: Schematic of an autothermal reformer for production of Syngas.**

The reactor is a refractory-lined pressure vessel. Therefore, higher pressures and temperatures can be applied than in steam reforming. Part of the feed is oxidized in the combustion zone (reactions 6 and 7). In the lower part, the remaining feed is catalytically reformed with

the produced carbon dioxide and  $H_2O$  (reactions 1 and 3). The endothermic reforming reaction duty is provided by the exothermic oxidation reaction.

Autothermal reforming of natural gas and light hydrocarbons is usually not applied on its own because of the high investment and operational costs. These are, for a large part, attributed to the cryogenic air separation plant needed for the production of oxygen. An autothermal reformer is frequently used, however, in the production of syngas for ammonia manufacture. In that case, this so-called secondary reformer is installed downstream of the steam reformer and air is used instead of oxygen. The advantage of this arrangement is that unreacted methane from the steam reformer is converted in the autothermal reformer, so that the steam reformer can be operated at lower temperature and higher pressure. These conditions are thermodynamically unfavourable. However, a high outlet pressure is advantageous because it decreases the costs for compression of the syngas to the pressure of the ammonia synthesis loop. Since air supplies the required nitrogen, no expensive oxygen plant is needed in this special case.

### 3.7 COAL GASIFICATION

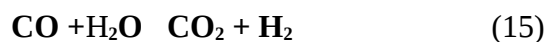
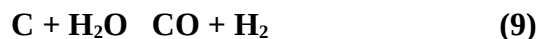
Gasification of coal to produce syngas (or coal gas or town gas) dates back to the end of the 18<sup>th</sup> Century. During the mid 1800s, coal gas was widely used for heating and lighting in urban areas. The development of large-scale processes began in the late 1930s and the process was gradually improved. Following World War II, however, interest in coal gasification dwindled because of the increasing availability of inexpensive oil and natural

gas. In 1973, when oil and gas prices increased sharply, interest in coal gasification was renewed and especially in the last 10 – 15 years, much effort has been put in improving this process. The main reason for this interest is the dramatic increase in oil and gas prices, which seem to be a continuing trend, together with the wide availability of coal compared to oil and natural gas.

Although coal gasification, like steam reforming of natural gas, produce, syngas, the incentive of the two processes is different. The goal of steam reforming is the production of carbon monoxide and hydrogen for chemical use, whereas coal gasification was primarily developed for the conversion of coal into a gas which happens to predominantly contain carbon monoxide and hydrogen.

### 3.8 GASIFICATION REACTIONS AND THERMODYNAMICS

In a broad sense, coal gasification is the conversion of the solid material (coal) into gas. The basic reactions are very similar to those that took place during the steam reforming. They are as follows:



Reactions (9) and (10) with carbon are endothermic whereas reactions (11), (12) and (13) are exothermic. Reactions (9 – 12) are heterogeneous reactions. It is a common practice to perform coal gasification in a autothermal way. The reaction is carried out with a mixture of O<sub>2</sub> (or air) and H<sub>2</sub>O so that combustion of part of the coal produces the heat needed for heating up to reaction temperature and for the endothermic steam gasification reaction. Besides these heterogeneous reactions, homogenous reactions occur. Reactions (14) and (15) are homogenous.

It will be clear that the structure of coal and its products is very complex. For convenience, in thermodynamic calculations, we assume that coal solely consists of carbon. Furthermore, under practical gasification conditions, it is usually assume that only the following species are present in the gas phase: H<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>. Of course, other hydrocarbons are also

present, but their concentrations are relatively small and in the thermodynamic calculations these are all represented by  $\text{CH}_4$ . With increasing temperature, the  $\text{CO}$  and  $\text{H}_2$  mole fraction increases due to increasing importance of the endothermic gasification reaction. Accordingly  $\text{H}_2\text{O}$  decreases with temperature. Both  $\text{CO}_2$  and  $\text{CH}_4$  go through a maximum as a result of the exothermicity of their formation and the endothermicity of their conversion. Hence, low pressure is favourable for  $\text{CO}$  and  $\text{H}_2$  forming reactions due to the increase in number of molecules. The  $\text{CO}_2$  and  $\text{CH}_4$  maxima shift to higher temperature with increasing pressure.

### 3.9 GASIFICATION TECHNOLOGIES

Three basic different reactor technologies are used for coal gasification namely: moving bed, fluidized bed and entrained flow gasifiers.

#### 3.10 MOVING BED GASIFIER

The Lurgi (now Sasol-Lurgi) moving bed gasifier is operated countercurrently; the coal enters the gasifier at the top and is slowly heated and dried (partial pyrolysis) on its way down while cooling the product gas as it exits the reactor. Fig. 5 shows the Schematic of a moving bed gasifier also known as Sasol-Lurgi moving bed gasifier.

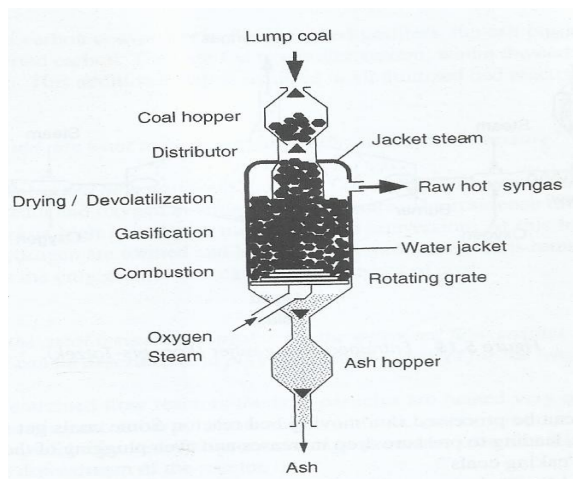


Fig. 5: Moving bed gasifier (Lurgi) (Higman and Burgt, 2007)

The coal is further heated and devolatilized as it descends. In the gasification zone, part of the coal is gasified into steam and carbon dioxide, which is formed in the combustion zone upon burning of the remaining part of the coal.

The highest temperatures (1300k) are reached in the combustion zone near the bottom of the reactor. All that remains of the original coal is ash. For most coals, 1300k is below the slagging temperature (the temperature at which the mineral matter becomes sticky or even

melts) of the ash, so the ash leaving the reaction zone is dry. The coal bed is supported on a rotating grate where the ash is cooled by releasing heat in the entering steam and oxygen. In this type of reactor, the temperature has to be kept low in order to protect the internals of the reactor. The consequence is that a rather large excess of steam has to be fed to the gasifier, which reduces the efficiency. A disadvantage of the moving bed reactor is that large amounts of by-products are formed, such as condensable hydrocarbons, phenols, ammonia tars, oils, naphtha, and dust. Therefore, gas cleaning for the Lurgi gasification process is much more elaborate than for the other gasification processes. On the other hand, the counter-current operation makes the process highly energy efficient.

Not all types of coal can be processed in the moving bed reactor. Some coals get sticky upon heating and form large agglomerates, leading to pressure drop increases, and even plugging of the reactor. Coals showing this behaviour are called caking coals.

### 3.11 FLUIDIZED BED GASIFIER

The Winkler fluidized bed gasifier (Fig. 6) is a back-mixed reactor in which coal particles in the feed are well mixed with coal particles already undergoing gasification. The intensive mixing results in excellent mass and heat transfer. This gasifier operates at atmospheric pressure and moderate uniform temperature.

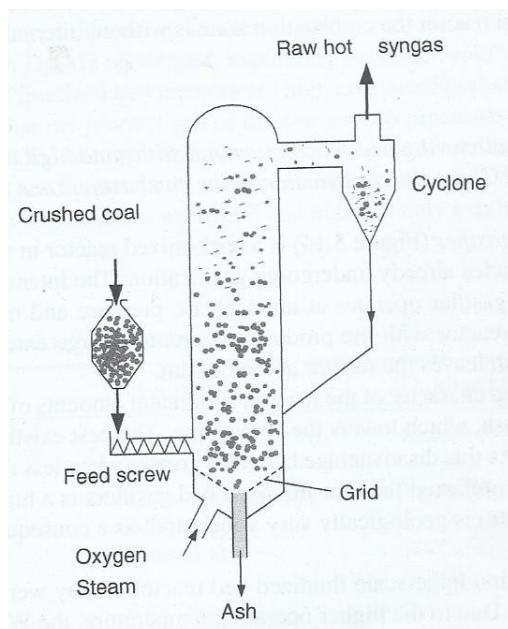


Figure 6: Fluidized bed gasifier (Winkler, high temperature) (Cornils, 1987)

Char particles that leave the reactor with the product gas are, to a large extent, recovered in cyclones and recycled to the reactor. Dry ash leaves the reactor at the bottom. As a result of

the back-mixed character of the reactor, significant amounts of unreacted carbon are removed with the product gas and the ash, which lowers the conversion. The best existing fluidized bed reactors offer a carbon conversion of 97%. As this disadvantage becomes greater when less reactive coal or coal with a low ash melting is used, the preferred feed for fluidized bed gasifiers is a highly reactive coal. Brown coal (often referred to as lignite) is geologically very young and, as a consequence, is highly functionalized, and therefore very reactive. Due to high operating temperature, the Winkler gasifier produces much lower quantities of impurities than the Lurgi gasifier. Because of the limited carbon conversion in fluidized bed gasifiers, the ash particles contain a relatively large amount of unconverted carbon. They are fed to a boiler system, where the carbon is burned, providing heat for steam generation. This additional step is required in all fluidized bed reactor system.

### 3.12 ENTRAINED FLOW GASIFIERS

The Koppers-Totzek entrained flow gasifier (Fig. 7) is a plug-flow system in which the coal particles react concurrently with steam and oxygen at atmospheric pressure. The residence time is a few seconds. The temperature is high in order to maximize coal conversion. At this high temperature, mainly carbon monoxide and hydrogen are formed and hardly any by-products. Ash is removed as molten slag. The entrained flow gasifier is the only gasifier that can handle all types of coal.

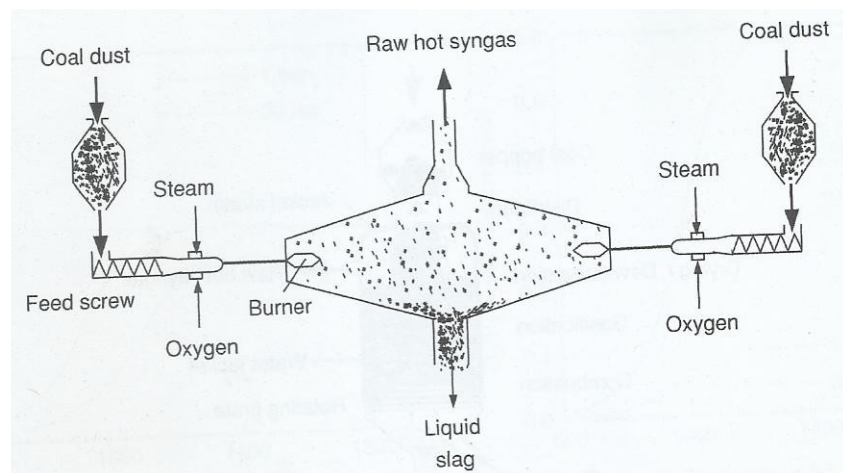


Figure 7: Entrained Flow Gasifier (Koppers-Totzek)

In fluidized bed and entrained flow reactors, the coal particles are heated very quickly. During heating, extensive pyrolysis occurs and when mixing is poor, considerable amounts of volatiles, cokes, and so on will be formed. The process design should be such that it will not lead to lowered efficiency and problems downstream of the reactor.

### 3.13 APPLICATIONS OF SYNGAS

Syngas finds its applications as follows:

1.  $H_2$  is mainly used in refinery, hydrotreating and hydrocracking.
2.  $3H_2:1N_2$  mixture in the production of ammonia.
3.  $2H_2:1CO$  mixture
  - (i) as substitute natural gas (SNG)
  - (ii) in production of alkenes
  - (iii) in production of methanol and higher alcohols
4.  $1H_2:1CO$  mixture for the production of aldehydes
5. CO is mainly used for the production of acids such as formic acids and acetic acids.

### 3.14 APPLICATIONS OF COAL GASIFICATION

When coal is gasified in air/steam mixtures, low calorific gas is produced (lean gas) which is usually used for heating or power generation. Coal-derived syngas is also applied in gas supply systems as Substitute Natural Gas or Synthetic Natural Gas (SNG).

#### **Coal CO/ $H_2$ $CH_4$**

Another important application of coal gasification is as a raw material for the chemical industry and for the production of liquid transportation fuels, for instance in Fisher-Tropsch type reactions.

#### **Coal CO/ $H_2$ hydrocarbons + alcohols**

Coal gasification is used primarily for the production of hydrogen.

#### **Coal CO/ $H_2$ Water – gas shift $H_2$**

Hydrogen can be used in a wide variety of processes applied in oil refining and in the chemical industry. However, about 95% of hydrogen production is based on steam reforming as a result of the much higher investment costs for a coal gasification plant compared to methane steam reforming plant.

### 3.15 OXO-PROCESS

Oxo-process is a homogeneous catalytic process for the production of aldehydes from the alkenes. The process is also known as hydroformylation. It was discovered by Otto Roelen in Germany before World War II in one of the many programs aimed at the use of coal-driven synthesis gas ( $CO/H_2$  mixtures). Roelen discovered that alkenes react with syngas, provided catalyst is present. Formyl, a formyl group or carbonyl group (CHO) and a hydrogen atom

are added to the double bond. Therefore, the reaction has been called hydroformylation or hydrocarbonylation analogous to hydrogenation being the addition of hydrogen. The most important products are in the range  $C_4 - C_{19}$  in the range of about 75% , the most significant is the hydroformylation of propene yielding two isomer

The products of hydroformylation usually are intermediates for the production of alcohols which are commonly known as oxo-alcohols. In most cases the normal aldehyde is the preferred product because it enjoys a much larger market than the branched aldehyde. For instance, normal butanol, produced by the direct hydrogenation of normal butyraldehyde, is used in the production of wide variety of chemical intermediates, while iso-butanol is predominantly used as a solvent. Furthermore, only normal butyraldehyde can be used to produce 2-ethylhexanol, which is the most widely used plasticizer alcohol. The oxo-alcohols in the  $C_{11} - C_{17}$  range are utilized in detergents.

Processes for the hydroformylation of propene are low pressure oxo process and process with a bifunctional catalyst system. Also processes for the hydroformylation of higher alkenes include conventional cobalt based process and low pressure cobalt-based process for the direct production of alcohols.

**Low Pressure Oxo Process:** Hydroformylation of lower alkenes, in particular propene is usually based on rhodium catalysts. By adding the right ligands the selectivity towards linear products is high. The reaction takes place in a continuous stirred tank reactor at much lower pressure than the processes with unmodified cobalt catalyst. The alkene and synthesis gas have to be purified thoroughly because the catalyst is extremely sensitive. This process is often called the low pressure oxo process.

The gaseous reactants are fed to the reactor through a sparger. The reactor contains the catalyst dissolved in product butyraldehyde and by-products. The gaseous reactor effluent passes through the demister, in which fine droplets of catalyst that are contained in the



product gases are removed and fed back to the reactor. The reaction products and unconverted propene are condensed and fed to the gas/liquid separator. Propene, apart from a small purge stream, is recycled to the reactor. The liquid reaction products are freed from residual propene in a stabilizer column and further purified by distillation.

A portion of the catalyst solution passes through a purification cycle for reactivation of inactive rhodium complexes and for removal of heavy ends and ligand decomposition products. The demisting device is an essential part of the reactor plant as it ensures that all rhodium remains in the reactor and in view of the high cost of rhodium, recovery should be as high as possible. In practice, the rhodiums lost in the process are very small.

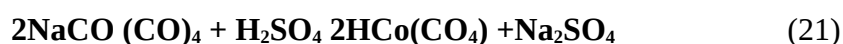
### **3.16 CONVENTIONAL COBALT-BASED PROCESS FOR HYDROFORMYLATION OF HIGHER ALKENES**

The first industrial oxo process was based on an unmodified cobalt catalyst ( $\text{HCo}(\text{CO})_4$ ). This catalyst system requires high pressures and temperature to ensure that stability of the catalyst. Hydroformylation of higher alkenes to produce plasticizer and detergent-range alcohols still uses this type of catalyst.

To minimize catalyst consumption and to avoid problems in downstream processing, it is very important that cobalt is recovered. A process that offers an elegant solution to the problem of catalyst separation is the Kuhlmann (now Exxon Mobil) process. This hydroformylation process is based on the following cobalt cycle.



The sodium salt is soluble in water. This enables recovery of the cobalt catalyst by scrubbing with water. The aqueous solution containing cobalt as the sodium salt is transformed to the active catalyst by reaction with sulphuric acid.



This complex is soluble in alkene, and as a consequence, it can be returned to the reactor dissolved in the reactant alkene flow. In the Kuhlmann hydroformylation process, the alkene with recycled and make up catalyst is fed to the hydroformylation reactor, (usually a stirred tank or a loop reactor) together with the synthesis gas. The crude product, after passing through the flash vessel, in which the gas is separated, is treated in countercurrent flow with

an aqueous sodium carbonate solution. The cobalt complex forms a water-soluble sodium salt. After scrubbing with water in the wash column, a virtually cobalt-free organic phase (crude aldehyde) and an aqueous phase containing sodium salt remain. The crude aldehydes are sent to a distillation section. Here, the excess alkenes are recovered and recycled to the reactor. The sodium salt is transformed to the original cobalt complex,  $\text{HCo}(\text{CO})_4$ , by adding sulphuric acid in the regenerator. This complex is extracted by the alkene feedstock and recycled to the reactor.

### 3.17 HYDROFORMYLATION PROCESSES

The rhodium catalyst is attractive for the conversion of propene to the linear aldehyde. The selectivity may be as high as 95%. The branched product also has a market, although a much smaller one than the linear product and its production is therefore desired in these small quantities. Hydroformylation of higher alkenes with internal double bonds requires isomerization activity and as a consequence, in that case cobalt catalysts are preferred. In all processes except the low-pressure cobalt based process for the direct production of alcohols, aldehydes are the primary products. These can be hydrogenated to alcohols in separate reactor. The modified cobalt catalyst is used for the direct production of alcohols rather than aldehydes because this catalyst, trialkylphosphine-cobalt complex ( $\text{Co/Phosp}$ ) promotes hydrogenation.

## 4.0 CONCLUSION

Hydrogen is the simplest element but versatile in application useful in synthesis gas, water and in other fuel economy. It plays an important role in acid base reactions because the reactions involve exchange of protons between soluble molecules. Carbon monoxide though very toxic to living things (animals and human), plays a role in the formation of ground-level ozone. Synthesis is produced by steam reforming of natural gas or light hydrocarbons

## 5.0 SUMMARY

Synthesis gas is produced from:

- (i) Steam reforming of natural gas;
- (ii) Partial oxidation of hydrocarbons; and
- (iii) Coal gasification.

## 6.0 TUTOR-MARKED QUESTIONS

1. List the processes for production of syngas.
2. Explain with diagram the steam reforming process for production of syngas.
  - i. Explain with diagram the following coal gasification technologies
  - ii. Moving bed gasifier.
  - iii. Fluidized bed gasifier.
  - iv. Entrained flow gasifier.
3. Discuss in detail but concisely what you understand by the term oxoprocess.
4. Explain the following terms
  - i. Allothermal reforming.
  - ii. Autothermal reforming.
5. Explain the thermodynamics in coal gasification reactions.
6. Explain in detail the process for hydroformylation of
  - i. Propene.
  - ii. Higher alkene with internal double bond.

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## **UNIT 2      WATER GAS, SOURCES OF HYDROGEN AND ITS APPLICATION**

### **CONTENT**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
  - 3.1 Water Gas
  - 3.2 Manufacture of Water Gas
  - 3.3 Sources of Hydrogen
  - 3.4 Application of Hydrogen
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Assignment
- 7.0 References/Further Reading

### **1.0 INTRODUCTION**

Fuels are naturally occurring or manufactured combustible organic substances which act as a source of heat or as raw materials for the chemical industry. Because of rapid growth of the organic synthesis industry (e. g. manufacture of plastics, synthetic fibres, synthetic rubber, varnishes, dyes, solvents e. t. c), huge amount of hydrocarbon materials are needed and these are mainly obtained by chemical processing of various fuels.

In the beginning, the principal and main source of raw materials for the synthesis of organic products was coal from which benzene, toluene, xylene, phenol, naphthalene, anthracene, hydrogen, methane; ethylene and many other products were obtained by the process of carbonization. Petroleum always contains dissolved gases which are separated when the petroleum is brought to the surface. These casing-head gases consist of methane, ethane, propane, butane and other hydrocarbons. The casing-head gases are extremely valuable raw materials of the chemical industry. Gases produced in the processing of petroleum are other important sources of hydrocarbon raw materials. Gases which are produced as a result of cracking, pyrolysis and reforming contain saturated (methane, ethane, propane, butane e. t. c) as well as unsaturated hydrocarbons (ethylene, propylene e. t. c). In addition, some aromatic hydrocarbons such as benzene, toluene, xylene and their mixtures may also be formed as a result of processing of petroleum.

All fuels can be classified according to their phase state as solid, liquid or gaseous and according to their origin as natural or synthetic. Coal, wood, shale, and peat are natural solid fuels. Petroleum is natural liquid fuel and natural gas and casing-head gas are the natural gaseous fuels. Synthetic fuels which are mainly produced by processing natural fuels are coke, low temperature semi coke, charcoal (solid fuels) petrol, kerosene, ligroine, fuel oil e. t. c (liquid fuels) and producer gas, coke oven gas, petroleum refinery gases, water gas e. t. c (gaseous fuels). This unit examines water gas as artificial gaseous fuel, water shift reaction which serves to increase the hydrogen gas/carbon monoxide ratio of the syngas for use in the production of various chemicals as well as sources of hydrogen and its applications.

## 2.0 OBJECTIVES

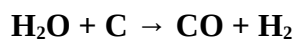
The students are expected to:

1. Explain different sources of hydrogen.
2. Explain the meaning of water gas.
3. Understand various applications of hydrogen.
4. Be acquainted with HT and LT shift reaction.
5. Discuss water-gas shift reaction and its application.

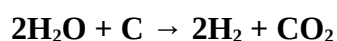
## 3.0 MAIN CONTENT

### 3.1 WATER GAS

Water gas is often called blue gas, because of the flame produced when it is burnt. Blue water gas consist mainly mixture of carbon mono oxide and hydrogen. It is produced by passing steam over red hot bed of coke at 1000°C.



The above reaction is strongly endothermic and hence the temperature gradually falls to about 1000°C. At this low temperature, steam reacts with carbon to form carbondioxide, according to the equation.



The resulting CO<sub>2</sub> has no calorific value and hence it is undesirable. At low temperature, a considerable amount of CO<sub>2</sub> goes on decreasing with an increase in temperature as a result of

conversion of  $\text{CO}_2$  to  $\text{CO}$ . The formation of water gas therefore depends on the decomposition of steam by the carbon. It has been observed that at  $758^\circ\text{C}$ , the percentage of steam decomposition is 25.3% and the composition of water gas formed is  $\text{H}_2 = 56.2\%$ ,  $\text{CO} = 7.8\%$  and  $\text{CO}_2 = 27\%$ . At  $1000^\circ\text{C}$ , the percentage of steam decomposed by coke becomes 93% and the composition of water gas becomes  $\text{H}_2 = 50.7\%$ ,  $\text{CO} = 48\%$  and  $\text{CO}_2 = 1.3\%$  whereas at  $1125^\circ\text{C}$ , the percentage of steam decomposition is 99.4% and the composition of water gas formed is  $\text{H}_2 = 50.9\%$ ,  $\text{CO} = 48.5\%$  and  $\text{CO}_2 = 0.6\%$ .

In practice, the rate of decomposition of steam and the formation of water gas are maintained by alternate run and blow periods. Hence, as soon as the temperature falls below  $1000^\circ\text{C}$ , the steam blast is stopped and air blast is passed through the red hot bed of coke for some time, to raise the temperature of the coke to about  $1400^\circ\text{C}$ . When this temperature is attained, the air blast is stopped and the steam blast again is resumed. In this manner, the process is alternated.

Since air forms an explosive mixture with water gas, water gas remaining in the generator is removed by passing steam for one minute. The steam sweeps off the water gas present in the generator. In the absence of the water gas in the plant, air is introduced. The steam passed for sweeping of the water gas is called Purage Steam. The period for which air is passed is called the hot blow. When the coke is sufficiently hot, steam is passed for 1.5 minutes. This period is called cold blow. After about one minute, the temperature falls below  $1000^\circ\text{C}$ , necessitating the hot blow again.

### **3.2 MANUFACTURE OF WATER GAS**

The gas generator consists of a steel cylinder lined with refractory lining. Coke, coal or any suitable fuel is introduced into the generator through an opening at the top. After charging, the top is covered or closed.

There are two inlet valve pipes joined to the steam generators. One of the pipes is below the top of the gas generator and the other is above the bottom. The air blast is sent through the inlet pipes as shown in fig 1. The operation is cyclic and consists of the following periods.

1. The up steam period (about 1.5 minutes): During this period, steam is blown through a distributor. The valve  $V_1$  remains open and the water gas produced by up steam goes out through an outlet pipe attached to the right side of the generator at the top.
2. The down steam period (about 1.5 minutes): In this period, steam is blown downward through the upper branch of the steam pipes, and the water gas produced leaves the generator through a pipe at the base via the valve  $V_2$ . This pipe is attached by a vertical pipe to the upper outlet pipe and hence, water gas produced by the downstream also passes out through the outlet provided at the top of the generator. The valves  $V_1$  and  $V_2$  are in the same plane and connected by a rod so that when  $V_1$  is opened,  $V_2$  remains closed and vice versa.
3. The three minutes steam period (1.5 minutes up steam + 1.5 minutes down steam): This three minutes steam period is followed by one minute of purge. During this period, steam passes at the top and sweeps off the remaining water gas in the generator and drives it to the gas holder.
4. Revival period: During the revival period, air blast is sent through the inlet pipe at the bottom and the temperature is brought back to about  $1400^{\circ}\text{C}$ . This operation takes about 2 minutes. The hot products of combustion formed during the air blast pass out through the top valve and are to waste.



## USES

Water gas is used as a source of industrial hydrogen in the manufacture of methyl alcohol and carbureted water gas, and for welding purposes.

## CARBURETED WATER GAS

To enhance the heating value or calorific value of blue water gas, the latter is carbureted by adding gaseous hydrocarbons obtained by cracking petroleum oils. The average composition of carbureted water gas is as follows:

$H_2 = 34 - 38\%$ ,  $CO = 23 - 28\%$

Saturated hydrocarbons = 17 – 21%

Unsaturated hydrocarbons = 13 – 16%

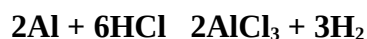
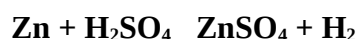
$CO_2 = 0.2 - 2.2\%$ ,  $N_2 = 2.5 - 5.0\%$

Carbureted water gas is used as a source of heat since it possesses high calorific value. It is generally employed for heating and illumination purposes.

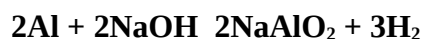
## 3.3 SOURCES OF HYDROGEN

The main sources of hydrogen are acids, alkalis, water and hydrocarbons. Hydrogen has also been found in sun's atmosphere.

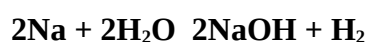
- (a) **From acids**, it can be prepared by reacting metals above hydrogen in the activity series with dilute or conc. HCl or dilute  $H_2SO_4$



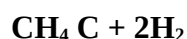
- (b) **From alkalis**, it can be prepared by the reaction of amphoteric metals such as Pb, Sn, Sb, As, Al and Zn with alkalies such as NaOH or KOH only



- (c) **Metals** above hydrogen in electrochemical series react with water to give hydrogen under different conditions



- (d) Cracking of hydrocarbons at high temperature gives hydrogen



Hydrogen can also be produced by various means and can be potential fuel resources.

At present, the main industrial methods of producing hydrogen are:

- a. Conversion techniques, that is, conversion of methane and its homologous with the subsequent conversion of the obtained CO or the conversion of water gas in the gasification of solid fuel
- b. Separation of coke oven gas by the consecutive liquefaction of all its components, except hydrogen.
- c. Electrolysis of water or aqueous solution of sodium chloride.

### 3.4 APPLICATION OF HYDROGEN

Hydrogen is used for industrial applications such as refining, treating metals and food processing. Liquid hydrogen is the fuel that once propelled the space shuttle and other rockets. Hydrogen fuel cells powered the shuttle's electrical systems producing pure water which was previously used as drinking water and in future, hydrogen will join electricity as an important energy carrier, since it can be made safely from renewable energy sources and is virtually non-polluting. It can also be used as fuel for zero-emissions vehicles to heat homes and offices to produce electricity and to fuel aircraft; although cost is the obstacle.

The first widespread use of hydrogen will probably be as additives to transportation fuel. Hydrogen can be combined with compressed natural gas (CNG) to increase performance and reduce pollution. Adding 20% hydrogen to CNG can reduce nitrogen oxides (NO<sub>x</sub>) emissions by 50% in today's engines. An engine converted to burn pure hydrogen provides only water and minor amounts of NO<sub>x</sub> as exhaust.

A few hydrogen-powered vehicles are on the road today, but will take some time before you can walk into your local car dealer and drive away in one. Today, 35 hydrogen fuel stations are operating in four states of the United State but not all are open to the public. With 32 stations, California has 91% of the nation's hydrogen fuel stations. Can you imagine how huge the task would be to quickly change the gasoline-powered transportation system we have today? Just think of the thousands of filling stations across the country and the production and distillation systems that serve them. Change will come slowly to this industry but hydrogen is a versatile fuel; it can be used in many ways.

Fuel cells (batteries) provide another useful option. Fuel cells basically reverse electrolysis-hydrogen and oxygen are combined to produce electricity. Hydrogen fuel cells are very

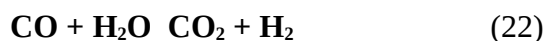
efficient and produce water as only by-product, but they are expensive to build. With technological advances, small fuel cells could someday power electric vehicles and larger fuel cells could provide electricity in remote areas. However, because of the cost, hydrogen will not produce electricity on a wide scale in the near future. It may though be added to natural gas, to reduce emissions from existing power plants.

As the production of electricity from renewable increases, so will the need for energy storage and transportation. Many of these sources especially solar and wind are located far from population centers and produce electricity only part of the time. Hydrogen may be the perfect carrier of this energy. It can store the energy and distribute it to wherever it is needed. Hydrogen also has many other uses. In the chemical industry, it is used to make ammonia for agricultural fertilizer (Haber process) and cyclohexane and methanol which are intermediates in the production of plastics and pharmaceuticals. It is also used to remove sulphur from fuel during oil refining process. Hydrogen is used daily as a gas and liquid by many industries including the petroleum industry and in manufacturing processes for producing chemicals, food, and electronics.

### **WATER-GAS SHIFT REACTION**

The water-gas shift reaction serves to increase the H<sub>2</sub>/CO ratio of the syngas for use in, for example, the production of various chemicals, Fischer-Tropsch liquids and SNG, or to enable the complete removal of carbon monoxide and carbon dioxide, for example in syngas for ammonia synthesis or hydrogen production and in power generation by the so-called Integrated Gasification Combined Cycle (IGCC) power plants with carbon capture.

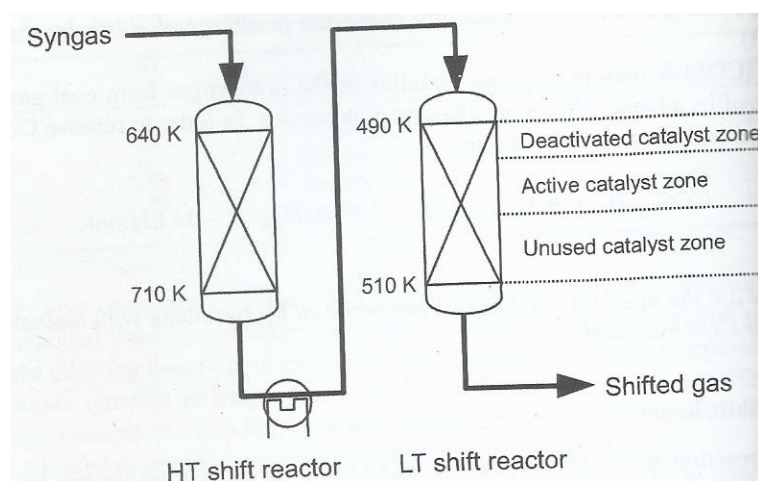
In the water-gas shift reaction, carbon monoxide is converted to carbondioxide.



Although the reaction is only moderately exothermic, the temperature has a great impact on the equilibrium.

Clearly, the temperature has to be low. In the past, catalysts were only active at temperatures above 600K. Later, more active catalysts were developed which were already active at temperature of 500K. These catalysts however require extremely pure gases because they are very sensitive to poisoning. Moreover, they are not stable at high temperatures. For many

practical purposes, the water-gas shift reaction is carried out using two adiabatic fixed bed reactors with cooling between the two reactors.



**Fig 2: Water-gas shift reactors with typical temperature and catalyst profile in the LT-shift reactor.**

In the first reactor, the high temperature (HT) shift reactor, (Fig. 2), most of the carbon monoxide is converted to carbon (iv) oxide. This reactor operates at a high temperature and contains a classical iron-oxide based catalyst. The second reactor, the low temperature (LT) shift reactor contains a more active copper based catalyst and operates at lower temperature. Here, the carbon monoxide content of the gas is further reduced.

The amount of catalyst in the LT shift reactor is much larger than the amount needed to achieve the required carbon monoxide conversion; extra catalyst, about 70% of the total catalyst volume is included to compensate for the inevitable deactivation and thus enable continuous plant operation for at least two to three years. Initially, almost all of the reactions takes place in the top part of the catalyst bed, but deactivation causes the reaction zone to move gradually down wards.

#### 4.0 CONCLUSION

Water gas is also called blue gas; it is produced by passing steam over red hot bed of coke at 1000°C. Hydrogen can be sourced from acids, alkalis, metals and cracking of hydrocarbons.

## 5.0 SUMMARY

Water-gas shift reactions are important in production of various chemicals. Its main objective is to produce hydrogen gas. Active catalysts at temperature of 500K were developed later as against those only active 600K. Today a few hydrogen-powered vehicles are on the road. It is also used industrially in refining, treating metal and food processing. Liquid hydrogen is the fuel for propelling space shuttle and other rockets.

## 6.0 TUTOR-MARKED QUESTIONS

1. Explain with equations the following processes:
  - i. Steam reforming.
  - ii. Water-gas shift reaction.
  - iii. Dry reforming reaction.
  - iv. Boudonard reaction.
2. Explain briefly but concisely the thermodynamics of the following reactions
  - i. Steam reforming.
  - ii. Partial oxidation of methane.
  - iii. Complete oxidation of methane.
  - iv. Dry reforming.

## 7.0 REFERENCES/FURTHER READING

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**MODULE 2****UNIT 1 INDUSTRIAL ORGANIC RAW MATERIALS****CONTENTS**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
  - 3.1 Organic Raw Material
  - 3.2 Biomass
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Question
- 7.0 Reference/Further Reading

**1.0 INTRODUCTION**

In the chemical industry, raw materials are converted into products for other industries and consumers. The range of products is enormous, but the vast majority of these chemicals are produced from a very limited number of simple chemicals called base chemicals, which in turn are produced from only about ten raw materials. These raw materials can be divided into inorganic and organic materials. Inorganic raw materials include air, water and minerals. Oil, coal, natural gas – together termed fossil fuels – and biomass belong to class of organic raw materials. Conversion of base chemicals can produce about 300 different intermediates, which are still relatively simple molecules. Both the base chemicals and the intermediates can be classified as bulk chemicals. A wide variety of advanced chemicals, industrial specialty chemicals and consumer products can be obtained by further reaction steps. From the foregoing, the organic raw materials are mainly fossil fuels and biomass.

**2.0 OBJECTIVES**

At the end of this unit, the students should be able to:

1. Understand the meaning of industrial raw materials particularly organic raw materials.
2. Differentiate between inorganic and organic raw materials.
3. Discuss natural gas as organic raw materials.
4. Relate crude oil, coal and biomass with industrial organic raw materials.

### **3.0 MAIN CONTENT**

#### **3.1 ORGANIC RAW MATERIALS**

All three fossil fuels (oil, coal and natural gas) have in common that they mainly consist of carbon and hydrogen, while also small amounts of hetero-atoms like nitrogen, oxygen, sulphur and metals are present. However, the ratio of these elements is very different, which manifests itself in the very different molecular compositions size, type etc) and physical properties. In addition to carbon and hydrogen, biomass contains a relatively large amount of oxygen. Biomass is the product of photosynthesis. The C/H ratio is a characteristics feature of hydrocarbons. Clearly, the relative amount of carbon in coal is much larger than in crude oil. Methane (CH<sub>4</sub>) obviously has the lowest C/H ratio of all hydrocarbons. The C/H ratio of natural gas is very similar to that of methane, because methane is the major constituent of natural gas.

#### **Natural Gas**

Natural gas is a mixture of hydrocarbons with methane as the main constituent. It can be found in porous reservoirs, either associated with crude oil (“associated gas”) or in reservoir in which no oil is present (non-associated gas). Natural gas is of great importance not only as a source of energy but also as a source of raw material for the petrochemical industry. Besides hydrocarbons, natural gas usually contains small (or sometimes large) amounts of non-hydrocarbon gases such as carbon dioxide, nitrogen and hydrogen sulphide.

Natural gas is classified as dry or wet. The term wet refers to water but to the fact that wet natural gas contains substantial amounts of ethane, propane, butane, pentane and higher hydrocarbons, which condense on compression at ambient temperature forming natural gas liquids. Dry natural gas contains only small quantities of condensable hydrocarbons. Associated gas is invariably wet, whereas non-associated gas is usually dry. The terms sweet and sour denote the absence or presence of hydrogen sulphide and carbon dioxide. Non associated gas can only be produced when a suitable local or export market is available. Associated natural gas, on the other hand, is a co-product of crude oil. Therefore, its production is determined by the rate of the accompanying oil. It has long been considered a waste product and most of it was flared for safety reasons.

Natural gas from the well is treated depending on the compounds present in the gas. A dry gas needs little or no treatment except for H<sub>2</sub>S and possibly CO<sub>2</sub> removal if the amounts are appreciable (sour gas). Condensable hydrocarbons are removed from a wet gas and part can be sold as liquefied petroleum gas (LPG), propane or butane may be used for the production of chemicals (ethane). The other part, C<sub>5</sub><sup>+</sup> hydrocarbons, can be blended with gasoline. So, once natural gas has been purified and separated, a large part of the gas is a single chemical compound, methane.

### Crude Oil

The composition of crude oil is much more complex than that of natural gas. Crude oil is not a uniform material with a simple molecular formula. It is a complex mixture of gaseous, liquid, and solid hydrocarbon compounds, occurring in sedimentary rock deposits throughout the world. The composition of the mixture depends on its location. Two adjacent wells may produce quite different crudes and even within a well the composition may vary significantly with depth. Nevertheless, the elemental composition of crude oil varies over a rather narrow range as shown in Table 1.

**Table 1: Elemental Composition of Crude Oil**

Element	Percent range (wt %)
C	83 – 87
H	0 – 14
N	0.2 – 3

Although, at first sight these variations seem small, the various crude oils are extremely different. The high proportion of carbon and hydrogen suggests that crude oil consist largely hydrocarbons, which indeed is the case. Detailed analysis shows that crude oil contains alkanes, cycloalkanes, aromatics, polycyclic aromatics, and nitrogen, oxygen-, sulphur- and metal-containing compounds. The larger part of the crude oil consists of alkanes, cycloalkanes, and aromatics. Both branched/linear alkanes are present. In gasoline applications the branched chain alkanes are desired. One of the aims of catalytic reforming is to shift the ratio of branched/linear alkanes in the desired direction. The heavier the crude, the more polycyclic aromatic compounds it will contain. Generally, heavier crudes yield a lower proportion of useful products. A further disadvantage of the heavier crude is that they contain more polynuclear aromatics (PNAs), which tend to lead to carbonaceous deposits (“coke”) during processing. The implications of coke formation play an important role.



Crudes do not consist exclusively of carbon and hydrogen; minor amounts of so-called heteroatoms are also present, the major ones being sulphur, nitrogen and oxygen. Of these, sulphur is highly undesirable because it leads to corrosion, poisons catalysts, and is environmentally harmful. Therefore, it must be removed. The nitrogen content of crude oil is lower than the sulphur content. Nevertheless, nitrogen compounds deserve attention because they disturb major catalytic processes, such as catalytic cracking and hydrocracking. Basic nitrogen compounds react with the acid sites of the cracking catalyst and thus destroy its acidic character. Heteroatomic compounds, such as aromatic sulphur compounds, are present in the higher boiling hydrocarbon fractions in particular.

Although, the oxygen content of crude oil usually is low, oxygen occurs in many different compounds. Metals are present in crude oil only in small amounts. Even so, their occurrence is of considerable interest, because they deposit on and thus deactivate catalysts for upgrading and converting oil products. One part of the metals is present in the water phase of crude oil emulsions and may be removed by physical techniques. The other part is present in oil-soluble organometallic compounds and can only be removed by catalytic processes. The most abundant metals are nickel, iron and vanadium.

## Coal

In contrast to natural gas and crude oil, the elemental composition of coal varies over a wide range as shown in the Table 2 below. The composition range is based on only the organic component of coal. In addition, coal contains an appreciable amount of inorganic materials (minerals), which forms ash during combustion and gasification.

**Table 2: Elemental Composition of organic materials in coal**

Element	Percentage range (wt %)
C	60 – 95
H	2 – 6
N	0.1 – 2
O	2 – 30
S	0.3 – 13

Furthermore, coal contains water, the moisture content of coal ranges from about 2 to nearly 70%. The high C/H ratio reflects the fact that a major part of the coal is built up of complex with aromatic rings.

### 3.2 BIOMASS

In a simplified analysis, biomass can be divided into three groups, that is, oils and fats, sugars, and lignocellulosic biomass. A simple economic analysis shows that lignocellulosics are most attractive, both with respect to resources and price.

Animal fats and vegetable oils are primarily composed of triglycerides, esters of fatty acids with glycerol. An example of a typical vegetable oil triglyceride is shown below:

Lignocellulosic biomass consists mainly of three components. Cellulose (35–50 wt %), hemicelluloses (15– 25 wt %) and lignin (15 – 30 wt %), plant oils, proteins, different extractives and ashes make up the rest of the lignocellulosic biomass structure. Although the material is very important, there is no full agreement on the structure yet. Recent researches suggest that the lignocellulosic biomass mainly consists of cell wall components built up from cellulose and hemicelluloses held together by lignin. The hemicellulose in turn is a matrix containing the cellulose fibres. Cellulose is the most abundant organic polymer on earth.

It consists of linear polymers of cellobiose, a dimer of glucose. The multiple hydroxyl groups of the glucose molecule form hydrogen bond with neighbour cellulose chains making cellulose microfibrils of high strength and crystallinity.

Hemicellulose is chemically related to cellulose in that it comprises a carbohydrate backbone. However, due to its random and branched structured hemicelluloses is amorphous. It also has a more complex composition than cellulose. Example of hemicelluloses is xylan. Whereas cellulose is completely built up from glucose monomers, hemicelluloses consists of a mixture of five-carbon sugars (xylose, arabinose), six-carbon sugars (glucose, manose, galactose) and uronic acids eg. glycoronic acid. Xylose is the monomer present in the largest amount.

Lignin, the third main component of the lignocelulosic biomass is an amorphous three dimensional polymer which fills the spaces in the cell wall between cellulose and hemicelluloses. It is aromatic and hydrophobic in comparison with cellulose and hemicellulose.

#### **4.0 CONCLUSION**

Base chemicals can be converted to produce up to 300 different intermediates. Raw materials are grouped into organic and inorganic. Fossil Fuels and biomass belong to the class of organic raw materials, while air, water and minerals are inorganic raw materials.

#### **5.0 SUMMARY**

Base chemicals and intermediates can be classified as bulk chemicals. Organic raw materials include natural gas, crude oil, coal, and biomass.

#### **6.0 TUTOR-MARKED QUESTIONS**

1. List any three organic raw materials in industrial production of materials.
2. Discuss fossil fuel as a raw material.

#### **7.0 REFERENCES/FURTHER READING**

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## **UNIT 2 TECHNICAL AND ECONOMIC PRINCIPLES OF PROCESSES AND PRODUCTS ROUTES, FLOW DIAGRAM**

**CONTENT**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
  - 3.1 Technical and Economic Principles of Processes
  - 3.2 Process Evaluation
  - 3.3 Product Routes/Flow Sheet/Flow Diagrams
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Question
- 7.0 References/Further Reading

**1.0 INTRODUCTION**

The basic function of any private company which aims to continue in business is to make profit. Without this, it cannot do other socially desirable things such as providing continuing employment, providing money for local services through rates and local taxes and providing money for national activities through corporate taxes and employee's taxes. In a planned economy or a nationalized industry, mixed economies which are currently operating in many countries, the profit motive is not the main imperative. Unprofitable activities may be continued for social or political reasons- to maintain employment in a depressed area or to maintain an industry, to avoid dependence on imports in strategically important areas of manufacture. However, any such unprofitable operations represent a drain on the national resources and must be supported and subsidized by the taxes paid by profitable activities.

In chemical industry, companies were founded and continued to exist, to produce profits by making and selling chemicals. The products made are those for which a need has been identified and which can be produced for sale at a price which the consumer is willing to pay and which adequately rewards the producer. The processes chosen to manufacture the desired products are those which are believed to offer the best profit to the producer. They may not be the most chemically elegant routes to the products or the most scientifically interesting processes but in this context these factors are unimportant. In case, it may be thought that the chemical producer operates his process to maximize his profits without concern for the effects on people or the environment, it must be emphasized that, today's production of chemicals is governed by numerous regulations. Construction standards, operating safety of

plant, the protection of employees from dangerous levels of chemicals exposure and the effect of effluents and products on the environment; including people outside the plant boundaries are all subject to control by local and national legislations. This factor particularly the control of atmospheric chemical levels within the plant and the safe disposal of gaseous and liquid effluents can have a significant influence on the choice of process. They can also significantly increase both the capital cost of the plant and the cost of operating process, as more equipment is required to meet increasingly stringent controls. The cost of operating a plant safely with minimum impact on the environment must ultimately be carried by the consumer in higher product price needed to keep the producer in business.

The strategy for developing new technologies or products is an important concern in Research and Development (R & D) departments for the chemical industry. The development of a particular process is successful if the desired product is produced in time at the planned rates, the projected manufacturing cost, and the desired quality standards. Included in the term cost are obvious items such as raw materials cost, but also safety and environmental compatibility. In consideration of technical economics principles of processes and product routes, flow diagrams are of vital importance. The flow diagram or process flow sheet summarizes a process from raw materials feed to finished product. The products routes end when the products get to the final consumer.

## **2.0 OBJECTIVES**

At the end of this unit, the students should be able to:

1. Understand the meaning of industrial raw materials particularly organic raw materials.
2. Differentiate between inorganic and organic raw materials.
3. Discuss natural gas as organic raw materials.
4. Relate crude oil, coal and biomass with industrial organic raw materials.

### **3.1 MAIN CONTENT**

### **3.2 TECHNICAL AND ECONOMIC PRINCIPLES OF PROCESSES**

**Cost of producing a chemical:** The profit which the manufacturer obtains by producing and selling his chemicals can be measured in various ways. However, in order to know whether or not a profit is being made from an existing plant or product or in the case of a project at the planning stage, whether the new product would show an acceptable profit, we need to know the actual or estimated costs involved in producing the chemical. So, let us consider how the cost of producing a chemical is built up. A considerable number of factors are involved in the production of chemicals ranging from the supply and storage and selling of the finished product. In between these steps is firstly all the complex and expensive equipment for carrying out chemical processes, separating and purifying the product. Secondly, the people who operate the plant and carry out maintenance work to keep the processes in operation. A simple way of combining information on these various cost factors into a useful economic model is the cost table. This presents information on an annual or per unit of product basis and is useful for indicating the relative importance of the various factors which make up the cost. There are various ways of sub dividing the components which make up the full cost of a chemical. The method used depends on the purpose for which the information is required. Traditionally, accountants like to divide cost into variables and fixed elements. This split is useful when considering the costs of an integrated works, an individual production unit or a single product. Variable costs comprises those factors which are only consumed (and therefore only charged to the operation) as product is being manufactured. As a result, the total variable cost during an operating period – day, quarter, year- will vary directly as the plant output during that period. Although the cost per unit of production will remain constant, fixed costs are those charges which have to be paid at the same annual rate whatever the rate of production, in fact even if the plant is shut down for a period for repairs, or any other cause, the fixed charges are still incurred. Since the total fixed costs are charged whatever the annual production from the plant, the cost per unit of output will increase significantly at output rates much below 100%.

There are different views as to which cost should be regarded as variable or fixed.

**Variable Cost:** The following are widely accepted as variable cost. They are Raw materials cost, Energy, input costs, Royalty and License payments.

**Raw material costs:** Where a process plant is operating the usage of feed stocks can be obtained by measurements of process flows during periods of steady operation. In the case of a new process, at the research stage or a project under development, raw material usages can be estimated from the process stoichiometry using assumed yield or yield obtained during process research experiments. In the latter cases, if yields are based on analysis of the reactor

products, allowances must be made for losses which occurred during the product recovery and purification stages. In an industrial situation, internal company data will usually be available for important feed stocks. Company technology strengths and strategic considerations can also influence the choice of feed stock and process route which will be selected to maximize commercial advantage. Thus, a company which uses an internally available feed stock or a minor modification to an existing process could be preferred to a possibly better alternative using a purchased feed stock or requiring a major investment in process development work. The cost of catalysts and materials not directly involved in the process of stoichiometry (solvents, acids or alkalis for pH adjustments etc) must also be included in the material cost. Catalyst costs are based on loss of catalyst per cycle for homogenous catalysts or cost of catalyst charge divided by output during charge life for heterogeneous catalyst. Catalyst materials recovered from purge streams or by reprocessing a spent catalyst reduces the net catalyst cost. Solvent losses can be either physical (loss in off-gas stream, pump leaks) or chemical due to decomposition or low reaction under process conditions. Such additional material consumption is difficult to estimate in the absence of plant operating data but are usually relatively small cost items.

**Energy input cost:** This item covers the multiple energy inputs necessary to carry out the chemical reaction and to separate the desired products at the level of purity demanded by the market. Steam, at various pressure levels depending on the temperature required, is used to provide heat input to reactors and distillation column reboilers. Fuel oil or gas is used to provide higher temperature heat inputs either directly by heat exchange between process streams and hot flux gases or indirectly by heating a circulating heat transfer medium. Electricity is used for motor drives for reactor agitators, pumps and gas circulators and compressors. Lighting of plant structures, tank farms and plant control rooms is an important but usually minor, use of electricity. Cooling water is required to remove reaction exotherms and control reactor temperature, condense and cool still overhead streams and cool process streams. Inert gas, usually nitrogen is used for purging equipment to provide an inert atmosphere over oxidizable or flammable materials. In the case of an operating process the consumption of energy inputs can again be obtained from process measurements during steady operation. For a process under development, estimates of major energy requirements can be made from the process energy balance and information process conditions in reactors and operating trains. The energy inputs available (e.g steam pressure available, use of fuel or gas) and the prices charged for them will vary from company to company and are very much site-dependent. A large integrated site could co-generate steam and electricity at high thermal

efficiency in a site power station. Use of waste streams (liquid or gaseous) could provide at least part of the fuel input, with the balance being purchased oil or gas. Steam would then be available at a number of pressure levels after staged let down from boiler pressure through turbines to generate electricity. In contrast, a small site or isolated production unit would have to raise steam in a package boiler, using purchased fuel oil or gas and buy electricity from the grid. The prices charged for energy inputs on the two sites would differ appreciably. In a highly competitive industry and also in the interests of environmental protection and resource conservation, efficient use of energy resources is important.

**Royalty/ License Payments:** If the process being used for production (or to be used in the case of a planned project) is based on purchased technology rather than process developed within the company, with royalty or process license fee will be incurred. This may be either a variable or fixed charge depending on the nature of the license agreement. Usually, a charge is made per unit of production and would appear in a cost sheet as a variable cost item. Alternatively, an annual license fee is related to the plant size (e.g N500 million per 100,000 tonne installed capacity) will be charged and this would then appear as a fixed charge. The size of the royalty payment or license fee is a matter of negotiations between the licensor and licensee. It would not be influenced by the nature of the technology, the advantages offered over competing processes and the number of alternative processes available for licensing.

**Fixed Costs:** These include labour charges, depreciation, rates and insurance and overhead charges.

**Labour Charges:** Operating labour and supervision charges, maintenance labour and supervision charges and analytical and laboratory staff. Emolument charges represent the manpower cost associated with the process and includes the team of process workers who operate the equipment. In the case of large, continuous process units, the operators work in shift teams to cover the 24hrs per day, 7days per week running of the unit. Maintenance labour includes: fitters, electricians, plumbers, instrument artificers and other engineering workers who keep the process equipment in good working order. Usually, maintenance work is planned and is generally carried out during normal day hours with only a small shift team to cover emergency breakdowns. Analytical manpower is also included. Again, a shift team of analytical staff involved to carry out checks on plant operation and product quality on a continuing basis.

The item for maintenance materials covers the cost of parts, replacement tools and similar items ranging from a replacement valve or pump to a new spanner. Only items to be expected



in normal maintenance are included, the replacement for example of a reactor as a result of accident or fire would require a special appropriation of capital.

**Depreciation:** Depreciation is a term used in a number of ways in different contexts. In the context of production costs of a chemical, the depreciation charge is regarded as an operating cost in the same way as material or energy usages. It represents the fact that the capital value of the plant is consumed over the operating life of the plant. Calculation of the annual depreciation charge requires an estimate of the expected life of the equipment, a figure of 10 to 15 years is generally used in the heavy chemical industry. The annual charge can then be calculated by a simple straight-line method in which the sum of money (equal to fixed capital costs / expected life) is charged each year. Another method of calculating the depreciation charge is the declining balance or fixed percentage of the remaining un-depreciated capital. Thus, in year 1, the depreciation charge would be 20% (for 20% rate with fixed capital C). The next year, the depreciation charge would be  $20\% \times 0.8C$  and so on. This method gives higher depreciation during the early years of plant life but does not depreciate to zero value at the end of expected service life. A high depreciation charge is then required at the final year of operating life to strike the balance. A second interpretation of depreciation is an allowance against tax. The annual income is reduced by an annual depreciation allowance before tax is charged thus reducing the tax payable. Calculation of the allowance is governed by the appropriate tax legislation and the depreciation shown for tax purposes may be a very different figure from that charged as an operating cost. The use of depreciation as an allowance against tax forms part of a net present value and discount cash flow measures of profitability.

**Rates and Insurance:** This item covers the local rates or local authority tax levied in the area in which the plant is situated together with the premium required to provide insurance cover for the facility. Actual charges will vary with the plant site and nature of the process being carried out (e.g a plant with a high fire risk will carry a high insured premium). Typical values for the rates and insurance item of cost lie in the range 0.5- 2.0% of plant capital.

**Overhead Charges:** Overhead or general charges cover those items not associated with any particular product or process but which are an essential part of the functioning of an individual site or a whole company. These charges are usually divided into two broad classifications- local works overhead and general management of works ( works, manager, secretarial services, plant records, planning, security, safety organizations, medical services, provision of offices, canteen facilities and so on). Company overheads include head office charges, central research and development activities, legal, patent, supply and purchasing and

other company wide activities. The allocation of company overheads to individual works and the further allocation of this charge and works overhead to individual plants or products is something of an arbitrary process allocation vary from company to company but are generally based on the plant capital and /or operating manning level for a plant relative to other plants in the works and of the works in overall relation to the company.

### 3.3 PROCESS EVALUATION

The basis for process evaluation is the documentation of the knowledge of the process gained from research. The important questions are:

- i. Is the production process technically feasible in principle?
- ii. What is the economic attractiveness of the process?
- iii. How big is the risk in economic and technical terms?

The technical feasibility of a process is proven by research in the laboratory, miniplant, and pilot plant. If certain process steps present difficulties, these problems should be solved either by improving these steps or by selecting a different procedure. Factors increasing the technical risk of a process are;

- a. Exceeding of limits (e.g. if the dimensions of the largest extraction column previously operated by a company are considerably exceeded).
- b. Unfamiliarity of the company with the particular technology (e.g. continuous processes, high pressure, per-acids, fluidized bed).
- c. Use of units that are difficult to scale up (e.g. for solids processing).
- d. Use of technical non-established equipment or unit operations (e.g. monolith reactors in multiphase applications).

The technical risk of a process can be reduced in a number of ways. The first is to increase the expenditure on research and development of the weak points, for example, pilot plants testing of the problematic unit, find well established alternative equipment or other ways to perform the unit operation. A second option is to develop failure scenarios that is to determine what can be done if problems should occur (e.g., backup units, additional instrumentation). The decision basically is an economic question; the costs of increased research and development expenditure have to be weighed against the cost of eliminating the risk when the plant started up or in operation. It should be noted that safety should have an

even higher weighing than economy. That is, processes that are unsafe should not be brought to commercialization.

An important factor in the decision to pursue or abandon the development of a process is the economic perspective of a process. As the purpose of investing money in a chemical plant is to earn money, some means of comparing the economic performance or profitability is needed. To be able to assess the profitability of a process, estimates of the investment and operating costs are required. For small projects and for simple choices between alternative processes or equipment, usually a comparison of the investment and operating costs is sufficient. More sophisticated techniques are required if a choice has to be made between large complex processes with different scope, time scale and type of product.

The economic evaluation of processes is based on criteria set by the company, such as Pay Back Time (PBT), Net Present Value (NPV) and so on. These kinds of evaluations are done by a specialist group within the company, but chemical engineers and industrial chemists should have a basic knowledge in order to communicate.

**Capital Cost Estimation:** Several methods are used to estimate capital cost required for a chemical plant. These range from preliminary estimates (or study estimates) or with accuracy of 20 – 30% to detailed estimates with accuracy of with 5%. The latter are only obtained in the final development stage of a process, when the engineering drawings have been completed and all equipment has been specified. Preliminary estimates usually starts with the use of cost charts for estimating the purchase cost of major equipment items, the other costs being estimated as factors of the equipment cost. Such other factors include cost for equipment design, material and such other related costs as site preparation, service facilities etc which lead to more accurate estimates. Total capital investment is also considered which consists of the total permanent investment (or total fixed cost) and the working capital. Purchase costs alone will not suffice to build a plant; the equipment has to be installed, including piping and instrumentation, there are costs for spare equipment items, storage vessels, initial catalyst load (if the catalyst cannot be reused), and so on.

Apart from the total capital investment, the annual operating costs and annual earnings (pre-tax and after tax) must be estimated in order to obtain an approximate measure of the profitability of the plant. Operating costs are divided into fixed cost and variable cost. The fixed costs do not vary with production rate and have to be paid whatever quantity produced.

The variable costs, on the other hand, depend on the quantity produced. The variable cost can be calculated from material and energy balances and material prices. Fixed costs are partly labour related and partly capital related. The latter are estimated as a percentage of fixed capital investment. The indirect operating costs are the company overheads, which include administration, general research and development, and sales expenses.

Raw material costs usually constitute a major part of the operating costs. The cost of raw materials follows from raw material consumption e.g., ton per ton (T/T product) and the unit cost of the particular raw material e.g., naira per ton (N/T). Utilities include steam, electricity, process water, and so on. Waste disposal is also often included in the utilities. Utility prices depend on the location and proximity of their source, as well as on whether they are purchased or generated on site. Operating labour costs are based on an estimation of the number of operators for the process and the cost to the company of one operator. The number of operators depends on the type and arrangement of the equipment, number of equipment items, number of instrumentation and control for the process, and company policy in establishing labour requirements. Supervision and other related costs are then estimated as a fraction of operating labour cost.

### **3.2 PRODUCT ROUTES/FLOW SHEET/FLOW DIAGRAM**

A process flow sheet is a schematic representation of a process which shows the equipment used and its interconnections. The flow sheet of a prototype chemical process is shown below. The stages involving preparation of feed and separation of products usually occupy most of the equipment in a plant.

**Fig 1: Prototype Chemical Process**

The reaction stage is of course crucial but is generally confined to a single vessel. It is convenient to have the flow rate, composition, temperature and pressure of each stream displayed on the flow diagram. An example of an actual process flow sheet is shown in Fig. 2. For a process of any complexity, this information would be in a tabular form next to the drawing.

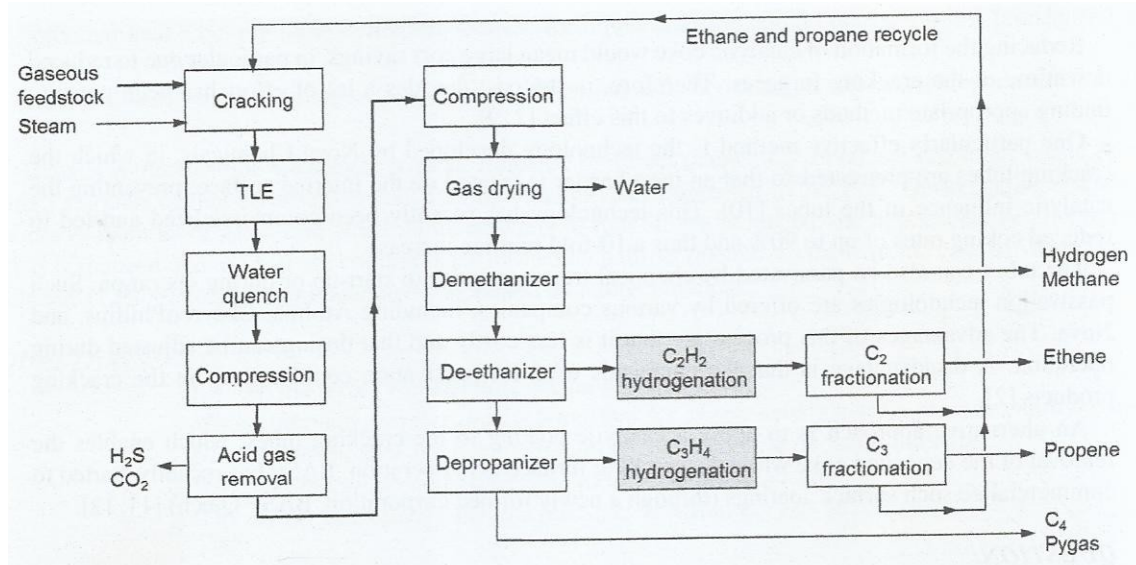


Fig. 2: Simplified process flow diagram for producing ethene via gas cracking

\*TLE = Transfer Line Exchanger

\* Pygas = Pyrolysis gasoline

### General Balance Equation

The material balance establishes relationship between flows and composition in different parts of a plant. It provides the principal tool for analyzing a process.

Consider the system shown in the Figure 3. Input and output of material are related by the equation

$$(1)$$

**Fig. 3: Material balance system**

Equation (1) may be applied in different ways according to the precise definition of “material” and the way in which the process is operated. If the balance is applied to the total mass of each element entering and leaving the system, the generation and consumption terms are zero (excluding nuclear reactions) and equation (1) becomes

(2)

Or

(3)

When considering quantities (mass or number of moles) of individual molecular species, material may be produced or consumed by chemical reaction. In the absence of chemical reactions equations like (2) apply also to the total number of moles of each molecular species. Process may be classified as continuous (open) or batch (closed). Most modern high volume processes operate with a continuous feed and form product continuously. In a batch process, materials are changed into a vessel and products withdrawn when the reaction is complete. Sometimes, as in batch distillation, products may be withdrawn continuously. Batch operation is usually used for low volume products, e.g., manufacture of pharmaceuticals.

The material balance equation for a batch process must necessarily include an accumulation term. Continuous processes are often assumed to operate at steady state, i.e., process variables such as flows do not change with time. There is therefore no accumulation and the general balance equation becomes

$$\text{Rate of input} + \text{rate of generation} = \text{rate of output} + \text{rate of consumption} \quad (4)$$

Or for the total mass,

$$\text{Mass flow in} = \text{mass flow out} \quad (5)$$

Alternatively, when considering the operation of a continuous steady-state process for a fixed period of time, each of the terms in equation (4) may be expressed simply as a mass or number of moles. Equation (2) thus becomes

$$\text{Total mass in} = \text{total mass out} \quad (6)$$

#### Example 1

10kgs<sup>-1</sup> of a 10% (by mass) NaCl solution is concentrated to 50% in a continuous evaporator. Calculate the production rate of concentrated solution (C) and the rate of water removal (W) from the evaporator

#### Solution

The flow sheet is shown in Fig. 4. The steady-state mass balance is given by equation (5). Balances can be made by individual species or total mass

#### Fig. 4: Flow sheet of concentration of NaCl

Because no chemical reaction takes place, we can write balances for molecular species rather than considering individual elements.

For each species, flowrate = mass fraction x total flowrate

Balance on NaCl:

$$0.1 \times 10 = 0.5 \times C$$

$$\square C = 2\text{Kgs}^{-1}$$

Total balance:

$$10 = W + C$$

$$\square W = 10 - 2 = 8\text{Kgs}^{-1}$$

**Material Balance Techniques:** It is usually helpful to follow a systematic procedure when tackling material balance problems. One possibility is outlined below.

- (1) Draw and label the process flow sheet: organize information into an easy to understand form. If possible show problems specifications on the flow sheet. Label unknown with algebraic symbols.
- (2) Select a basis for the calculation: the basis is an amount or flow rate of a particular stream or component in a stream. Other quantities are determined in terms of the basis. E.g. for example 1 above, the flow rates of product and water were obtained on a basis of  $10\text{kg s}^{-1}$  of feed. It is usually most convenient to choose an amount of feed to the process as a basis. Molar units are preferable if chemical reactions occur, otherwise the units in the problem statement (mass or molar) are probably best.
- (3) Convert units/amounts: as necessary to be consistent with the basis.
- (4) Write material balance equations: for each unit in the process or for the overall process. In the absence of chemical reactions the number of independent equations for each balance is equal to the number of components.
- (5) Solve equations: for unknown quantities. This can be difficult, particularly if nonlinear equations are involved. Overall balances usually give simpler equations. For complex flow sheets computer methods offer the only practicable solution.
- (6) Scale the results: If the basis selected is not one of the flow rates in the problem specification, the result must be scaled appropriately.

Example 2:

An equimolar mixture of propane and butane is fed to a distillation column at the rate of  $67\text{mols}^{-1}$ . 90% of the propane is recovered in the top product which has a propane mole fraction of 0.95. Calculate the flow rates of top and bottom products and the composition of the bottom product.



## Solution

- (1) Draw the flow sheet

- (2) Select basis

10 mol of feed i.e.  $F = 10$  mol. This basis is somewhat easier to work with than the specified feed flow rate. By selecting a quantity of feed (rather than a flow rate), we are, implicitly, considering the operation of the process for a fixed period of time.

- (3) Conversion of units-not necessary, all units are molar

- (4) Equations: there are no reactions and the steady-state balance equation for total or component flows is

$$\text{Input} = \text{output} \quad (1)$$

- (i) Total material balance

$$F = D + B \quad (2)$$

- (ii) Component balances:

Propane:

Butane:

It is evident that these equations are not independent. The total balance can be obtained by summing the component balances. Inserting specified values into the first two equations gives

$$10 - D + B \quad (5)$$

$$5 = 0.95D + Bx_B \quad (6)$$

A third independent equation is provided by the specification on propane recovery:

$$X_D D = 0.90 F x_F \quad (7)$$

$$\text{Or } 0.95D = 0.90 \times 0.5 \quad (8)$$

$$\square 0.95D = 4.5 \quad (9)$$

(5) Solution:

From equation 9,  $D = 4.74 \text{ mol}$

Substituting in (5)  $B = 5.26 \text{ mol}$ .

And equation (6) is now solved for the bottom stream composition,  $X_B = 0.095$ .

(6) Scaling – compositions are unchanged by the choice of basis. The quantities obtained above must be scaled by

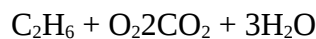
To solve the problem as stated i.e

$$\text{Bottom flowrate} = 5.26 \times 6.7 = 3.5 \text{ mols}^{-1}$$

$$\text{Top flowrate} = 4.74 \times 6.7 = 31.8 \text{ mols}^{-1}$$

**Chemical Reactions:** The treatment for material balances for systems in which chemical reactions take place involves some new considerations. Generation and consumption terms must be included for molecular species and the stoichiometric constraints must be observed.

**Stoichiometry:** The stoichiometric equation of a reaction defines the ratios in which molecules of different species are consumed or formed in the reaction e.g.



For the purpose of defining stoichiometric coefficients  $v_i$ , it is convenient to write the stoichiometric equation with all species,  $i$  on the right hand side i.e.



The stoichiometric coefficients are:

A general stoichiometric equation may be written as

Where  $A_i$  is the participating species and  $v_i$  is negative for reactants, positive for products and zero for inerts (substances unchanged in the reaction).

**Extent of Reaction:** It is useful to have a measure of the amount of material consumed or produced in a chemical reaction. The most convenient quantity is the extent, consider a material balance for a chemical reactor

Fig. 5: Material balance for a chemical reactor

The extent  $\xi$  is defined by the equation

$$f_{i,\text{out}} = f_{i,\text{in}} + V_i \xi$$

Where

$f_{i,\text{out}}$  is the number of moles of species  $i$  leaving the reactor

$f_{i,\text{in}}$  is the number of moles of  $i$  entering

$v_i$  is the stoichiometric coefficient

The extent has the same units as  $f_i$ , i.e. mole or mol/unit time. It is always a positive quantity because of the sign convention for  $v_i$  and has the same value for all species because  $(f_{i,\text{in}} - f_{i,\text{out}})$  is proportional to  $v_i$ .

Most chemical reactions do not result in complete conversion of reactants to products. The maximum possible extent depends on the equilibrium constant but it is often more convenient to define a fractional conversion based on the quantities present in the feed.

Unless the feed composition is stoichiometric, the fractional conversion will be different from each species. Even for a reaction which goes to completion the fractional conversion will not be unity except for the limiting reactant.

Example 3:

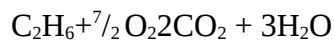
200 mol of ethane are burned in a furnace with 50% excess air. A conversion of 95% is achieved. Calculate the composition of the stack gases.

Soln:

Flowsheet

Fig. 6: Simple flow sheet

The stated quantity of ethane will be used as bases, i.e. 200mol. The stoichiometric equation is



A stoichiometric feed, would require

$$\text{C}_2\text{H}_6 = 200\text{mol C}_2\text{H}_6 \text{ in the feed.}$$

$$\text{O}_2 = 200 \text{ mol} \times \frac{7}{2} = 700 \text{ mol O}_2. \text{ Thus } 50\% \text{ excess air} = 150\% \text{ O}_2 \frac{150}{100} \times 700\text{mol} \\ = 1050\text{mol.O}_2 \text{ in the feed}$$

Air is 21% molar O<sub>2</sub> and 79% molar N<sub>2</sub>

$$\text{N}_2/\text{O}_2 \text{ ratio} = 79/21 = 3.76$$

$$\text{i.e. } 1050 \times 3.76 = 3948 \text{ mol N}_2 \text{ in the feed}$$

The conversion is 95%; since no reactant is specified, we assume that it refers to the limiting reactant (ethane in this case).

Since stoichiometric coefficient of C<sub>2</sub>H<sub>6</sub> is -1.

**The material balance is summarized in the Table 1 below:**

Feed	In mol	Mol (fin-)	Out mol
C <sub>2</sub> H <sub>6</sub>	200	200-	10
O <sub>2</sub>	1050	1050 - 7/2	385
N <sub>2</sub>	3948	3948	3948
CO <sub>2</sub>	0	2	380
H <sub>2</sub> O	0	3	570

Table 1: Summary of material balance

#### **4.0 CONCLUSION**

Chemical industries were established to make profits by making and selling chemicals. The products are those with proven needs of the society and consumers are willing to pay at an affordable price. The cost of producing a chemical involves variable cost, energy cost, royalty/ license payment, fixed cost, labour charges, depreciation, rates and insurance. The process evaluation is based on documentation of knowledge of the process obtained from research. Flow diagram is a schematic representation of a process that shows the equipment used and its interconnections.

#### **5.0 SUMMARY**

Raw material costs usually constitute a major part of the operating costs. Utilities include steam, electricity, process water, waste disposal, etc. An important factor in the decision to pursue or abandon the development of a process is the economic perspective of the process. The technical feasibility of a process is proven by research in the laboratory, mini plant and pilot. The material balance establishes a relationship between flows and composition in different parts of a plant.

#### **6.0 TUTOR-MARKED QUESTIONS**

1. Explain what you understand by a process flow sheet.
2. Show the production of ethane via gas cracking using flow diagram.
3. Differentiate between variable and fixed costs.
4. Classify the following under variable and fixed costs
  - i. Labour charges.
  - ii. Energy input.
  - iii. Royalty.
  - iv. Overhead charges.
  - v. Rates and insurance.
  - vi. Raw materials.
  - vii. Depreciations.
5. Discuss any variable and fixed costs.
- 6a. Explain some of the factors that increase technical risk of a process.
- 6b. How can these risks be minimized?

7. 250KgS<sup>-1</sup> of 25% (by mass) NaCl solution is concentrated to 60% in a continuous evaporator. Calculate the production rate of concentrated solution and the rate of water removed from the evaporator.
8. An equimolar mixture of ethane and propane is fed to a distillation column at the rate of 60molS<sup>-1</sup>. 75% of the ethane is recovered in the top product which has an ethane mole fraction of 0.9. Calculate the flow rates top and bottom products and the composition of the bottom product.
9. 80mol of ethane is burned in a furnace with 50% excess air. A conversion of 90% is achieved. Calculate the composition of the stack gas.

### 7.0 REFERENCES/FURTHER READING

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## **MODULE 3**

Unit 1: Selected Oil and Fats

Unit 2 Soaps and Detergents, Sugar and Varnishes, Glass, Ceramics and Cement

Unit 3 Plastics, Wood pulp and paper

### **UNIT 1 SELECTED OILS AND FATS, SOAPS, DETERGENTS, SUGARS, VARNISHES AND PLASTICIZERS**

#### **CONTENTS**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
  - 3.1 Selected Oils and Fats
  - 3.2 Essential oils
  - 3.3 Detergents
  - 3.4 Soaps
  - 3.5 Sugars
  - 3.6 Varnishes
  - 3.7 Plasticizers
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Question
- 7.0 Reference/Further Reading

#### **1.0 INTRODUCTION**

Fats and oils are esters of higher fatty acids and other acids with glycerol. Thus, oils and fats are esters of glycerol and fatty acids. The esters of glycerol are commonly known as glycerides. Fatty acids are both saturated and unsaturated. We know that soap lowers the surface tension of water and lowering the surface tension can easily be affected by dissolving soap in water. This property of soap is an important factor in the cleansing action. There is another important property of soap solutions which plays more important action in the cleansing property of soap. This property is the emulsification of fats and oils.

In the light of the two important properties of the cleansing power of soap, attempts were made in Germany and other countries owing to shortage of fats during the First World War,

to produce other substances called detergents, very different in chemical nature from ordinary soap or salt of a fatty acid. For example, some acids were first prepared by the action of sulphuric acid on higher unsaturated hydrocarbons containing 10-18 carbon atoms. The sodium salts of these acids were found to reduce the surface tension of water and to have valuable wetting and detergent properties. Substances which lower the surface tension of water are commonly known as surface active substances. Surface active substances when dissolved in water, dispersed in liquid and wash a surface clean by removing oil in which dirt particles are dispersed. A detergent may be regarded as a chemical formulation which essentially consists of surface active agent or surfactants and subsidiary constituents such as fillers, builders, boosters etc.

Cane sugar is used all over the world as a sweetening agent, being the important sugar economically. Cane sugar or sucrose ( $C_{12}H_{22}O_{11}$ ) occurs in sugar cane, beat maple, sweet sorghum and some species of palm. Many sweet fruits, such as pineapple, apricot, ripe banana, etc. also contain sugar or sucrose. Sugar supplies man with about 13% of the energy required for existence. Sucrose occurs in nature in sugar cane and sugar beet. Its concentration in lower part of sugar cane is greater than that in the upper parts. The cane sugar or sucrose industrially is based on extraction of sucrose from sugar cane and sugar beet. Sugar cane contains 70-75% water, 10-15% crystalline sugar, 0.5-1.0% reducing sugar, 10-18% fibre, 1% ash and 1% organic acid.

A varnish may be regarded as an un-pigmented colloidal dispersion or solution of natural or synthetic or both resins in oil in absence or presence of thinners. They are used as a protective or decorating coating for various surfaces. They dry on the surface by evaporation, oxidation and polymerization of its constituents.

## 2.0 OBJECTIVES

The objectives of this unit include the following:

1. To distinguish between fats and oils.
2. Explain in detail some selected oils and fats.
3. Understand the use of fats and oils in the production of soap and detergents.
4. Discuss the use of cane sugar in the manufacture of sucrose.
5. Explain the types of varnishes, how to manufacture varnishes and their uses.



### 3.0 MAIN CONTENT

#### 3.1 SELECTED OILS AND FATS

Oils are generally characterized by being water repellent and insoluble in water. They are emulsifiable and have solvent properties for organic substances. They are emollient and greasy to the touch. They have low volatility and are liquid at 20°C.

Fats are similar to oils but being solid at 20°C, spreading properties are limited. There is no difference between a fat and oil as far as chemical properties are concerned. Researchers have shown that all natural fats and oils consist of mixed glycerides. The difference between a fat and oil is merely physical, one of consistency. Those melting above 20°C are called fat by convention and those melting below 20°C are called oils. Oils contain large proportion of glycerides of unsaturated acids while fats contain a large portion of saturated fatty acids. Coconut oil and ghee are fat in winter and oil in summer. The fatty acids in natural fats and oils have almost invariably an even number of carbon atoms.

#### **Vegetable oils**

The important oil of this category are castor oil, cotton seed oil, coconut oil, soya bean oil, hempseed oil, palm oil, peanut oil, rapeseed oil, tung oil e.t.c. The two general methods for the manufacture of vegetable oils and fats are expression and solvent extraction. The solvent extraction method is widely used.

#### **Manufacture of Soya bean oil by solvent extraction.**

The seeds of the soya bean are cleaned by screening and small thin sticks, chaff and dirt are removed by blowing with air. The cleaned weighed seeds are first cracked or crushed by feeding through a hopper into the crushing chamber of corrugated rolls. These rolls are provided with grinding plates. The seeds falling from above on appropriate guide plates are gradually crushed between the rolls. The crushed material is then cooked or conditioned at low temperature in a stacked cooker or a rotary steam tube heater. Heating is necessary for easy flow of oil and coagulation of the albumin. The heated crushed material called **Meat** is then rolled into thin flakes of equal weight in moulding machines and slowly charged into a solvent extractor which works on a counter current extraction principle. The extractor consists of a number of baskets moving in a circular, vertical or horizontal direction. The crushed seeds are placed on a perforated false bottom of the extractor and the benzene or the hexane (solvent) is superheated to appropriate temperature and passed through the perforated baskets into the material. A portion of the solvent together with oil or fat condenses in the

space below the false bottom. The uncondensed solvent vapour along with that expelled from the oil or fat is led away through an outlet pipe by steam coils. This vapour of the solvent is again condensed together with water in a condenser. The solvent is separated from the water in a separator and the separated solvent is transferred to the vapouriser. The extraction is complete when no steam passes out with the solvent vapour. The oil or fat collected at the bottom of the extractor is blown with steam in order to remove solvent associated with oil or fat. The latter is taken out of the extractor, screened, filtered and stored for refining. The crude oil obtained is further refined to **remove (i) suspended, dispersed and dissolved impurities (ii) colour and odour (iii) saturated glycerides**. The overall processing of crude vegetable oils usually involves alkali refining, water washing and drying, bleaching, hydrogenation and deodorizing.

### **Animal oils**

These are fatty acid glycerides isolated from animal sources. They may be land animal oils such as neat foot oil, marine animal oil such as cod liver oil, sardine oil and blubber oils such as whale oil. Neat foot oil is used for lubricating delicate parts of sewing machine, clocks, mobile base gums etc. Cod liver oil is used in medicine and blubber oils are used as illuminants and in soap making. Lower grade blubber oils are used in leather dressing, lubrication and tempering of steels.

### **Cod liver oil**

This oil was first prepared by storing the fish in barrels and then allowing them to rot until the oil floats on the top. It is now prepared by live steam cooking of the livers and other parts of the cod and halibut for about half an hour. As a result of steam cooking white scum floats on top, which is allowed to settle for some time, then decanted and finally strained. It is used in leather dressing for poultry feed and for medicine (it contains vitamins A and D). Before the oil is used as medicine it is filtered, bleached and then used.

### **Mineral oils**

The oils are generally isolated from petroleum. Hence, they are mineral in origin. These are mixtures of various hydrocarbons of different molecular weights and varying degrees of volatilities. These oils are used as illuminants, as fuels in automobiles and power industry. They are also starting materials for gaseous fuels, as source of petrochemicals and fertilizers,

as solvent in dry cleaning, as source of carbon black and for making lubricants of various grades. Example of mineral oil is Kerosene oil.

### **Hydrocarbon oils**

Crude petroleum is essentially a mixture of gaseous, liquid and solid hydrocarbons obtained from oil wells. It appears as a dark brown, strong smelling fluid. Often some organic compounds other than hydrocarbons are also present in varying amounts. For example, sulphur compounds with strong unpleasant odour, occur in petroleum in varying amounts. According to the nature of the crude, the first step in refining is either a wash with caustic soda solution or distillation. The lighter liquid fractions are distilled off at atmospheric pressure and later high boiling fractions are separated under reduced pressure to get solvent spirit, naphtha, kerosene, motor spirit, gas oil, diesel oil, stock for conversion into white oil and finally lubricating oil. The stock which provides the white oil is high lubricating oil fractions collected at a controlled viscosity and represents about 8% of the crude. Although, all crudes do not contain paraffin wax but when it is present, it distills over with the lubricating oil fractions including the white oil stock and it can be removed by making use of special process. Some crude oils leave residues after distillation which can be filtered through bleaching earths to give petroleum jelly or petroleum as a colloidal jelly. When paraffin wax is present in the white oil stock in significant amount, it can be extracted along with aromatic hydrocarbons by washing once or twice with liquid  $\text{SO}_2$  under pressure at 30-50°C. The paraffin wax and the aromatic stock extracted is next treated in several stages with oleum and the sludge is separated after each stage of centrifuging. Valuable aromatic sulphonates are recovered from sludge. The oil is then washed with dilute caustic soda solution in a mixture of water and alcohol to remove acidic substances and it is finally brightened by treating with bleaching earth. Deodorized kerosene is not derived from white oil but it is highly refined kerosene fraction.

### **3.2 ESSENTIAL OILS**

These are pleasant smelling, highly volatile liquids, widely distributed in various types of plants and are also known as volatile liquids. Examples are turpentine oil, oil of cloves, oil of eucalyptus etc. Common natural sources of these oils are buds, flower petals, bark, leaves, roots etc. Their chemical origin varies widely because of the different functional groups present in them. For example, linalool (sandal oil, lavender oil) contains alcoholic groups,

Citral (lemon grass oil) contains aldehyde group, Eucalyptus oil of the winter green contains ester group, cymene contains hydrocarbons and eugenol (Bay oil) contains phenolic group.

Essential oils are colourless in pure state but light yellow in crude state. They are soluble in organic solvents in all proportions. They are steam volatile with decomposition in some cases. They impart a greasy stain on paper which disappears on warming or on solvent washing. The oils are generally isolated by the following techniques:

(a) Expression method (b) Distillation method (c) cold fat extraction method (d) extraction with volatile solvent

In expression method, the fruit is halved and then placed in water for some 5-6 hours and then pressed against a sponge. As a result, oil ejects out.

In distillation method, the steam distillation is carried out under atmospheric pressure and then the condensate is fractionated.

In cold fat extraction method, an extraction mixture consisting of 1 part of tallow, 2 parts of lard and 0.6% benzoin is spread in thin layers on rectangular wooden frames over which flower petals are distributed and allowed to remain there for about 8-10 weeks. During this period, the fat becomes saturated with the oil. The alcoholic solution of the fat extracts deposits fat on cooling, leaving oil in the solution. The oil is recovered by evaporating the solvent.

Extraction with a volatile solvent e.g. petroleum ether and evaporation of solvent gives the oil in the semi solid form, because of much accompanying wax. Fractionation of the semisolid oil gives the oil. The solvent used for the purpose should be non flammable, chemically inert and highly volatile.

Essential oils are widely used in making perfumes, toilet waters, chewing gums, toothpastes, beverages and in the manufacture of lacquers, inks, varnishes, greases, and lubricating oils.

### 3.3 DETERGENTS

The detergent may be in the form of a solid, liquid, paste or powder. The modern concept of surface active agents or surfactants includes soaps, detergents, emulsifier, wetting agents and penetrants. This is probably due to the fact that these chemicals owe their industrial application to their ability to modify the surface properties of liquids in which they are dissolved. Hence, these substances which have the property of altering the conditions at interfaces are called surface 'active agents or surfactants'. The modern theory of the action of surface active agents or surfactants relates to the process of adsorption. The inherent property of surface active agents to adsorb at interfaces results from their molecular structure. There

are essentially two parts of the molecule – a hydrocarbon chain and a polar group. The hydrocarbon chain consists of 12-18 carbon atoms and the polar group may be carboxylate, sulphate or sulphonate e.t.c. If the hydrocarbon chain is smaller than this, the compound is expected to be lacking in surface activity but if the carbon chain is too long, it will result in the surface active agent having a limited solubility in water. The hydrocarbon chain has an affinity for fatty acids, greases and similar long chain compounds, whereas the attached polar group will have an attraction for water or aqueous solution. If solvent is water, the hydrocarbon chain may be regarded as the hydrophobic group and polar group. The hydrophobic group may be of complex nature and may contain both straight chain and ring compounds. Soaps are important class of surface active agents. They can be represented as RCOOX where R is the hydrophobic group and X is usually an alkali metal. Example is sodium laurate,

$\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$ , Soap ionize in water to some extent as:



The active hydrophilic group in it is anion  $-\text{COO}^-$ . Hence, soaps are classified as anionic surfactants. For a long time, soaps were only known surfactants and they were not only different but inexpensive too. Sodium and potassium soaps, used in proper conditions are probably the best available detergents and wetting agents. However, they have two serious disadvantages. They form insoluble Ca and Mg salts.



**Ca**



This condition is particularly troublesome for washing purposes in areas where water is hard. Soap is lost by precipitation as the calcium salt which also tends to settle as scum on washed clothes or textiles. Secondly, soaps are inactivated in acid conditions in which hydrolysis takes place to give un-dissociated fatty acids.



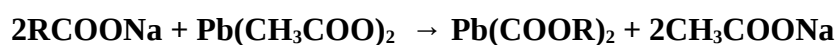
In order to remove these deficiencies of soaps, search for other surface active agents started so that they can perform efficiently in hard water. In Germany, in 1930, researchers observed that the sodium salts of the higher molecular weight of alcohol sulphates had properties similar to those of soaps. These new surface active agents were found to be similar to

detergency, wetting and foaming power to soap, but their Ca and Mg salts were found to be soluble in water.

The substitutions of the sulphate group  $-\text{OSO}_2\text{O}^-$ , or the sulphonate group  $-\text{SO}_2\text{O}^-$  in place of  $-\text{COOH}$  group of soap gave products of greater water solubility. This discovery gave impetus to the search for further surface active agents and to the development of the synthetic detergent industry. Synthetic detergents and wetting agents of varied chemical nature and with properties which make them especially suitable for specific purposes are now being manufactured. They find extensive use not only as detergent substitutes for soaps but also as wetting agents in dyeing to increase the effectiveness of insecticide spray and for many other purposes. A large amount of edible oils and fats, which is being consumed in the manufacture of soap, has now become available for human consumption by the introduction of soapless detergents. In general, the synthetic detergent is used to indicate a synthetic material which is used for cleaning and usually does not include soap. The cleansing action of surface active agents (present in detergents) depends upon the property of decreasing surface tension or interfacial tension at the boundary surface between two phases of matter (liquid-gas or liquid-liquid). The most important advantage of the synthetic detergents is better wetting and cleansing action and low solubility in hard water because of higher solubility of their  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.

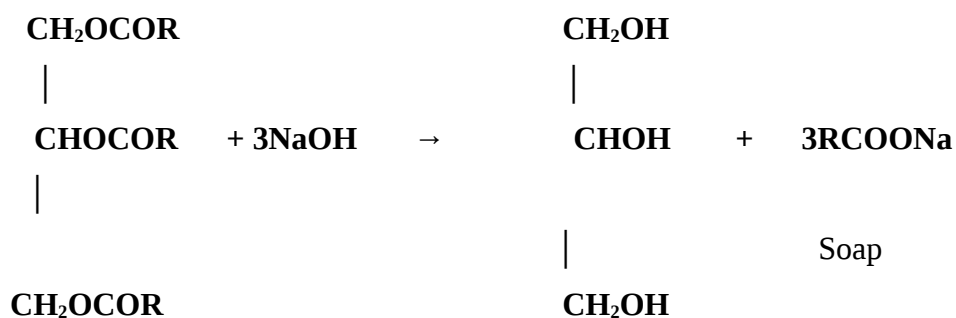
### 3.4 SOAPS

Soaps are the members of anionic class of surfactants because active hydrophilic group in these are the anions  $-\text{COO}^-$  group. Water soluble soaps are formed when fatty acids are neutralized with KOH or NaOH. A large proportion of soap used for cleansing is sodium soap which is the neutralization product of fatty acids such as Lauric, Palmitic, Oleic and Myristic acids. The sodium soaps are called hard soaps and may be in form of bars, cakes, powders and flakes. The potassium soaps are called soft soaps and have a greater solubility in water. These are generally used in liquid soaps. Among the non-cleansing metal soaps are the aluminum, calcium, magnesium and zinc soaps. These soaps have been used in polishes, printing inks, paints, lubricating oils and emulsions. Soaps of heavy metals are generally prepared by double decomposition.



Sodium soap    lead acetate            lead soap                    sodium acetate

Oils and fats consist essentially of triglycerides of fatty acids and are used as raw materials in the manufacture of soaps. When the oil or fat molecule is allowed to react with NaOH in the presence of water, soap and glycerol are formed.



### Glycerol

Selection of oil and fat blend for this reaction needs a careful study so that a product of desired properties can be obtained. The final product will depend on the fatty acid composition of the oil or fat. For example, a blend of 80% tallow and 20% coconut oil will produce a product suitable for toilet soaps when subjected to saponification but 80% tallow and 20% olive oil would give an entirely different product. The range of oils and fats used in soap making depends on the availability and composition of the raw material. The most common soap making fats include: tallow, coconut oil, fish oil, cotton seed oil, whale oil, palm kernel oil, soya bean oil, castor oil and linseed oil. A serious problem in soap making is the rancidity of oils and fats, perhaps due to the oxidation of the free fatty acids produced by partial hydrolysis. Rancidity can be prevented by

- 1) Storing the fats and oils in a moisture free atmosphere.
- 2) Using stainless steel containers
- 3) Bleaching
- 4) Hydrogenation of oils and fats
- 5) Adding an anti-oxidant

One of the most common methods of manufacturing soaps is full boiled process. This process produces good quality soap and glycerol will be recovered as an important byproduct. In this process, oils and fats are boiled in open kettles using steam coils with NaOH until all the fats are completely saponified. Large amount of NaCl are then added and the sodium soap is precipitated from the reaction mixture. Because of salting out process, the soap rises to the surface and is skimmed off. Soaps made by this process are superior in colour and texture. Potassium soaps can be salted out easily and are usually prepared by the semi boiled process

in which the fats and equivalent amount of KOH are added. It is difficult to ensure that the proportions of the two reactants are correct so that there will be no excess of either.

### 3.5 SUGAR

#### Manufacture of Cane Sugar

Procedures of manufacture of sucrose from cane sugar are as follows:

- 1) Extraction of juice
- (2) Purification of juice
- (3) Concentration of juice
- (4) Crystallization
- (5) Separation of crystals
- (6) Drying and bagging

**Extraction of Juice:** The cane is first washed to remove mud and trash. It is then cut into small lengths by means of sharp rapidly moving knives (500-600rpm) fitted on a horizontal shaft and then dropped over a moving belt, called cane carrier to be carried to the extractor consisting of one-two rolled toothed crusher and four three rolled grooved mills. The crusher fitted with a set of revolving knives makes diagonal cuts, converting the cuts into chips. The juice is then extracted by passing the crushed cane or chips through a series of mills each of which consists of three groomed rolls that exert pressure of about 3 to 6 tonnes per square inch. When the chips are fed into the crusher, they pass through the rollers to extract about 50% of the juice. The bagasse containing 50% of the juice is then introduced into the first mill. Before passing the bagasse to the first mill, the juice from the second mill is sprayed on the bagasse for efficient pressing. Juice extracted in the first mill is collected in the strainer below, from where the juice is transferred to the raw juice tanker. About 90-96% juice is extracted from the cane and the spent cane baggasse is collected in the storage which is burned as fuel or is used in the manufacture of paper, hard board or insulating material.

**Purification of Juice:** The liquor is defected i.e prepared for filtration and classification by removing solid impurities. After removal of suspended impurities, the juice is at once transferred into defection tank. The syrup is then neutralized by adding adequate amount of milk ( $\text{Ca}(\text{OH})_2$ )

Of lime till the pH reaches 7-7.3. The limed juice is then passed through a tubular heater where it is heated to boiling. The hot limed juice is then poured into settling tanks, where it separates into three layers. The precipitated matter, which forms a thick scum at the surface forms the upper layer, and lies below the top layer and above the bottom layer, the middle layer is clear juice. The mud containing heavy precipitates forms the bottom layer. The thick scum layer (top layer) and mud layer (bottom layer) are removed mechanically by passing through a filter press. It has been found that simple defection process by making use of lime does not eliminate all the impurities completely. Hence, by crystallizing the concentrated



juice called syrup, a coloured, crystalline sugar, known as raw sugar is obtained instead of white crystalline sugar. The raw sugar is then clarified by conversion into white crystalline sugar by a refining process i.e by either sulphatation or carbonation process or both processes used simultaneously.

**Concentration:** The clarified juice is concentrated into thick syrup under reduced pressure in multi effect vacuum evaporators. From the last evaporator in the multi effect vacuum evaporators, pale yellow thick syrup is led into the syrup tank as concentrated raw sugar.

**Crystallization:** The syrup liquid is further concentrated by removing most of the water by heating in a single effect evaporator called vacuum pan. The concentrated syrup is then led to crystallizing tanks and cooled slowly when crystals of sugar separate out.

**Separation of Crystals:** Crystals of sugar are then separated from molasses (mother liquor) by whirling in centrifugal machine, which is composed of a perforated basket revolving at a speed of 1200-1450rpm suspended on the lower end of a vertical shaft, the upper end of which is held on a roller bearing. As a result of high revolving motion, the catalysts are easily separated and liquid portion drains out. Last traces of molasses still sticking with the crystals are removed by spraying cold water on the crystals and whirling again in the centrifugal machines. Single centrifuging is sufficient if raw sugar is manufactured. Double centrifuging becomes necessary when white sugar is produced in the sugar factory and not by refining raw sugar.

**Drying:** The crystals of raw sugar obtained after centrifuging are dried by dropping them in a long pipe through which hot air or super heated steam is passed and finally bagged.

### 3.6 VARNISHES

#### Types of Varnishes

- 1) **Spirit Varnishes:** These are solutions of natural resins such as shellac, rosin, copal, damer, kauri gum etc in methylated spirit or other completely volatile non film forming solvent. These varnishes dry more rapidly but undergo cracking and peeling in the absence of plasticizers.
- 2) **Oleoresinous Varnishes:** These are solutions of one or more natural or synthetic resins in a drying oil and a volatile solvent. Some plasticizers may also be added to the oil. Urea formaldehyde resin, phenol formaldehyde resin, vinyl resin, melamine formaldehyde resin etc are the synthetic resins that have been used for making these varnishes. Oils used are linseed oil, soya bean oil, tung oil, castor oil and tail oil etc. Turpentine or solvent naphtha is used as a solvent.

Since varnishes do not contain any pigment, they are less resistant to light than are paints, enamels and pigmented lacquers. Thus, varnishes differ from paints in that they have no pigments. In varnishes, a part or whole of the oil is substituted by resin. Drying of oils result in the formation of highly polymerized products which are quite similar to resin, so oil is replaced by resin

Raw materials used in the manufacture of varnishes include the following:

- a) **Film Forming Materials:** These are drying oils and resins. The drying oil may be of vegetable origin such as linseed oil, tung oil, castor oil, soya bean oil, coconut oil, cotton seed oil etc and fish oil such as sardine oil. The resins used may be natural such as copal, manila, shellac etc or synthetic such as oil soluble phenol, formaldehyde resin, alkyds, chlorinated rubbers, and melamine and urea formaldehyde resins. Cellulose derivatives such as cellulose nitrate, cellulose acetate, ethyl cellulose etc are also used in the film forming material. The purpose and function of the film forming materials is to form protective film. They also act as binders for pigments when the solvents are evaporated and the varnish oil is dried.
- b) **Solvents and Thinners:** These are necessary for dissolving the resins and control of flow characteristics i.e. viscosity of film-forming materials. The common solvents used are turpentine oil, petroleum spirits, kerosene, dipentene, aromatic and aliphatic naphtha, xylol, alcohols, toluol etc
- c) **Driers:** These are used only in case of oleoresinous varnishes to increase the rate of drying or hardening of the varnish film. Driers are inorganic such as oxides carbonates and borates of Co, Pb and Mn, or organic such as oil soluble linoleates, napthanates, resonates and tallates of Pb, Mn, Co and Zn
- d) **Antiskinning Agents:** These are guaiacol and tertiary amyl phenol
- e) **Plasticizers:** These are used in the manufacture of spirit varnishes to prevent film brittleness. Tricresyl phosphate, dibutylphthalate etc are used as plasticizers.

### 3.7 PLASTICIZERS

Spirit varnishes are solutions of natural resins in volatile solvents such as methylated spirit, hydrocarbons, ketones etc. Spirit is used in presence of suitable plasticizers (otherwise they are likely to be cracked and peel off from the surface). The preparation involves active stirring and sometimes heating to bring about the desired solution.

Spirit varnishes are prepared by simply mixing the natural resin and solvent in a barrel. Stirring is continued till the resin is completely dissolved. The solution is allowed to settle,

filtered and the filtrate is heated for thorough mixing of resin and solvent and to attain a desired viscosity. For spirit varnishes with synthetic resins, it is necessary to bake the resin for some desired characteristics to be followed by tempering with plasticizers for achieving the desired adhesion properties. In the preparation of spirit varnishes, if the resin is cellulosic, use of mixture of more than one solvent in small amounts is a common practice. An example of spirit varnish is the solution of natural resin, shellac in alcohol.

Oleoresinous varnishes are solutions of natural or synthetic resin in a drying oil containing driers and thinners. Some natural resins such as kauri gum are not soluble in oil. In such cases, varnish is prepared by de-polymerizing of the resins by heating with constant stirring at 300-350°C until the foaming ceases. The hot natural resin is then mixed with preheated drying oil and again heated until correct viscosity is attained. The solution is then cooled to about 200°C and then thinner and drier are added. If the natural resin is soluble in oil, then the resin is heated with preheated oil at about 300°C up to correct viscosity.

In the case of synthetic resins, preheating of the oil is not necessary. The resins and the oils are heated together until homogenous solution of desired viscosity is obtained. The solution is then cooled to 200°C and thinner and drier are added. The solution is again cooled to room temperature and clarified by titration or centrifuging, followed by ageing in long tanks to remove insoluble matters. Liquid driers such as metallic naphthenates may be mixed at the time of cooking, if there is no marked tendency of the varnish to go skin formulation. If a varnish undergoes some degree of skin formation, some anti-skinning agents such as aguaiacol, catechol or their derivatives along with driers are desirable to be added just before packing in evacuated containers.

#### **4.0 CONCLUSION**

The manufacturing processes for some selected oils and fats as well as their applications in industrial production were well established especially in the production of detergents and soaps. Firm forming materials, solvents, thinners, driers, anti-skinning agents and plasticizers are the principal raw materials in the manufacture of varnishes.

#### **5.0 SUMMARY**

Some selected oils and fats have been studied. They include vegetable oils (cocoa nut, soybean oil, castor oil etc), animal oil (neat oil, cod-liver oil, whale oil etc), mineral oil, hydrocarbon oil and essential oil. Also detergents and soap were treated as well as sugar. The procedure for the manufacture of sucrose from cane sugar involves extraction, purification, concentration, crystallization, separation of crystals and drying and bagging. There are two types of varnishes viz spirit varnishes and oleo resinous varnishes. These varnishes are made principally from firm forming materials, solvents and thinners, driers, anti-skinning agents and plasticisers. The preparation of varnishes was also discussed.

## 6.0 TUTOR-MARKED QUESTIONS

1. Differentiate between fats and oils.
2. Give examples of each of the following
  - i. Animal oil.
  - ii. Vegetable oil.
  - iii. Hydrocarbon oil.
  - iv. Mineral oil.
  - v. Essential oil.
3. Discuss any technique for isolation of essential oils.
4. With equations, explain in detail production of soap.
5. Explain how rancidity of oils and fats can be prevented.
6. Discuss the manufacture of sucrose from cane sugar.
7. State and explain any two types of varnishes.
8. Discuss the raw materials used in production of varnishes.

## 7.0 FURTHER READING

1. Sharma, B. K (2014). Industrial chemistry, including chemical engineering, 18<sup>th</sup> edition, Krishna Prakashan Media Ltd, India

## **UNIT 2 GRASS, CERAMIC AND CEMENT**

### **CONTENT**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
  - 3.1 Glass
  - 3.2 Ceramics
  - 3.3 Cement
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Question
- 7.0 References/Further Readings

### **1.0 INTRODUCTION**

Physically, glass may be defined as a hard, rigid, under-cooled, brittle, non- crystalline substance having no definite melting point and sufficiently high viscosity to prevent crystallization. It is usually transparent but sometimes opaque or translucent. Chemically, glass may be defined as a fused mixture of silicates, alkali and alkaline earth compounds and other constituents such as calcium oxide, magnesium oxide, tin oxide, barium oxide and lead oxide. Glass is completely a vitrified product. As can be seen, glass has no definite composition. However, glass consists of major and minor ingredients. Major ingredients are sand, lime and soda ash. Minor ingredients include borax, boric acid, potash, zinc oxide e.t.c. These minor ingredients are added to give certain properties to glass. Lime, silica and ash still form over 90% of all the glasses of the world; and are considered as the major ingredients.

Ceramics include all articles which are essentially silicates. In a restricted sense, those articles which are made of clay are mainly known as ceramics. The term ceramics is derived

from the old Greek word keramos, meaning pottery and has its root in older Sanskrit word meaning to burn. Ceramics are therefore called clay products or pottery products. Nowadays, we understand ceramics not only as the manufacturing of pottery articles but also as the manufacture of all those articles in which clay or similar plastic raw material is used and which after having been shaped and dried, are subjected to a firing process to make them hard or give them the desired mechanical strength. The definition is very broad and covers a large variety of products such as table ware, crockery and decorative ware, sanitary ware and industrial ware etc.

## 2.0 OBJECTIVES

The objectives of this unit are to:

1. Understand the meaning of glass.
2. Be able to explain some physicochemical properties of glass.
3. Discuss the steps used for the manufacture of glass.
4. Identify industrial applications of glass.
5. Explain the meaning of ceramics.
6. Discuss the properties and uses of ceramics.

## 3.0 MAIN CONTENT

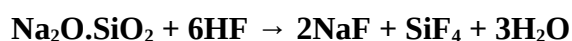
### 3.1 PROPERTIES OF GLASS

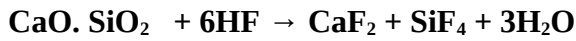
#### Physical properties of Glass

- 1) They are usually transparent amorphous solid.
- 2) Glass is completely a vitrified product.
- 3) They are hard and rigid; and they have no definite melting point.
- 4) They have sufficiently high viscosity
- 5) They are insulator of heat and electricity.
- 6) They can incorporate colouring material, preserving transparency.

#### Chemical properties

- 1) Glass is not attacked by air or oxidizing agents.
- 2) Ordinary glass is readily attacked by alkalis but very resistant to acids, except hydrofluoric acid. Glass is a silicate and HF reacts with it to form  $\text{SiF}_4$  and fluorides of metals.





- 3) Ordinary glass is alkaline in reaction. Water slowly reacts on glass to form NaOH. This reaction is enhanced in the presence of acids. If glass bottles containing acids are kept for a long time, silicic acid will be found to be deposited on the glass of the bottles. The glass known as neutral glass of which Pyrex is an example contains very small amount of silicates.

### Characteristics of Glass

The most important characteristics of glass can be summarized as follows:

- (a) Hardness (b) Transparency (c) Refractive capacity (d) Dispersive capacity (e) Low coefficient of cubical expansion (f) High electrical insulation (g) Low thermal conductivity (h) Capacity of absorbing decorative colours without loss of transparency (i) Chemical inertness under ordinary conditions. In order to suit different purposes, it is possible to modify any or all the above characteristics of glass.

### Methods of Manufacture

The following steps are used for the manufacture of glass.

- 1) Formation of batch material
- 2) Melting
- 3) Shaping
- 4) Annealing
- 5) Finishing

### Formation of Batch Material

The lumps of ingredients such as limestone, burnt limestone, dolomite, feldspar e.t.c are crushed to coarse powder. Other ingredients such as quartz sand, soda ash e.t.c are also obtained in proper particle size. The requisite quantities of different ingredients are separately weighed and then mixed uniformly in the form of coarse powder. The mixture of powdered ingredients is called batch material. For white glass, the batch material is given in the Table 1. Batch for other types of glass can be seen elsewhere.

Table 1: Batch material for white glass

Ingredients	Parts
Sand (SiO <sub>2</sub> )	1000
Red lead (Pb <sub>3</sub> O <sub>4</sub> )	440

Potash	290
Borax (Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> )	200
Gold chloride	0.36

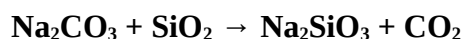
The batch is now transferred either to the tank of a tank furnace or to the pot of a pot furnace for melting purposes.

### Melting

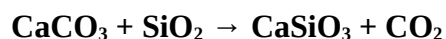
The batch is mixed with cullet to lower the melting point. The pot or tank is filled to the desired height. The pot or tank is heated to about 1400°C. At this temperature, the material melts and reacts to form molten glass. As the charge melts, test samples are drawn out from the tank or pot on an iron hook. When the melted glass is transparent and free from bubbles of CO<sub>2</sub> and SO<sub>2</sub>, it is said to be plain. The tank or pot gradually fills up with the molten glass. When the glass line level in the furnace is reached, the process of heating is stopped and the furnace is allowed to cool. The process of charging, melting, refining and drawing for shaping proceeds continuously. The molten glass is sent to the refining end. At the refining end, the molten glass becomes free from small bubbles of gas called *Seeds*. From the refining end, the melt passes to the drawing chamber surrounded by working pits. The temperature in the drawing chamber and working pit is maintained at about 980°C. Undecomposed sulphates and chlorides of calcium, alkali metals and aluminium along with various other ingredients rise to the top in the form of a scum called GLASS GALL. The glass gall is easily skimmed off. The shaping is done by drawing the melt from the working pits.

### Chemical reactions in the furnace

Glass is a solid solution with no definite composition. However, ordinary glass may approximately be written as **Na<sub>2</sub>O.CaO.6SiO<sub>2</sub>**. When quartz or silica is heated with soda ash (Na<sub>2</sub>CO<sub>3</sub>), the silica being an acidic oxide displaces the carbonic acid from the carbonate, and a compound known as Sodium Silicate is formed.

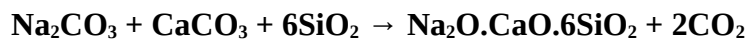


When this is allowed to cool, it solidifies to a glassy mass known as water glass, which is soluble in water. The limestone (CaCO<sub>3</sub>) also reacts with silica to give a glassy mass on cooling known as calcium silicate which is insoluble in water but soluble in acids.

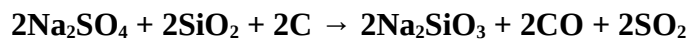




But if silica is simultaneously fused with  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$  (soda ash + limestone), sodium calcium silicate is obtained which sets to a glassy mass on cooling and it is insoluble in both water and acids.



Sometimes, a mixture of salt cake, sodium sulphate and charcoal is fused with sand and limestone to get glassy mass.



However, because of the above reactions, gases are produced and the gases remain in the melted glass and set the melt to a state of ebullition, thereby achieving a uniform heat distribution throughout the melt. They also serve to homogenize the composition of the melt, which slowly progresses towards the consistency of glass. If the gas is in the form of small bubbles, seeds are said to be there in the glass but if the gas is in the form of big bubbles, molten glass is said to have boils. These defects are always skimmed off from the top of working pits. The process of removing these defects (seeds and boils) is called *Refining*.

### **Shaping or Forming**

The manufacture of different types of glass wares from the molten glass is shaping or forming. Glass may be shaped either by hand moulding or by machine.

Hand moulding involves blowing both the wares and sheet or plate glass with the air from the lungs. Continuous mechanical process is a mechanized process of shaping or forming in which collection of glass, blowing of the article with the help of moulds, removal of the article from the moulds after final shaping e.t.c are all carried out continuously and automatically. Forcault and Colburn processes have widely been used as mechanized processes for the production of sheet or window glass.

### **Annealing**

If the articles manufactured above are cooled suddenly, glass being a bad conductor of heat is likely to develop great internal strain and likely to crack or break on heating or even on keeping for some time. The glass cannot withstand change of temperature or shock. The internal strain is also caused due to lack of uniformity. In order to avoid this cause, all the articles should be kept above the critical or annealing temperature for a sufficiently long time. Since glass is an insulator, rapid cooling will cool the surface of the glass more quickly than the internal portion, causing an internal strain. To avoid this, glass must be cooled very

slowly with this process of slow cooling which is used to reduce strain is known as *Annealing*. It is therefore necessary to anneal all types of glass whether formed by machine or hand mould methods. For every type of glass, there is a definite annealing temperature and if glass is maintained as near this temperature as possible, strain is rapidly removed. Annealing is usually carried out by passing the article through several hot chambers (lehrs) around the furnace, the temperatures of which gradually falls. Thus, annealing makes the glass wares more durable and resistant to shock and change of temperature. The chambers in which glass ware is stacked and the chamber is heated up and then cooled slowly by closing the chamber from all sides is called **Annealing chamber**.

### **Finishing**

All types of annealed glass require finishing. Finishing is usually carried out by cleaning, washing, grinding, polishing, cutting, sand blasting, enameling, grading and gagging. Washing and cleaning are of course, applied to all kinds of articles, although the methods are adopted according to the requirements.

### **Uses of Glass**

Glass is used in diverse areas of human needs namely in:

- 1) Building for protective and decoration purposes.
- 2) The laboratories e.g chemical laboratories for construction of laboratories wares.
- 3) The food and beverage industries for packaging of products.
- 4) Pharmaceuticals and hospitals for packaging and construction of hospital equipment.
- 5) Households for domestic uses.
- 6) The oil and gas industries for sundry appliances.
- 7) Electrical, electronic and computer industries and in many other industrial applications.

## **3.2 CERAMICS**

“CERAMICS” originates from Greek word – “keramos” meaning burnt stuff, previously referring to products from natural earths that have been exposed to high temperatures. Modern definition refers to all engineering materials or products (or portions thereof) that are chemically inorganic, except metals and alloys that are made serviceable through high temperature processing.

### **History of Ceramics**

The first products were hand-moulded articles baked by the sun or campfire. It was suspected that ceramics (pottery) was accidental instead of by design; the early man used baskets made of reeds and lined with mud. When one of such baskets fell into fire, the basket burnt off but the clay became harder and rock like, with that singular event triggered off the ceramic industry as we know it today.

Pottery making is traced to the Egyptians, in that they produced vessels that were red in colour and they later added figures and patterns. It was during the reign of Pharaoh Amenhotep III (2718BC) that pottery became very decorative. Chinese ceramic authorities claim their enameled ware was produced around 2698BC. The Greeks had theirs around 2200BC. While the Egyptians wares had red patterns, the Chinese improved on this and produced cobalt-blue colours but the Greeks produced highly polished wares. The industrial revolution ushered in a critical demand for ceramic products. Ceramic materials are very useful inputs for chemical, electronic and allied industries.

### **Types of Ceramics**

The first classification is based on temperatures at which the ceramics materials are used and sub classified on their porosity.

The other classification groups ceramic material according to method of production and placing in order of increasing economic use. Such as:

- a. **Abrasives:** An abrasive is any substance that is applied for grinding, rubbing down or polishing surfaces. Natural abrasives are further classified into; high grade natural abrasives, siliceous natural abrasives and the miscellaneous forms (diamond, emery, boron and garnet) are all natural abrasive materials.
- b. **Porcelain Enamel:** It is defined as a glazed or unglazed vitreous ceramic white-ware that is used for technical purposes while china is used for non-technical purposes as in house-hold utensils, baths, etc.
- c. **Refractories:** A refractory material is defined as that material that is capable of withstanding high temperatures without undergoing any perceptible deformation or breakage. They are used for lining of kilns, furnaces and ovens
- d. **White wares:** As the name suggests, are a class of materials that are white (often cream) in colour after firing. The white colour is due to the mineral content or complete absence of iron oxide. White wares are a blend of refractory bodies and glossy coatings.

- e. **Structural Clay Products:** They are low-cost but very durable products. They contain high percentage of iron oxide ( $\text{Fe}_2\text{O}_3$ ).
- f. **Electronic and Technical Ceramic Products:** They serve wide range of industries. The aerospace industry utilizes alumina ceramics for missile and rockets cones. About 90% of all nuclear power installation contains enriched uranium dioxide ( $\text{UO}_2$ ), a ceramic material as a fuel element.

### Fig. 1 Classification of Ceramic Materials

#### Raw Materials

Raw materials for ceramic products were first derived from a given location around the world e.g. English China and ball clay valued for good grade porcelain, but increase in knowledge of chemical features of these materials, it was easy to replace geologically “prepared” with synthetic ones. Economically, natural minerals are lower in cost and the proportion of synthetic ceramics is still small. The principal raw material for the ceramic industry is clay (primary or secondary). Other less important raw materials are silica and feldspar. Raw materials are classified as clay, non-clay or special materials. Clay-containing raw materials are known to account for a greater tonnage of ceramics than all other raw materials put together. Clay is one of the most widespread and earliest mineral substances utilized by man.

Clay is an earthly substance consisting chiefly of hydrated aluminium silicate, with colloidal materials and specks of rock fragments. They become plastic when wet and stone-like under fire. Widespread accessibility, ease of extraction and adaptability to several end-users has made products of clay very acceptable in modern industrialization. Clay is not a mineral but an aggregate of minerals and colloidal substances with other finer constituents. It is from igneous rock of the granite type which has three compositions:

1. Feldspar –  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
2. Mica –  $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
3. Silica –  $\text{SiO}_2$

#### Nature of Ceramic Materials

They possess a number of unique features that account for their enduring utility. They include:

- 1) High mechanical strength in spite of brittleness, strong resistance against corrosion and various reagents.
- 2) Their ability to be decorated by a wide range of colours, textures and designs.
- 3) Their ability to withstand high temperatures.
- 4) There is no clear boundary that separate ceramics from metallic or polymeric materials. As a glass, ceramics are better electrical and thermal insulators and are chemically and thermally inert even at high temperatures, shown by their good oxidation state and reduction resistance.
- 5) They exhibit greater rigidity than polymers and are known to withstand compression very well.

## **Methods of Producing Ceramics**

### **1. Extrusion**

This technique is mainly used in the manufacture of structural clay products and more recently for white wares and refractories. The method has the advantage of rapid and economic formation of ware. It is used for products that have high percentage of clay and 12 – 20% of water.

Extrusion involves three close steps:

- i) Pugging
- ii) deairing
- iii) extrusion through a die.

In the process, dry material is continuously supplied at one end of a long trough that has been sprayed with water. The feed is then cut and pugged by rotating knives into a homogenous plastic mass. This mass moves slowly down to the deairing chamber where there is a vacuum. The vacuum is to remove any air entrapped in the plastic mix during the shredding operation. Deairing improves plasticity and strength and permits the formation of a denser ware. The plastic body is then forced through a die of appropriate cross-section and the extruded column is cut into pieces of suitable length.

### **2. Soft Plastic Forming**

It consists of a variety of making methods, all relying on the development of plasticity in the material used. Clay content of most bodies gives rise to their plasticity. Therefore they have high proportion of clay (20-30%). The following techniques are employed:

- a. **Jiggering:** This is used for producing flatware. Flat disc of body is first formed by spreading the body on a flat, revolving plaster head brought down into the body from above.

- b. **Throwing:** This is mainly of historical importance as its use today is limited to studio potties. It entails shaping of a plastic body by hand while rotating on a potter's wheel.
- c. **Moulding and Ramming:** Moulding is mainly used to produce special refractories. It involves throwing a piece of the ceramic bath into a mould and cutting off the excess clay with the top of the mould.

Ramming is the modification of the hand moulding techniques. The shape is built up gradually by placing successive tools as it added. Ramming is used to produce wares that are too big to be formed by other techniques.

- d. **Dry Pressing:** This method finds extensive use in the white wares, refractories, and abrasive industries and for the manufacture of cements (a blend of metal and ceramics). It is used where many parts of relatively simple shapes are to be made. It has the dual advantage of eliminating the making process and permitting greater accuracy of size, since little or no dry shrinkage is involved. The material to be dry-pressed must be dry or contains 12% moisture content at the most. The required amount of material is fed to the die cavity with the lower punch partially inserted in the die and the granules flow readily and tend to fill the die cavity uniformly.
- e. **Slip Casting:** A slip (a free flowing suspension of powdered ceramic material in water) is poured into a porous plaster of Paris with the required shape. Water from the slip is absorbed into a porous mould and as this process proceeds, the interior surfaces of the mould conform to the exterior surface of the desired ware. For solid casting, the process is continued until the walls of the ware meet the centre for drain casting, until the slip is drained from the mould when the walls reach desired thickness.
- f. **Firing and Finishing:** These are the final stages of manufacture, normally referred to as the finishing touches to the ceramic ware. Firing converts the weak and a soft article into a strong and hard product. It is achieved by the reaction between the fluxing material and other body constituents, thereby resulting in a liquid which on cooling solidifies into a glass, bonding together particles or crystals which have not melted. Various methods of firing exist and they differ according to the temperature of maturity, size, quality, and type of the required ware. Ceramic articles are often subjected to a second firing after the initial. This is predominant in a pottery ware that requires glazing (covering with a glass-like surface). The second firing is to allow the glaze to mature. Wares which are not glazed require only a single firing.

Decoration is often applied mostly for dinner wares and other upholstery articles. Further firing is required to mature the colours. Decorative firing is perhaps the hardest to control since different colours have different maturing temperatures. It is perhaps necessary to have several decorating fires.

### Reactions on Firing

The reaction site for the entire process is the kiln where the temperatures attained facilitates a series of reaction which are progressive.

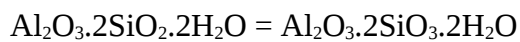
1. At 100°C – dehydration

Any moisture in the ceramic ware and all other hygroscopic moisture are evaporated.



2. At 450°C - 500°C (Dehydroxylation)

The hydroxyl group present in the clay structure is driven off as water molecules e.g.



Kaolinite                      Metakaolin

This reaction weakens the body because the metakaolin formed does not possess binding capability of clay.

3. At 300°C – 700°C (oxidation of organic matter). All organic matter is burnt off at the temperature range of 300°C - 700°C, but in rare circumstances, higher temperatures are required. The case of burning is dependent on the type of organic matter and the rate of heating.

4. At 900°C and above – vitrification

Vitrification or glass formation commences at temperatures that begin from 900°C and above depending on the body composition particles of fluxing. Materials react with particles of other body constituents with which they are in contact to form a liquid. New materials may crystallize from the liquid as the temperature is increased.

**Fig. 2: Flow chart for manufacture of ceramics**

### GENERAL PROPERTIES OF CERAMICS

- 1) Chemical and Physical Properties: The components present in ceramics such as oxides, carbides, etc give high chemical stability to ceramics most of the constituent oxides are usually resistant to highly oxidizing and reducing atmospheres and also to flocculation in temperatures. Compactness of the crystal structure, high directional character of chemical

bonding and high field strengths of small cations of high charge are also responsible for the stability of ceramics.

- 2) **Optical Properties:** Ceramics are opaque as well as transparent. However, most of the ceramics are transparent over a wide range of wave length regions of the electromagnetic radiations. Optical transmission or absorbance is due to the interaction of the electromagnetic field of the incident beam with the polarisable electron fields of the constituent atoms or ions present in the crystal lattice of the ceramics. The optical properties of ceramics depend upon its composition and crystal structure, because extent of polarization mainly depends upon or controlled by ionic size, bonding energy and crystallographic direction. It should be noted that isotropic crystals which have higher refractive index, exhibit properties only along the closed packed crystallographic directions. The presence of vacant electronic energy bond impurities with donor and acceptor sites also contribute to the absorption in the visible region. These impurities cause colour centres in a colourless material because of non-stoichiometry cation-anion ratio. The translucency or opacity in a ceramic body is due to scattering of light resulting due to difference in the refraction at the boundaries of a polyphase polycrystalline material. For example dispersion of  $\text{SnO}_2$  and  $\text{ZnSiO}_4$  in the slip causes opacity in the product due to their capacity to increase the difference in refractive indices of the host matrix and the dispersed phase.
- 3) **Mechanical properties:** Ceramics are brittle solids which are very resistance to compression. The strength of ceramics is mainly controlled by the following important factors (i) temperature (ii) size and shape (iii) compositions (iv) surface condition (iv) surface condition (v) micro structure.
- 4) **Electrical and Magnetic properties. Oxides:** Ceramics are generally bad conductors for insulators in their normal oxidation states. The non-oxides ceramics, however act as semi conductors. Ceramics containing transition metal ions have also been found to show magnetic properties because of spins associated with unpaired electrons. Magnetic ceramics are those which contain molecules with odd number of electrons and incompletely filled 3f, 4f and 5f ions. Unlike magnetic metals, magnetic ceramics are bad conductors of electricity and hence do not conduct electricity. Magnetic ceramics respond to magnetic field known as magnetic susceptibility.

### **USES OF CERAMICS**

Ceramic products are extensively used;

- a) In the construction and decoration of buildings



- b) In the manufacture of metals (refractory materials)
- c) In the manufacture of chemical products (stoneware and porcelain)
- d) In drainage of water and storage (stonewares)
- e) In the sanitation (earthenware and vitreous china)
- f) As insulators in the electrical industry (porcelain and steatite)

The pottery branch of ceramic industry supplies various domestic requirements from the kitchen to the dining room (porcelain, china, earthen ware, etc). On the other hand, particularly all types of ceramic materials are used from terra cotta to fine china, in the manufacture of art wares. Glass, cement and plastics could also be included in the ceramic materials.

Therefore, ceramics is that branch of technology which deals with the manufacture of ceramic articles, their technical characteristics and the raw materials used.

Silicate industry has several independent branches of which the most important are the manufacture of ceramics and refractories, cements, plasters, glass and pyrocerams. Ceramic materials and wares are divided into the following basic groups, according to their main field of use:

- 1) Structural Ceramics: Articles used mainly in constructing buildings and various other structures. Examples building bricks – common bricks, brick block, hollow tile, roof tile, drain tile etc. Rock goods such as clinker brick, ceramic slabs for floors, sewer pipes etc
- 2) Facing materials: Articles used for internal and external facing of buildings and structures. Examples – facing bricks, slabs and oven tiles.
- 3) Refractories: Materials which retain their mechanical properties at 100°C or high temperatures. These are also used in making various parts of industrial furnaces, ovens and apparatus for operating at high temperatures.
- 4) Fine Ceramics: Porcelain wares and glazed pottery are included in this class. They are used domestically (dishes, wash basins, sinks, decorative articles), electrically (electrochemical porcelain) and in laboratories (chemical ware and apparatus)
- 5) Special Ceramics: A group of articles with specific properties utilized in radio industry, aviation instruments manufacture etc.

### **3.3 CEMENT**

The word cement comes from the latin word “Caementum” – meaning anything that binds or unites two bodies together. It can be defined as powdered ceramic material which when mixed with water, sets and develops adhesive and cohesive property into a compact mass.

## Development

Cement was developed in stages. Portland cement was invented by Joseph Aspadin in 1824 who patented artificial cement made by calcinations of an argillaceous limestone. He called it Portland cement because of the concrete made from Portland stone, a famous building stone obtained from Isle of Portland, near England. He used low temperature and obtained product of poor quality. In 1845, Johnson worked on Aspadins product, applied a much higher firing temperature to the mixture, this gave a product of superior hardness and colour, by further experimentations, the correct formulations and temperature were established and led to the arrival of the Portland cement industry as we have today. Over the years, knowledge increased. In 1877, the German cement manufacturers association was set up.

In 1904, the first British Standard Portland Cement was drawn up. This was later revised. However the process remains one of burning an intimate mixture of calcareous limestone or chalk and argillaceous clay or shale.

## Definition of Portland cement

British and Nigerian standards state that the Portland cement is a product obtained by intimately mixing together calcareous (chalk) and argillaceous clay or other silica and alumina and iron-bearing materials, burning at clinkering temperature and grinding the resulting clinker. Gypsum (4-5%) is added in small amount during grinding to control setting and enhance strength development. Only gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is to be added after burning.

## Types of Cements

There are many types of cements classified according to their compositions and uses. The main classes are expansive, high-alumina and ordinary Portland cements.

### Fig 1: Classification of cement

**Expansive (Non-shrinking) Cement** - These are cements which expand slightly on hardening or have no net shrinkage on further air-drying. They are used mainly in USA and Russia. High alumina cement (H.A.C) is hydraulic cement in which the principal components are calcium aluminates as against calcium silicates which are the major ingredients of Portland cement. It is manufactured by heating until molten, a mixture of equal amounts of limestone and bauxite. The product is cooled and pulverized. The initial setting time is 2-6hrs

and final setting time of not more than 2hrs after initial setting. It sets slowly but hardens quickly. This makes ordinary Portland cement unfit for marine use. Its acid resistance and good refractory properties increase with increasing temperature, therefore it can be used as kiln lining material.

**Ordinary Portland cement** - Obtained by intimately mixing together calcareous and argillaceous or other silica, alumina and iron oxide-bearing materials, burned at a clinkering temperature and grinding the resulting clinker. The only major component is gypsum or other derivatives of calcium sulphate. The surface area is not less than  $225\text{m}^2/\text{kg}$ .

**Quick-setting Portland cement** –This slightly differs from Portland cement in that its setting time is less. Hardening time is similar to that of rapid-hardening Portland cement.

**White Portland Cement** - The chemical characteristics of the white Portland and ordinary Portland cements are alike but the essential is that white Portland are nearly free from iron, manganese and chromium oxides, which impart colouration. White cement is produced from raw materials low in colouring elements such as iron, manganese and chromium. It utilizes high grade limestone, white clay and pure silica as raw materials. It is useful in architectural application needing white concrete.

**Sulphate Resisting Portland Cement** - Obtained by mixing together materials containing mainly lime ( $\text{CaO}$ ) and silica ( $\text{SiO}_2$ ) with small proportions of alumina ( $\text{Al}_2\text{O}_3$ ) and iron oxide ( $\text{Fe}_2\text{O}_3$ ), burning the mixture at small amount of gypsum. Its surface area is not less than  $250\text{m}^2/\text{Kg}$ .

**Super-Sulphate Cement** –This is obtained by mixing together granulated blast furnace slag, calcium sulphate and a small percentage of Portland cement.

**Oil-well Cements** - Produced by grinding Portland cement more coarsely than normal and mixing with special retarders, like starches, sugars or organic hydroxyl acids. They are produced and used for cementing the steel casing of gas and oil wells to the walls of the borehole and seal porous formations. The cement slurry is pumped into position pressure before it sets under high temperature and pressure.

**Masonry Cement** - They are produced by grinding more finely than usual, a mixture of Portland cement and limestone, together with plasticiser that contain air. It gives more plastic mortar than ordinary Portland cement.

### **Cement Manufacturing Processes**

The composition of ordinary Portland cement is similar to other classes of cement. The only major differences in the properties of various types of cements are due to the addition of different chemical substances depending on the intended use of the cements.

### **Raw Materials**

The major raw materials for cement production are calcium carbonate and clay.

### **Methods**

Five essential stages are involved in cement manufacture:

- a. Quarrying and crushing of the raw materials;
- b. Grinding of the carefully proportioned materials to high fineness;
- c. Subjecting the homogenized mix to pyroprocessing (heating at high temperature) in a kiln to form clinkers;
- d. Grinding of the resulting clinker to a fine powder with addition of small proportion of gypsum; and
- e. Milling.

### **The Wet Process**

Here, the raw materials (chalk and marl are broken up and sent into the wash mills. The chalk and clay are fed in the required proportions to the wash-mill, with sufficient water to form slurry. When the raw materials are limestone and clay, the clay is usually fed, already dispersed in water to the tube mill.

### **Dry Process**

In dry process, the raw material, usually limestone is conveyed from the quarry to a stone crusher where the lump size is reduced, and smoothens out any chemical variations that may occur in the, raw materials are smoothed out. The stacked limestone is reclaimed and blended further before grinding to fine powder.

## Properties

As a security to the manufacturer and a guarantee of quality to the consumer, cement is usually sold under the standard specification of each country. If the burning temperature in the kiln is too low, the reactions will not proceed to completion; hence the clinker will not be well sintered and will be dull and chalky in appearance. Such clinker is termed “under burnt”, it will not be sound due to presence of some uncombined lime and will not develop the normal strength. It is actually a mixture of cement and incompletely combined material.

If the temperature is higher than necessary, the clinker will be more molten and harder to grind and will contain free calcium oxide (lime). Such clinker is termed “Over burnt”. Properly burnt clinker (termed normal) shows the appearance of small rounded irregular balls, velvety or grey-black with sparkling crystals.

The clinker colour depends on a number of factors:

If ferric oxide is present – dark grey but if absent, it is white or near white.

Other elements such as titanium, manganese, chromium, also impart different shades of colour.

The fineness of cement influences its rate of hydration since reactions occur at its interface with water.

<b>Cement</b>	<b>Surface area</b>
Ordinary Portland cement	300 – 350m <sup>2</sup> /Kg
Rapid-hardening Portland cement	400 – 450m <sup>2</sup> /Kg
British standard specify minima	225m <sup>2</sup> /Kg
Maxima	325m <sup>2</sup> /Kg
Nigerian standards specify a value of not less than	250m <sup>2</sup> /Kg

Soundness of cement is also an important feature that can affect the final concrete structure. Defective cement expands after setting, sometimes after weeks, months or years and leads to weak concrete and destruction of structures.

## 4.0 CONCLUSION

From this unit, we studied the physical and chemical properties of glass extensively as well as the physical and chemical properties of ceramic. Moreover, the use of ceramics in building decoration and other numerous applications of ceramics were also established.

## 5.0 SUMMARY

Physical and chemical properties of glass were treated in this unit. Physical properties include transparent and amorphous solid, vitrified product, hard and rigid with no definite melting point, sufficiently high viscosity. They are insulator of heat and electricity as well as incorporation of coloring materials. Characteristics of glass are hardness, transparency, refractive capacity, dispersive capacity, low thermal conductivity as well as inertness. Processes involved in the manufacturing of glass are formation of batch material, melting, shaping, annealing and finishing. Chemical and physical properties of ceramics as well as optical properties were discussed. The application of ceramics in building decoration and manufacturing of other relevant products was examined. Ceramics materials are divided into structural ceramics, facing materials, refractories, fine ceramic and special ceramics. Also a brief history and development of cement were discussed. Types and classification of cement were treated.

## 6.0 TUTOR-MARKED QUESTIONS

- 1a. Discuss glass under the following headings
  - i. Properties.
  - ii. Methods of manufacture.
  - iii. Uses.
- b. List and explain the most important characteristics of glass.
  1. List
    - i. The uses of ceramics.
    - ii. The types of ceramic
  2. Discuss ceramics under the following headings
    - i. Properties.
    - ii. Division according to main field of use.
- 2a. Using a flow chart, explain the manufacture of ceramics
- 2b. State and explain the most important properties of ceramics
3. List the five essential stages involved in cement manufacture.
- 4a. Write short notes on

- i. Wet process
  - ii. Dry process
4. With a well labeled diagram, explain the classification of cement

**7.0 REFERENCES/FURTHER READING**

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**UNIT 3      PLASTICS, WOOD PULP AND PAPER****CONTENT**

- 1.1 Introduction
- 2.0 Objectives
- 3.0 Main Content
- 3.1 Plastics
- 3.2 Wood Pulp
- 3.3 Paper
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Question
- 7.0 References/Further Readings

**1.0 INTRODUCTION**

The name plastic denotes materials containing higher molecular resins as their main component, which are capable of changing into a plastic state at high temperatures and pressures. They can be moulded under the influence of external force and retain their shape in service. Many plastics are composite that in addition to a binding resin or resins contain fillers, plasticizers, stabilizers, lubricants, pigments, dyes and hardeners. Each of these compounds imparts definite properties to plastics. The properties imparted are plasticity, capacity to be moulded, electrical insulation, anti-corrosive nature and others. Besides synthetic polymers, cellulose esters, protein substances, asphalts and tars have also been used for getting these properties. Plastics are materials with a set of valuable properties making it possible to solve problems of modern engineering and to manufacture abundant consumers' goods. Plastics are used as construction materials in making diverse parts of all kinds of machines, apparatus, instruments and other technical devices including those which must operate under high corrosive conditions over a long period of time.

Plastics have excellent mechanical strength which in some cases is as high as that of ferrous metals. Plastics are excellent insulators, stable to aggressive media, and have a low thermal and sound conductivity. Plastics are available with a low coefficient of friction and with high friction properties. An important merit of plastics is the simplicity of processing them into articles with a high coefficient of material utilization up to 0.90-0.95 against 0.5-0.6 for



metals. A distinctive feature of plastics is their excellent di-electrical properties and low heat conductivity, which is 100-150 times less than that of metals. Many plastics are heat resistant and do not burn. Some of them are highly conductive for light and radio waves.

Cellulose is an important organic raw material widely used in the paper and pulp industry for the manufacture of paper and other related materials. Wood is the principal source of cellulose. Paper is manufactured chiefly from fibrous materials like wood-pulp, esparto grass, corn stalks, cordage and rough waste of textile industry.

### **Advantages of plastics**

Most important advantages of plastics are:

- a) Their high resistance to the effects of environmental factors and various corrosive media  
Their capability of being processed into ware of complex shape by the most efficient modern methods.

Some important disadvantages of plastics are:

- a) Their low resistance to heat as compared to metals; most plastics can be used only at temperature up to 150°C.
- b) Most plastics undergo aging as a result of oxidation, darkening, reduction of hardness and strength.

The working temperature of most plastics is 60-150°C. Above it, they undergo deformation and lose their strength properties (the parent elongation increases). The loss of strength is also associated with their ability of ageing under the effect of light, oxidizing agents and aggressive media.

### **Classification of Plastics**

Depending on the chemical composition of the resins, almost all kinds of plastics can be divided into four classes namely:

- 1) Plastics based on high molecular compounds formed by polycondensation, eg phenolformaldehyde resin (phenolic plastics), amino and amino formaldehyde resins (amino-plastics), organosilicopolymers, polyesters etc.
- 2) Plastics based on modified naturally occurring polymers. Examples are ethers and esters of cellulose (celluloid, celloid, etrol, etc), protein substances, etc.

- 3) Plastics which contain high molecular compounds produced by chain polymerization. Examples are plastic based on polymers of ethylene and its various derivatives, polymers of vinyl alcohol and its derivatives, polymers of esters of ethylene carboxylic acids, etc.
- 4) Plastics based on naturally occurring and petroleum asphalts.

Plastics of mixed nature, that is, plastics containing resins of different classes can also be produced to manufacture materials of even more diverse properties. The most commonly used polymerization resins are polyethylene, polystyrene, polymers and co-polymers of vinyl chloride, polymers of fluoro derivatives of ethylene, polyacrylates, polypropylene, polyvinyl acetate, polyisobutylene, polyformaldehyde etc, plastics based on these resins are thermoplastics and they are made without filters. They possess excellent dielectric properties, high impact strength (with the exception of polystyrene), but the majority of them have low resistance to high temperature. The polycondensation group of plastics include: phenol aldehydes, aminoformaldehyde, polyester, epoxy, polyamide and silicone resins. Some of them are thermoplastics, but most of them are thermosetting. Wares made from plastics based on these resins can be used for long periods of time at a wide range of temperature. At high temperatures, the changes in their physical and mechanical properties are not so pronounced as in the case of articles made of most polymerization resins.

## **2.0 OBJECTIVES**

At the end of this unit, students should be able to:

1. Give a concise definition of plastics.
2. Explain concisely the advantages of plastics.
3. Classify plastics depending on the chemical composition as well as manner of setting.
4. Discuss various processes for the manufacture of wood pulp.
5. Describe how to manufacture paper.
6. List some uses of paper.

### **3.1 MAIN CONTENT**

#### **3.2 PLASTICS**

#### **CLASSIFICATION OF PLASTICS**

Plastic materials or plastic articles obtained from the moulding powders are classified into two classes, namely: thermosetting and thermoplastic, according to the manner of setting,

- 1) **Thermosetting Plastics:** As discussed earlier thermosetting plastics are those which change irreversibly into hard and rigid materials on heating. After cooling, if the set article is again heated, it will not soften again, hence it is irreversible. They are permanent setting resins and during moulding acquire three dimensional cross linked structures with predominantly strong covalent bonds. These bonds retain their strength, even on heating. Thermosetting resins are usually harder, stronger, and more brittle than thermoplastic resins and they cannot be reclaimed from waste. The resins are formed by condensation polymerization and consist of three dimensional network structure joined by strong covalent bonds. They are almost insoluble in all organic solvents, due to cross-linking and strong bonds. Examples of thermosetting plastics are phenol formaldehyde plastic or bakelite, amino plastics and alkyd plastics, epoxy plastics, silicone plastics etc.
- 2) **Thermoplastic Plastics:** These plastics or resins soften on heating and regain their original properties on cooling. Their hardness is a temporary property subject to change with increase or decrease in temperature. Repeated heating or cooling does not alter the chemical nature of thermoplastic resins, because the changes involved are of physical nature. They soften on heating and remain soft as long as they are hot. They regain their original rigidity and hardness on cooling. Thermoplastic resins are usually soft, weak and less brittle and can be reclaimed from the wastes. These resins are formed by addition polymerization only and consist of long chain linear polymers with little or no cross linking. These resins are usually soluble in some organic solvents. Examples of thermoplastic plastics are cellulose nitrate, cellulose acetate butyrates, ethyl cellulose, polyacrylates, polyvinyl resins, styrene or polystyrene resins, polyamides (nylon), polyethers, polypropylene, polyethylene etc. Commercial resins and plastics can also be classified into three classes according to their derivations.
  - a) Resins derived from natural products: These are usually thermoplastics and derivatives of natural products such as natural resins (resins, shellac). Cellulose derivatives (vicose, cuprammonium), cellulose esters (nitrate, acetate, propionate etc), other cellulose esters (methyl, ethyl, carboxymethyl, etc) and protein derivatives (casein-formaldehyde, soya bean-protein formaldehyde, etc)
  - b) Synthetic resins formed as a result of condensation polymerization: These are usually thermosetting and formed by condensation polymerization. Examples are phenol resins (phenol formaldehyde, phenol furfural etc), amino resins (urea formaldehyde, melanine formaldehyde, etc). Some thermoplastic resins can also be obtained by condensation

polymerization under certain conditions. Examples are polyethers (polyformaldehydes, polyglycols), polyurethanes, polyamides and silicone resins etc.

- c) Synthetic resins formed as a result of addition polymerization: These are usually thermoplastic and formed by addition polymerization. Examples are polyethylene, polypropylene, polyisobutylene, fluorocarbon resins, polyvinyl acetate and its derivatives, vinyl polymers such as polyvinyl ethers, divinyl polymers etc., polystyrene and polyvinylidene chloride.

## 3.2 WOOD PULP AND PAPER

### MANUFACTURE OF PULP

This is the first step in paper manufacturing in which raw wood and other materials are converted to pulp. Pulp from fibrous raw material is manufactured either by mechanical process or chemical process. About 80-85% pulping is carried out by chemical process and only about 8-10% by mechanical process.

**Mechanical Process:** Mechanically, wood pulp is obtained from pine and other soft wood such as spruce and balsam. The wood is first slashed and debarked. The debarking is usually carried out by two methods.

- 1) Continuous rotating cylindrical drums or stationary machines fitted with agitating cam are used. In this case, the wood is introduced into the upper end of a rotating drum immersed in a tank partly filled with water where it is tumbled. The bark is rubbed off and the clean wood discharged at the other end.
- 2) Mechanical friction i.e by applying high pressure water jets to individual logs by means of hydraulic barkers. Water jets are directed against the log by means of hydraulic barkers in such a manner that the bark is broken up and removed.

The debarked wood is then subjected to mechanical grinding in presence of water in grinders to remove the heat of friction and to float the extremely small pieces of fibers. The pulp and water mixture thus obtained contains all the lignocellulose of the original wood. The mixture from the grinders is withdrawn into a stock sewer, below the grinders and then conveyed to the silver screen. The fine particles, thus screened by these screens are then concentrated in thickeners to get commercial mechanical pulp. The larger particle retained by silver screen and the fine screen are treated in refiners and then returned to the screens again to recover more mechanical pulp.

The white water, overflowing from the thickeners contain about 15-20% of the original fibres. It is used in grinding and to aid flow in the stock sewer. The remaining fibres are strained from the white water before it is run to waste. The fibres so strained are conveyed to thickeners for concentration to mechanical pulp. As mechanical pulp cannot be completely bleached, it is employed in the manufacture of cheap grade of paper, such as required for newspaper and wrapping. Its colour can however, be considerably lightened by the use of bleaching agents, such as sodium or calcium bisulphite, hydrogen peroxide or sodium peroxide.

**Chemical Process:** This process is used to obtain high grade paper. Various types of pulps, such as sulphate pulp, soda pulp, sulphite pulp etc are prepared by chemical process.

**Sulphite Pulp:** The wood is slashed, debarked, cleaned and chipped. The disintegrated chips are then digested with an aqueous solution of calcium bisulphite or magnesium bisulphite and an excess of sulphur dioxide. The sulphite process involves sulphonation, and solubilizing of the lignin with the bisulphite and the hydrolytic decomposition of cellulose lignin complex. The newer and technically more acceptable sulphite process is based on magnesium bisulphite instead of calcium bisulphite due to the following important reasons.

- 1) The waste liquor from the calcium bisulphite process cannot be used again as calcium bisulphite would not decompose to  $\text{SO}_2$ , whereas magnesium bisulphite does. The magnesium bisulphite waste liquor is therefore recoverable and reusable.
- 2) The disposal of calcium bisulphite waste liquor is a serious pollution problem since more than half the raw material entering the process appears as dissolved organic solids. The magnesium bisulphite waste liquor, on the other hand, reduces pollution because of the fact that it can be used again and it is recoverable. Moreover, a large number of by-products such as lignin, vanillin, tanning materials, rod binders, portland cement, accelerator, plastics from the lignin present, and food yeast etc can be obtained from the waste liquor of magnesium bisulphite process.

In the process, sulphur is heated in a tank by the rotary burner, and the vapours of the sulphur are allowed to enter a combustion chamber, where they are re-oxidised by air to sulphur dioxide.



The amount of air is carefully controlled in order to prevent the further oxidation of SO<sub>2</sub> to SO<sub>3</sub>. The hot sulphur dioxide thus formed is immediately cooled in coolers, surrounded by water cooled pipes. The cooled SO<sub>2</sub> gas is then passed through a series of two or more absorption towers or acid making tanks containing magnesium carbonate. A fine spray of water trickles down the tower system and meets sulphur dioxide gas in a counter current manner (SO<sub>2</sub> gas is blown up through the tower)



The final liquid containing a solution of magnesium bisulphite and some free unabsorbed sulphur dioxide is charged to the digester. It should be noted that free SO<sub>2</sub> gas vented from the digesters is also bubbled through acid making towers. Hence, the amount of SO<sub>2</sub> in the liquor is increased from time to time. The digester is filled with the chip and the acid cooking liquor is introduced through the bottom of the digester. To prevent corrosive action of the cooking liquor, the digesters are lined with crushed quartz or acid resisting bricks. The digester may be heated with steam, but it causes dilution of the liquor. In order to achieve a better temperature distribution pattern throughout the system and to prevent dilution of the liquor, the cooking liquor is heated outside stainless steel tube heater with forced outside circulation of steam and the heated liquor is then circulated through the charge by making use of pumps. The cooking is carried out at about 70-80°C and takes about 6-12 hours.

After the completion of the cooking process, the pulp is washed with fresh water in a large round tank having a false bottom. The cooking or red liquor is evaporated and burnt in boiler to MgO and SO<sub>2</sub>. The MgO is slaked into Mg(OH)<sub>2</sub> and are pumped to the cooling and acid tower down from which SO<sub>2</sub> gas (formed as a result of burning) is passed to produce fresh bisulphite liquor.



The pulp is collected in a tank from where it is pumped to a series of screens. Knots and large lumps of fibre are retained by the screens and the desired fibre screened is conveyed to the centrifuge so as to remove foreign impurities. The pulp is then concentrated in a cylindrical thickener and retained on the screen and water passes through. The thickened pulp is bleached with chlorine or chlorine dioxide and then bleached pulp is treated with milk of lime to neutralize the mass. The resulting stock is again washed with water, thickened and passed

to the machine stock chest. The chest gives pulp laps containing about 30-35% dry fibre. These laps are dried in a pulp dryer by means of steam heated rolls to get a product containing 80-90% dry fibre.

Sulphite pulp is a high quality pulp and used in the manufacture of some finest papers, including sunlit bond.

### **3.3 PAPER**

#### **MANUFACTURE OF PAPER**

The pulp mixed with filling, sizing, and colouring material is called soup. The soup is first sent through screens into a stock box having a thin slit at the bottom. It is forced through the slit to fall on an endless band of exceedingly fine bronze wire screen in motion. During the forward movement of the screen, the pulp fibres remain on the screen while a great portion of water drains from the soup. As the screen moves forward, it has a sidewise shaking motion which acts to orient some of the fibres and provide better felting action and more strength to the sheet. It causes the minute shreds to mat together. The removal of water is further facilitated by vacuum pumps connected to suction booths, over which the wire screen moves.

The fibrous sheet from the wire screen is transferred to the felt blanket, which carries it through a series of press rolls. Pressure of the rollers removes more water and makes the paper more compact leaving the first felt, the paper passes through steel smoothing rolls, where it is subjected to more pressure under rollers and then picked up by the second felt which carries it to a series of drying cylinders. The paper enters the steam heated drying cylinders with a moisture content of 60-70% and leaves with 90-94% dry. If the sizing material has not been added, it can be applied in the form of a paste on one or both sides of the sheet before or after drying. The paper runs through the bath of the size material and then through squeezing rolls to remove excess material and finally runs over drying rolls. The sheets of paper obtained above is rough and irregular. They become compact, smoother and receive fine glaze when they are passed through a series of hot and polished rolls, called polish cylinders. This process is called *Calendaring*

Raw paper stock thus obtained may further be converted to its end use by various means depending upon the final form of the paper desired. For example, the printability of paper may be improved by applying mineral or pigment surface coating. For basic pigment coating, clay is used while for colour coatings, dyes are added. After calendaring and finishing, sheets of papers are wound on reels into large roll. These are then taken to slitting machine to cut

them into rolls of paper size. The manufacture of heavy paper, card board paper or non-uniform paper is carried out by making use of cylindrical machines. It consists of 4-7 parallel vats. Each vat is charged with similar or dissimilar paper stocks. A wire covered rotating cylinder dips into each vat. The paper stock is deposited on the turning screen as the water inside the cylinder is removed. The cylinder is so moved further that the paper stock reaches the top where wet layer adheres to a moving felt, which carries it to a press roll, to remove some of the water. This felt and paper come in contact with the top of the next cylinder and pick up another layer of wet paper. In this manner, several layers are united together into one compact wet sheet. This is passed through press rolls and on to the steam heated drying rolls and smoothing rolls to get a dry, smooth heavy sheet.

### **USES OF PAPER**

Paper is used for writing, for printing of books, periodicals and newspapers etc, for making bags, envelopes and other packing materials. Tissue paper has been used in making napkins, toilet papers, and light weight wrappings. Coloured tissue papers are used for decoration purposes and paper flowers.

### **4.0 CONCLUSION**

The advantages and disadvantages of plastic in addition to classification of plastic materials based on their various properties were well established. The processes for the manufacture of wood pulp used in the production of paper were enumerated.

### **5.0 SUMMARY**

The most important advantages of plastics as well as their disadvantages were enumerated. The four classes of plastics depending on their chemical properties include plastics based on high molecular compound, plastics based on modified naturally occurring polymers, plastic which contain high molecular compounds produced by chain polymerization and plastics based on naturally occurring and petroleum asphalts. Plastics are also classified into thermosetting plastics and thermoplastic plastics depending on their moulding materials or articles. Classification of commercial resins and plastics based on their derivations are resins derived for natural product, synthetic resins as a result of condensation polymerization and synthesis resins formed as a result of addition polymerization. Processes involved in making pulp and manufacture of paper were extensively discussed.



## **6.0 TUTOR-MARKED QUESTIONS**

1. List the advantages of plastics.
2. Classify plastics according to:
  - i. Manner of setting.
  - ii. Derivation.
- 3a. Discuss the following for production of pulp
  - i. Mechanical process.
  - ii. Chemical process.
- 3b. which process is more economical?

Give reason(s).

- 4a. Outline the stages in the manufacturing process of paper.
- 4b. List any five uses of paper.

## **7.0 REFERENCES/FURTHER READING**

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**UNIT 4 ENVIRONMENTAL POLLUTION****CONTENT**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
  - 3.1 Air Pollution
  - 3.2 Water Pollution
  - 3.3 Energy and Environment
  - 3.4 Nuclear Waste
  - 3.5 Acid Rain

**1.0 INTRODUCTION**

The earth is a complex and dynamic system, involving the transfer of material on both micro and macro scales. The processes operating on and within the earth can be simply viewed as a series of interlinked compartments with the links allowing material and energy flow in different directions.

Human activity on the surface of the earth has had an environmental impact since the first tools and manipulations of resources occurred, but only since the industrial revolution of the 18<sup>th</sup> and 19<sup>th</sup> centuries have human activities have a measurable effect on a global scale. To support the maintenance and development of society, humans have developed and refined means to utilize the resources available from within and upon the surface of the earth. This utilization has developed from, in the most part, agricultural practices towards an industrially and technologically dominated society.

So within any developing society there is an underlying need to capture resources from the earth, process raw materials and utilize the products. The environmental effects of these activities can be severe and can arise at a number of stages, including: the removal from natural location.

1. Handling at the point of removal.

2. Transport and storage.
3. Process handling.
4. The generation and disposal of waste.

An increasing world population and technological advancing society increase the net pressure of human activity on the environment. Ultimately, the fate of anything used by humans is that it becomes waste material. If the primary activity of an industry is to produce a product, which has a use in the activity, has the potential to generate waste at many stages in the process. The waste material may be released to the environment at the point of generation or at a later stage. It is important to understand the interaction of any release with the environment and particularly in relation to the biogeochemical cycles, so that any likely environmental impact can be assessed. If that impact is negative, then the release is generally viewed as being a pollution index.

As a consequence of the complexity of environmental processes, the diversity of industrial activities and inter-relationships between humans and the environment, the term pollution has a wide range of implication. In a formal sense, a pollutant may be defined as a substance or effect which adversely alters the environment by changing the growth rate of species, interferes with the food chain, is toxic or interferes with the health, comfort, amenities or property values of people.

When this definition is considered with the description of waste, it is apparent, that any human activity generates both waste and pollution. Differentiating between the two is difficult. It is generally accepted now, that humans must be more efficient in managing their activities on the surface of the planet if there will be a sustainable development of society and the preservation of the quality of life. As a result of past practices, scientific research and an improving understanding of our own impact on the environment, recent legislative changes have meant that industry, often viewed as the primary polluter is pressurized to clean up and minimize its environmental impact.

This unit gives a short introductory overview of the industrial sources of pollution, present practices, and the constraints of minimizing the environmental impact with particular reference to the chemical industry.

## 2.1 OBJECTIVES

The objectives of this unit are to:

1. Identify various industrial sources of air pollution
2. Explain how air pollution can be controlled
3. Discuss air pollution analysis
4. Identify sources of water pollution and categorize these sources
5. Identify some sources of nuclear waste and its disposal
6. Explain some phenomena such as photochemical smog, acid rain and green house effect.

## 3.0 MAIN CONTENT

### 3.1 AIR POLLUTION

Air Pollution is the qualitative and quantitative alteration of the natural composition of air. The alteration occurs when pollutants are introduced into air.

The pollution of air is that of smoke and soot. Recently, the pollution of air is becoming complex because of industrialization. Some of the major pollutants of air are listed below.

#### Major Pollutants

- (i) Particulate Materials
- (ii) Oxides of Sulphur      London Smog
- (iii) Oxides of Nitrogen
- (iv) Photochemical Oxides
- (v) Carbon monoxide      Photochemical smog
- (vi) Gaseous Hydrocarbon

#### Minor Pollutants

- (i) Fluorohydrocabons
- (ii) H<sub>2</sub>S, NH<sub>3</sub>, Flourides, Asbestors, Mine, Lead and Mercury.

#### Major Causes of Air Pollution

- (a) Combustion of fossil fuel containing sulphur in thermal power station.
- (b) Incomplete combustion in incinerators.
- (c) Incomplete combustion of gasoline in internal combustion engine.
- (d) Emission of gases from chemical and allied industries.

**Table 1: Industrial Sources of Air Pollutants**

Industry	Air Pollution Gases	Loss Rate
Power generating	Dust CO <sub>x</sub> Fumes SO <sub>x</sub> Fly ashes NO <sub>x</sub>	0.05 – 1.5% fuel by weight
Petroleum Refinery	Dust H <sub>2</sub> S Mist CO <sub>x</sub> , SO <sub>x</sub> , NH <sub>3</sub> hydrocarbon	0.5 – 1.5% Of crude
Mineral Processing	Dust Process Fume dependent	1 – 3% Weight material
Metallurgical industry	Dust SO <sub>x</sub> , CO <sub>x</sub> Fumes fluorides	0.5 – 2% weight of material
Cement	Dust factors particulate matter SO <sub>x</sub> , CO <sub>x</sub>	

**Table 2: Comparison of London Smog and Photochemical Smog**

Characteristics	Photochemical Smog	London Smog
Temperature	24 to 32°C	-1 to 4°C
Relative humidity	< 70%	□ 85%
Months	August to September	Dec – Jan.
Visibility	<0.8 to 1.6cm	<30 cm
Main Constituent	NO <sub>x</sub> , CO oxidant, O <sub>3</sub>	Particulate material SO <sub>x</sub> , CO
Type of chemical reaction	Oxidative	Reductive
Fuels	Petroleum (gasoline)	Coal and petroleum products
Time of Maximum occurrence	Mid- day	Early morning
Health hazards	Eye irritant (PAN)	Eye irritant as well as bronchitis coughing
Environmental hazard	Polymers Rubbers	Iron and steel cement

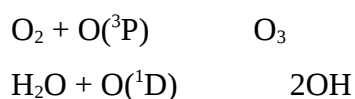
Because of this pollution there is the presence of CO<sub>2</sub> which is responsible for greenhouse effect. Also, because of the presence of oxides of sulphur, nitrogen etc. we have acid rain. Particulate materials are one of the constituent of the London Smog.

### Main Steps in Photochemical Smog

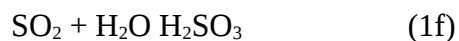
- (1) Emission of oxides of Nitrogen and hydrocarbons ( $\text{NO}_x$  and HC) Absorption of solar radiation by  $\text{NO}_x$  will help the HC to react.
- (2) The absorption of solar energy causing photochemical dissociation of  $\text{NO}_x$ .
- (3) Absorption of  $\text{NO}_x$  and simultaneous building up of oxidant. These oxidants are the  $\text{O}_3$ ,  $\text{O}_2$  and peroxide (-O-O-).
- (4) Oxidation of hydrocarbons to produce wide variety of products. These products are pollutants.
- (5) Dispersion of pollutants.

Reactions of Oxides of sulphur in the atmosphere

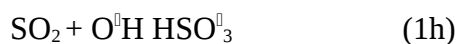
These reactions take place in the lower layer region of the atmosphere.



This reaction and similar ones are responsible for phenomenon of acid rain.



In all these reactions, solar energy is always absorbed



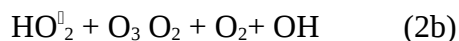
### Reactions of $\text{H}_2\text{S}$



$\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{NaCl}$ ,  $\text{NH}_3$  are also present in the atmosphere as particulate material and can therefore react with the emitted gas e.g.

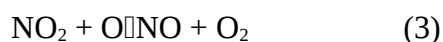


### Reactions of Water Vapour



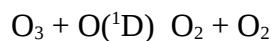
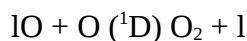
The reaction continues because the OH produced keeps reacting with O<sub>3</sub> as in (2a)

### Reactions of Oxides of Nitrogen (NO<sub>x</sub>)

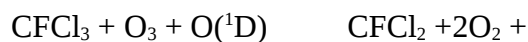


Once O<sub>2</sub> is formed, O<sub>3</sub> will be depleted.

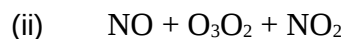
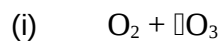
### Reactions of CFCl<sub>3</sub>



Overall reaction:



I is responsible for the destruction of O<sub>3</sub> layer in the atmosphere by recycling.



The two reactions are responsible for photo stationary state.

## CONTROL OF AIR POLLUTION

There are three general approaches to the control of air pollution.

- (i) Alter the nature of combustion of industrial process to reduce the amount of pollutants Example, in the combustion of fuel, SO<sub>2</sub> is a source of air pollution. In

industry therefore, low sulphur content instead of high sulphur content is used during the process.

(ii) Disperse emitted pollutants over a large area using tall stack thereby diluting their effects. Tall chimneys to disperse gases to higher atmosphere in a high large area. When this is done, the concentration here is automatically reduced, but the total burden of the pollutant remains the same.

(iii) Install additional device for the removal of pollutants from the waste gases prior to their release into the atmosphere.

The applicability of any of the three methods will depend on the type and sizes of polluting sources.

### **SOURCES OF AIR POLLUTANTS**

- (1) Stationary sources
- (2) Mobile sources

Stationary Sources: Chemical industries and refineries among others like incinerators that are found in sites (industrial sites) release pollutants in the air.

Mobile Sources: This includes the automobiles, trains, airplanes, ships, etc. that move from place to place releasing a lot of air pollutants during their respective engine combustion.

### **Methods of Reducing Air Pollution**

- (1) **Physical Method.** Physical methods of reducing air pollution includes

- (a) Settling chambers
- (b) Air filters
- (c) Electrostatic precipitators
- (d) Cyclone separator
- (e) Wet scrubbers

- (2) **Chemical Methods:** Chemical methods are applied for the remedy of chemical pollutants which are in gaseous form. Examples are SO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S etc

Chemical methods includes

- (i) Precipitation
- (ii) Absorption: Here, the pollutants are absorbed in liquid form. Wet scrubbers are used in industries.



- (iii) Adsorption: Here the pollutants are adsorbed in solid form. Dry scrubbing is applied using dry scrubbers.
- (iv) Neutralization
- (v) Flash hydrolysis used for the solid waste.
- (vi) Ion-Exchange method.

### **Particulate Materials**

The choice of method for reducing particulate materials depends on:

- (a) Volume of gas and its variation with time in the material.
- (b) Pressure and temperature of the particulate material
- (c) The amount and the nature of particulate materials.

Some of the particulate materials are inactive e.g. sand does not give any problem. If they are reactive, they give problems.

### **PHYSICAL METHODS**

#### **Settling Chambers**

Settling Chambers can separate dust from useful gas thereby reducing particulate materials in the atmosphere.

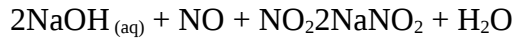
(a)

**Fig. 1: Settling Chamber**

**CHEMICAL METHODS**

**Elimination of Oxides of Nitrogen:** There are a number of ways of removing the oxides of nitrogen.

(1) Alkaline absorption



The market for the  $\text{NaNO}_2$  is very limited.

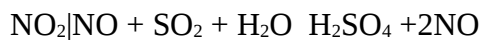
(2) Instead of  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$  solution can be used.



$2\text{NH}_4\text{NO}_2$  decomposes to liberate  $\text{NH}_3$ . Therefore this method is not very good one since  $\text{NH}_3$  is a chemical pollutant.

(3) Another method involves series of steps

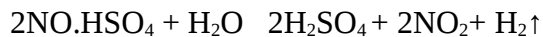
(i) Oxidation



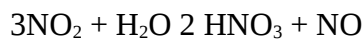
(ii) Scrubbing



(iii) Decomposition

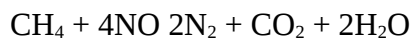
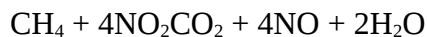


(iv). Conversion of  $\text{NO}_2$  to  $\text{HNO}_3$



The  $\text{NO}$  generated is recycled and the process continues. The demand for  $\text{HNO}_3$  is very high.

(4) Catalytic reduction: This is usually carried out by mixing hydrogen and hydrocarbon gases. Most often methane is used to carry out the reaction on industrial scale.



All these reactions are exothermic and therefore a lot of heat is generated.

**Removal of Fluorides**

Many industries emit fluorides into the atmosphere especially fertilizer and aluminium smelting industries.

Their removal is classified into two major classes.

(i) Dry method. Absorbant –  $\text{CaO}$

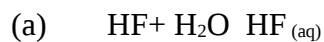
(ii) Wet method



The  $\text{CaF}_2$  is a good market for the production of cryolite ( $\text{NaAlF}_4$ )

### Fig 1: Scheme for removal of Fluoride

In the wet method HF is absorbed or made soluble in water.



Sometimes  $\text{SiF}_4$  is also emitted along with the HF. In that case we have

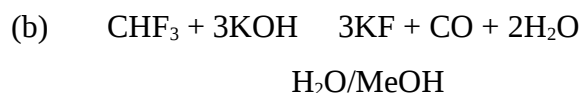


### Removal of $\text{CHF}_3$

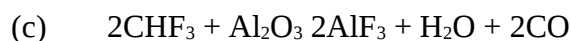
There are a number of methods available for the removal of  $\text{CHF}_3$ . They are considered responsible for the depletion of  $\text{O}_3$ .



This method is not very safe because of the formation of HF except the method of removal of the HF formed is used immediately to eliminate the HF.



This method can only be used for small scale removal of the pollutant and cannot be applied to large scale.



This is the most appropriate method.

Adsorption of  $\text{CHF}_3$  on Aluminium oxide since  $\text{AlF}_3$  is used in Aluminium smelting.

### Importance and advantages of using solid $\text{Al}_2\text{O}_3$ in the removal of $\text{CHF}_3$

$\text{AlF}_3$  has a ready market since it is used in aluminum smelting

$\text{Al}_2\text{O}_3$  is readily available

The method is relatively simple.

## ANALYSIS AND MONITORING OF AIR POLLUTANTS

This is very important for the following reasons

- (1) To establish levels of pollutants in the environment
- (2) To appraise contamination of air from a source or a process.
- (3) To determine efficiency of methods for the removal of pollutants.

The monitoring of air pollutants requires two steps:

- (i) Sampling
- (ii) Analysis

**Sampling:** Several steps are involved e.g. collection of samples; while collecting samples, a number of factors will be put into account which include

- (a) Size of sample
- (b) Rate of sampling
- (c) The duration of sampling
- (d) The effect of storage that is, whether it decomposes or whether it can last for a longer time.

There are various methods for the devices available for the sampling of air.

The devices will consist of number of items or the sampling equipment consists of a number of devices e.g.

- (i) Sampling collector
- (ii) Metering device: Mostly used is rotometer. Venturimeter is also used.
- (iii) Vacuum source
- (iv) Essential supplementary devices

In the air, there are two types of pollutants viz:

- (i) Particulate materials
- (ii) Gases

There are different devices for these two pollutants.

For the particulate material, we have the following device

- (i) Filters (Air filter)
- (ii) Electrostatic precipitators
- (iii) Centrifugal separators (Cyclone separator)
- (iv) Impingers

Devices for the sampling of gases include the following

- (a) Absorbing Tower (liquid)
- (b) Adsorbing Tower (solid)

**Analysis:** Either it is carried out in the field (sources) or in the laboratory which is dependent on the nature of pollutants. Stable pollutants can be carried out in the laboratory while the unstable pollutants are carried out in the field *in situ*.

Analytical methods fall into two major classes

- (i) Chemical method
- (ii) Spectroscopic method

Chemical Method, includes volumetric and gravimetric methods while spectroscopic method involves the use of instruments. It is also called instrumental method.

### 3.2 WATER POLLUTION

Like air, water is very important to support systems. It is very important both for civilized societies, industries and agriculture.

#### Uses of Water

This can be classified into domestic and industrial uses.

#### Industrial Uses

- (i) It is used in generation of steam
- (ii) In cooling medium to eliminate heat
- (iii) For washing and for transportation of fluid or for suspending medium as a reactant.
- (iv) Water is an essential component of drinks (used in breweries)
- (v) Water is used in food industries

#### Sources of Water Pollution

The major sources are:

- (a) Industrial effluents
- (b) Agricultural drainage
- (c) Mine drainage (from mine metallurgical industries)
- (d) Trade effluents
- (e) Domestic effluents

The trade and domestic effluents are normally accepted for disposal by the municipal sewers. The industrial effluents cannot be accepted without treatment because the nature of the effluents depends on the industries. So it needs to be treated to remove the toxic wastes e.g.

petrochemical industries' effluents may contain acids; fertilizer industries' effluents may contain phosphates, nitrates etc.

### **Categories of Waste Pollutants**

Waste pollutants can be categorized into three sources.

- (1) Toxic materials – These include pesticides, herbicides heavy metals, PCB (polychlorinated biphenyls, chlorinated hydrocarbons), true chemicals, petrochemicals, amines, pyridines, and radioactive materials
- (2) Substances which increase oxygen depletion in the water or is necessary for the survival of microorganism. When some of these materials are discharged into the water, they are degraded by microorganisms in the water, thus biological degradation results in the depletion of oxygen in the water resulting to competitive struggle for oxygen in water

The transfer of oxygen from the air is temperature dependent because at higher temperature, the solubility of  $O_2$  in water decreases. The consequent decrease of  $O_2$  (due to biodegradation) and increase (due to transfer from air) constitute a phenomenon called Oxygen Sag.

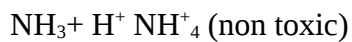
This phenomenon helps us to know the interval of discharge of effluents into the water to maintain oxygen equilibrium in the water. These effluents are reducing agents, biologically labile substance surface acting agent which interfere with the solubility of  $O_2$  in  $H_2O$ .

- (3) Substances in this category are indirectly harmful. These include suspended solids which are chemically inert or uncreative inorganic salts, soluble and insoluble salts, colouring agents and dyes.

### **Criteria for Polluting Strength**

(i) Temperature: The temperature is around 30°C and it is the temperature at which most effluents are permitted to be discharged into aquatic medium. At high temperatures the aquatic life is affected. At high temperature, the solubility of O<sub>2</sub> in H<sub>2</sub>O is decreased; thus O<sub>2</sub> concentration is reduced. Increase in temperature also affects the rate of chemical reactions and indirectly affects the rate of physiological processes e.g. respiration rate. Again, at high temperatures, enzymes produced for biochemical processes may be degraded or destroyed.

(ii) pH: The pH of the effluent should be around 7 (neutral). It can be varied between 5 and 9 i.e. not too basic and not too acidic. The pH has profound effect on the toxicity of chemicals e.g. NH<sub>3</sub> which is toxic can be made non toxic by reaction of H<sup>+</sup>.



(iii) Suspended Solids: These are usually chemically inactive insoluble impurities causing turbidity and sedimentation. The high concentration of suspended solids poses a potential danger to aquatic life.

(iv) Biochemical oxygen demand (BOD): This is a measure of O<sub>2</sub> requirement to oxidize organic material to harmless molecules under aerobic condition at standardized time and temperature. BOD indicates polluting strength of the effluents in terms of O<sub>2</sub> which will be consumed by microorganisms when the effluents are discharged to neutral water resources. e.g. river, stream. The biochemical oxygen demand is useful to design biological treatment units, to control quality of effluents and to determine the cost of treatment.

(v) Chemical oxygen demand (COD): This is a measure of the total oxygen requirement to oxidized both organic and inorganic materials by an oxidizing agent such as sodium dichromate. It is a superior or better method than the biochemical oxygen demand because it can be carried out in a short time (in a day) unlike the biochemical which takes about five days.

### **Effluent Treatment Plans and methods**

It is easier to consider steps which help to minimize the volume of industrial effluents while considering the methods for treatment and disposal. These steps include the following concepts:

(i) **Recycling of Process Water:** Recycling of process water containing little waste materials may achieve considerable savings in the cost of water as well as reduction in the volume of effluents.

(ii) **Balancing the volume and strength of effluents:** An appropriate balance between the volume and the strength of waste water may help in reducing harmful effect of pollutants as well as to minimize the treatment cost.

(iii) **Segregation of Waste Products:** The segregation of waste product stream containing toxic materials from the main stream limits the polluting effect of the toxic materials. The stream containing toxic material can then be treated by detoxication (detoxification).

### **Treatment of Effluents**

The methods for the treatment of effluents can be grouped into the categories

- (a) Primary treatment
  - (b) Secondary treatment
  - (c) Tertiary treatment
- (a) **Primary Treatment:** This involves sedimentation, flocculation and filtration of suspended materials and their effluents. This is usually a physical treatment. Centrifugation may also be used for tiny particles.
- (b) **Secondary treatment:** This involves biological, aerobic degradation of the soluble organic materials. The basic idea is to allow microorganism to consume organic materials in the effluent for primary treatment.
- (c) **Tertiary treatment:** It involves the removal of more biodegradable chemicals and neutrons from the effluents of the secondary treatment. The techniques available for chemical treatment are chemical precipitation, reverse osmosis, ion-exchange and distillation.

The effectiveness of these methods is measured in a number of ways:

- (i) B.O.D (Biological Oxygen demand)
- (ii) C.O.D (Chemical oxygen demand)



- (iii) D.O. (Dissolved oxygen)
- (iv) S.S (Suspended solid)

The table below shows percentage removal of BOD, SS and COD through primary and secondary treatment procedures.

% Removal of	Primary	Secondary
SS	60%	90%
BOD	35%	90%
COD	30%	80%

The remaining impurities are easily removed by the tertiary treatment. Example, say the impurity of phosphate is removed by chemical precipitation. This chemical precipitation involves adding of lime and aluminium sulphate. The precipitates of phosphate are allowed to settle down before the effluents are discharged. These phosphates precipitated are lost and phosphates recovered are used for fertilizer manufacture.

The efficiency of the tertiary treatment varies from 80% - 90%. If we take chemical precipitation, the filtration efficiency will be 90%. The cost of the tertiary treatment is quite high compared with the primary or secondary methods of treatment. The impurities of heavy metals from industrial effluents are easily removed by chemical precipitation as metal hydroxides at an appropriate pH. The Table below shows the pH at which hydroxides of the metals are precipitated.

M <sup>+</sup>	pH
Fe <sup>3+</sup>	2.0
Al <sup>3+</sup>	4.1
Fe <sup>2+</sup>	5.5

The pH is adjusted in order to precipitate the hydroxides. In industries, industrial workers try to follow zero waste materials and hence the pollutants are considered resource materials.

### **Pollutants as Resource Materials**

It is a productive approach to the method of environmental pollution. A number of pollutants such as lead, mercury, zinc, aluminium, nickel are available materials. And their recovery could not only be the problem of toxic pollution but also their demand from primary source of pollution.

**Disposal of Acid Tar from Petroleum Work**

The acid tar has the following distinct concentration and depending on the type of process, the concentration will vary. Example, acid for  $\text{H}_2\text{SO}_4$  will be in the range of 40 – 60% wt. 2-10% wt is dissolved organic matter and the remaining is free water.

The acid tar is fairly viscous.

There are possible methods of disposing these acid tars:

- (i) Burning the tar direct under the boiler to generate a steam.
- (ii) Hydrolysis of the acid tar and then recovering neutral organic oil and dilute acid ( $\text{H}_2\text{SO}_4$ ).
- (iii) Decomposing the acid tar to coke and recovering  $\text{SO}_2$  liberated for reconversion to  $\text{H}_2\text{SO}_4$ .

Sometimes, these acid tars containing these acids can also be reacted with  $\text{NH}_3$  and steam to get  $(\text{NH}_4)_2\text{SO}_4$ . The reaction is carried out at high temperature and pressure. The remaining aqueous layer, the acid layer can then be separated – a way of recovering the waste material.

- (iv) Pickling liquor in steel mills. These pickling liquors will contain various salts. If it is iron, it will contain iron sulphate. It is useful to remove the iron sulphate from this pickling liquor.

**Zhan Process**

The rotatory drum will enable the hot vapour to be removed. Centrifugation will help to remove the  $\text{H}_2\text{SO}_4$  from  $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ . The  $\text{H}_2\text{SO}_4$  can also be used to manufacture sulphuric acid. The process is developed by the British Iron Steel Research Association (BISRA) and it involves roasting of  $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$  and absorbing  $\text{SO}_2$  into  $\text{H}_2\text{O}$  and catalyzing  $\text{SO}_2$  to  $\text{SO}_3$  which then dissolve in  $\text{H}_2\text{O}$  to give  $\text{H}_2\text{SO}_4$  acid concentration up to 40%. Recovery of these materials involves cost. It is useful to recover these materials to avoid the problem of disposal.



## **Monitoring and Control**

This involves measurement of effluent flow rate, sampling of effluents, analysis and composition. There are two ways for sampling:

- (i) Random sampling
- (ii) Periodic sampling

From the analysis of the samples collected one can determine the level of concentration of the pollutants. The physical characteristics of the samples such as temperature of pollutants and concentration of suspended solids can also be determined.

Chemical characteristics of the effluents such as the pH, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) can be determined.

Also, analytical techniques like flame photometry, IR, NMR, UV etc are used for analysis of effluents. There can also be chromatographic methods

- (i) Gas chromatography (G.C)
- (ii) Gas Liquid chromatography method (G.L.C)
- (iii) High pressure liquid chromatography method (H.P.L.C)
- (iv) Gas Chromatography-Mass Spectrophotometry (GC/MS)

## **3.3 ENERGY AND THE ENVIRONMENT**

### **Sources**

Thermal power station: Fossil fuels, coal, oil and gas.

Nuclear power plant: nuclear fuels, Uranium and Plutonium

Hydroelectric power plant: Water

Of these three, the nuclear and hydroelectric power plants are the lesser sources of pollution. However, thermal power station leads to the emission of much more pollutants e.g.  $\text{SO}_x$ ,  $\text{NO}_x$  and  $\text{CO}_x$ . The power generated by coal is always cheaper than the amount generated by Uranium. Recently the control of the emission of  $\text{SO}_x$  and  $\text{NO}_x$  combustion technique has been modified to reduce the emission of  $\text{SO}_x$  and  $\text{NO}_x$ .  $\text{SO}_2$  can be removed during combustion.

### **Methods of Removal of Sulphur Compounds from Flue Gases**

- (1) Flue gas desulphurization

Flue gas containing  $\text{SO}_2$  is brought in contact with lime water in an absorbing tower.

Flue gas ( $\text{SO}_2$ ) +  $\text{Ca}(\text{OH})_2$   $\text{CaSO}_3$  +  $\text{H}_2\text{O}$   $\text{CaSO}_4$

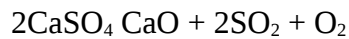
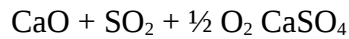
$\text{CaSO}_4$  produced is a good form of gypsum which is used in the manufacture of Plaster of Paris (POP)

## (2) Fluidized Bed Combustion.

In fluidized Bed Combustion (FBC), limestone ( $\text{CaCO}_3$ ) is used as bed materials. The technology burns fuel at temperatures of  $750^\circ\text{C}$  to  $900^\circ\text{C}$ . The mixing action of the fluidized bed brings flue gases into contact with sulphur absorbing chemicals such as quicklime ( $\text{CaO}$ ), a product of the decomposition of  $\text{CaCO}_3$  in the bed. At last,  $\text{CaSO}_4$  is formed which on decomposition gives  $\text{CaO}$ ,  $\text{SO}_2$  and  $\text{O}_2$ . The  $\text{SO}_2$  formed is used to produce  $\text{H}_2\text{SO}_4$ . By so doing, its emission into the atmosphere is minimized. Advantages of the FBC include low sintering process (melting of ash), low production of  $\text{NO}_x$  due to low temperature and low production of  $\text{SO}_x$  due to capture by limestone. So FBC reduces the amount of sulphur emitted in the form of  $\text{SO}_x$  emission.

## Fluidized Bed Combustion





$\text{SO}_2$  produced is used to produce  $\text{H}_2\text{SO}_4$ . By so doing its emission into the atmosphere is then minimized.

### **Control of Oxides of Nitrogen ( $\text{NO}_x$ )**

Oxides of nitrogen emission are usually controlled by converting them to Nitrogen gas. This can be achieved by modifying the combustion process. One of the methods is staged combustion, which is described below:

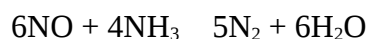
#### **Methods**

##### (1) Staged Combustion

Limited amount of oxygen is supplied to the apparatus thereby the amount supplied is used to burn carbon from the coal leaving the Nitrogen unburned.

##### (2) Reaction of oxides of Nitrogen with $\text{NH}_3$ .

Selective catalytic reduction method



$\text{NH}_3$  can be injected into the reaction zone, during the reaction or prior to the reaction.

Disadvantages:

- (i) It requires large quantity of  $\text{NH}_3$ .
- (ii) There is a possibility that  $\text{NH}_3$  can be oxidized producing oxides of Nitrogen.

$4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$ , this is more rapid when catalyst is not used and reaction temperature is at  $900^\circ\text{C}$ . When  $\text{V}_2\text{O}_5$  is used at  $300 - 400^\circ\text{C}$ , 70% of  $\text{NO}_x$  is taken care of.

### **3.4 DISPOSAL OF NUCLEAR WASTE**

When nuclear fuel is used in reactors (nuclear power plants), some materials such as uranium, plutonium, minor actinides (neptunium, americium and curium) and fission products (radioactive isotopes of wide variety of elements including alkali metals,

transition metals, halogens and even noble gases) are left as pollutants. These pollutants are referred to as nuclear waste. These wastes are sometimes called used fuel and are dangerously radioactive and remain so for thousands of years. When they first come out of the reactor, they are so toxic that if one stood close to them while they were unshielded, the person would receive a lethal radioactive dose within a few seconds and would die within few years.

#### SOURCES OF NUCLEAR WASTE

1. Use of nuclear energy. The use of nuclear energy as a source of energy is a major source of nuclear waste. This form of energy is very cheap.
2. Processing plant. Uranium and plutonium processing is a good source of nuclear waste.
3. Laundering of contaminated materials. This includes clothes and other materials worn by processing workers and nuclear energy managers.
4. Hospitals. This is another serious source of nuclear waste. In hospitals, radioactive materials are used for treatment of some illness.

#### CATEGORIES OF NUCLEAR WASTES

Nuclear waste originated from nuclear power plant. They are categorized into three levels.

- (i) Low level waste (L.L.W) such as iodine and phosphorous isotopes
- (ii) Intermediate level waste (I.L.W) or medium level waste (MLW). Examples include those nuclear wastes that are hospital origin.
- (iii) High level waste (H.L.W) such as nuclear waste from fuel element processing for nuclear energy.

#### TREATMENT OF NUCLEAR WASTE

Treatment of nuclear waste from processing plant is possible from processing plant is possible by storing it so that it disintegrate completely after life cycle. Ion exchange treatment method could be applied for low to medium nuclear waste. Another method of treatment of nuclear waste is through detention of the waste over a long time.

#### METHODS OF NUCLEAR WASTE DISPOSAL

There are two practical methods for the disposal of nuclear wastes. They are:

- (a) Concentrate and Contain

- (b) Dilute and Disperse

### **Temporary storage to permit decay of short lived fission products**

#### Industrial Wastes

In industries, we have three types of waste which are;

- (i) Gaseous
- (ii) Liquid
- (iii) Solid

#### **Gaseous Waste**

- (1) Gaseous waste or the particulate materials are usually removed by any of the following methods.
  - (i) Filtration
  - (ii) Absorption and scrubbing
  - (iii) Reaction with solid
  
- (3) Liquid waste: Most of the liquid wastes are treated by dilution and dispersion technique. Dilution is often preceded by storage to permit the decay of short lived fission products. The liquid waste with high level of radioactivity usually converts to solids for long time storage. This conversion is by 1 or 2 methods:
  - (i) Evaporation: In an evaporator or simple distillation (where the vapour is condensed and solidified)
  - (ii) Precipitation (coal precipitation method). Precipitation of soluble materials with insoluble precipitates. This insoluble precipitates acts as a carrier to radioactive

materials. The solution is adjusted to an alkaline pH to precipitate an insoluble metal hydroxide. The precipitates are separated as slug and the slug is dried and stored.

- (1) Solid Waste: They are disposed of by (a) Burial in approved ground (b) Incineration
- (2) Radioactive solids are stored in a stainless container with continuous monitoring.

### **Air Pollution and Pesticides**

Sources of Atmospheric input:

- (i) Mechanism of Aerial spray: These are applied directly to the air and in a large quantity.
- (ii) Volatilization: Volatilization of the pesticides applied in the soil or the plants. Factors that affect volatilization of the soil are temperature, relative humidity of air and velocity of wind.
- (iii) Manufacturing: Formulation, packing and distribution. During manufacturing, there could be spillages and during other processes enumerated above, there could be emission of the pesticides into the atmosphere.
- (iv) Disposal: This is done in two ways:
  - (a) Incineration
  - (b) Burying underground

Incineration is a combustion process and when this is done gaseous elements are liberated e.g.

DDT CO, CO<sub>2</sub> and HCl

### **Removal Processes of Pesticides introduced in the Air**

- (a) Physical process
  - (i) Sedimentation
  - (ii) Precipitation
- (b) Chemical Process
  - (i) Oxidation and photo degradation. During photo degradation, energy of the order of 290 – 400nm are absorbed by the pesticides. Molecular O<sub>2</sub> in the atmosphere can react with degraded products or photo excited pesticides to form peroxides and bauxites.

### **Degradation of Pesticides**



Many pesticides contain aromatic compounds and they also contain heteroatom such as S, N, P, O.

Pesticides that contains Aromatic compounds

2,4,5-Trichlorophenoxy Acetic Acid

==>2,4,5 TAA

A product of 2,4,5-TAA known as Dioxan, is very poisonous and toxic.

(ii)

2,3,7,8 tetrachloro-dibenzo

**Manufacture of 2,4,5-Triphenoxy benzoic acid**

Mechanism

Phosalone: Degradation of this compound takes place either by oxidation or hydrolysis or both.

Phosalone is an organophosphate chemical commonly used as pesticide and acaricide. It was developed by Phone-Poulenc in France but EU eliminated its pesticide registration in December 2006.

$\text{H}_3\text{PO}_4$  is produced whether the compound takes oxidative path or hydrolysis path.

### **Other Environmental Concerns**

- (1) Photochemical Smog

(2) Greenhouse Effect

(3) Acid Rain

### **Photochemical Smog**

Photochemical smog is produced when pollutants from the combustion of fossil fuels reacts with sunlight, converts the pollutants into other toxic chemicals. For photochemical smog to form there must be other pollutants in the air, specifically nitrous oxide and other volatile organic compounds (VOCs). Photochemical smog therefore comprises oxides of nitrogen, photochemical oxides, carbon monoxide and gaseous hydrocarbon. Major steps in photochemical smog formation are as follows:

1. Emission of oxides of nitrogen (NO<sub>x</sub>) and hydrocarbons. Absorption of solar radiation by NO<sub>x</sub> with the hydrocarbons to react.
2. The absorption of solar energy causing photochemical dissociation of NO<sub>x</sub>
3. Absorption of NO<sub>x</sub> and simultaneous building up of oxidants. These oxidants are O<sub>3</sub>, O<sub>2</sub> -O-O- (peroxides).
4. Oxidation of hydrocarbons to form wide variety of products. These products are pollutants.
5. Dispersion of pollutants as smog

**2. Greenhouse Effect:** This is the warming of the earth's surface and lower layers of the atmosphere that tends to increase with increasing atmospheric carbon dioxide. This is caused by conversion of solar radiation into heat in a process involving selective transmission of short wave solar radiation by the atmosphere, its absorption by the earth's surface and re-radiation as infra red. The infra red is absorbed and partly re-radiated back to the surface by carbon dioxide, methane, nitrous oxide and water vapour in the air.

### 3.5 ACID RAIN

Acid rain refers to the deposition of wet (rain, snow, sleet, fog, cloudy water, and dew) and dry (acidifying particles and gases) acidic compounds. "Clean" or unpolluted rain has an acidic pH, but usually no lower than 5.7, because carbon dioxide and water in the air react together to form carbonic acid, a weak acid according to the equation;



Carbonic acid then can ionize in water forming low concentrations of hydroxonium and bicarbonate ions.



However, unpolluted rain can also contain other chemicals which affect its pH. A common example is nitric acid produced by electric discharge in the atmosphere such as lightning. Acid deposition as an environmental issue would include additional acids to  $\text{H}_2\text{CO}_3$ . Particulates, gases and aerosol in the atmosphere are commonly regarded as determinants of wet deposition chemistry. Anthropogenic emissions can be oxidized to produce oxides carbon, sulphur and nitrogen compounds in the atmosphere; which are balanced stoichiometrically by a net production of hydrogen ion ( $\text{H}^+$ ). Gaseous sulfuric and nitric acids are partially neutralized by gaseous  $\text{NH}_3$  to form  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ , both common

components of rainfall influenced by anthropogenic sources. Nitric and sulphuric acids are regarded as the sole contributors of nitrate and sulfate in precipitation, and these are assumed to be the major sources of acidity in precipitation influenced by combusted hydrocarbons. The major acid precursor gases (SO<sub>x</sub> and NO<sub>x</sub>) that cause acid rain in Niger Delta region of Nigeria are production of hydrocarbon combustion (gas flaring and crude oil refining). Other economic activities in the area that can synergize acidic precipitation also abound. Oxides of nitrogen (NO<sub>x</sub>) are by-products of firing processes of extremely high temperature (automobiles, utility plant(s) and in chemical industries (fertilizer production, aluminum smelting). Natural processes such as bacterial action in soils, forest fires, and lightning can contribute significantly to the high value of this acid-forming gas in the atmosphere. Sulphur dioxide (SO<sub>2</sub>) can be produced by iron and steel production, smelting of metal sulphate ore, plankton, and rotten vegetation, are all common features in the Niger Delta region of Nigeria. Combustion of fuels produces sulphur dioxide and nitric oxides. They are converted into sulphuric and nitric acids.

In the gas phase, sulphur dioxide is oxidized by reaction with the hydroxyl radical in an intermolecular reaction (Seinfeld and Pandis, 1998).



This is followed by:



In the presence of water, sulphur trioxide (SO<sub>3</sub>) is converted rapidly to sulphuric acid



Nitrogen dioxide reacts with OH to form nitric acids



When clouds are present, the loss rates of SO<sub>2</sub> are faster than can be explained by gas phase chemistry alone. This is due to reactions in the liquid water droplets. Hydrolysis is important in this respect.

Sulphur dioxide dissolves in water and then hydrolyses in a series of equilibrium reactions:

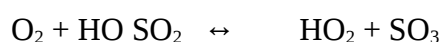


There are a large number of aqueous reactions that oxidize sulphur from sulphur (iv) to sulphur (vi) leading to the formation of sulphuric acid. The most important oxidation

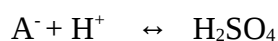
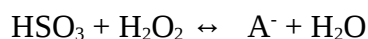
reactions are with ozone, hydrogen peroxide and oxygen, reactions with oxygen being catalysed by iron and manganese in the cloud (Seinfeld and Pandis, 1998).

Atmospheric reactions that lead to acid precipitation can take place in gas or aqueous phases.

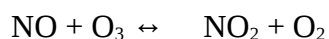
In gas phase, photolysis is important in the day time. The main oxidant for SO<sub>2</sub> conversion to sulphuric acid is hydroxyl radical (OH<sup>·</sup>), represented as:



Diurnal variation in OH makes the above less important at night. Hydrogen peroxide is the principal oxidant in the aqueous phase, such as



Where A<sup>·</sup> is intermediate specie, Gas phase oxidation of nitrogen oxides to nitric acid is important in the daytime, with hydroxyl radical as principal oxidants and proceeds as



#### 4.0 CONCLUSION

The major environmental pollution namely; air, water, nuclear in addition to industrial effluents, energy and environment, and industrial waste was thoroughly studied. Again, other environmental concerns such as ozone layer depletion, acid rain, green house effect and photochemical smog were also addressed.

#### 5.0 SUMMARY

This unit covers air pollution, water pollution, nuclear waste and other environmental concerns. In dealing with air pollution, air pollutants, sources of air pollutant were discussed. Methods of control and reduction of air pollution were also treated. Industrial uses of water and sources of water pollution were also discussed. Waste pollutants and their categories as well as criteria for polluting strength were treated. Effluent treatment plans and methods, pollutants as resource materials, disposal of acid tar from petroleum work, effluent flow rate, sampling effluents, analysis and composition were studied. Energy and the environment, sources of nuclear waste, disposal of nuclear waste as well as industrial wastes such as

gaseous, liquid and solid wastes and method of their removal were discussed in detail. Other environmental concerns like the green house effect, acid rain, ozone layer depletion and photochemical smog were dealt with in this unit.

## 6.0 TUTOR MARKED QUESTION

1. List the major and minor air pollutants.
2. What are the major causes of air pollution?
- 3a. Explain with diagrams the following methods of reducing air pollution
  - i. Dry scrubbing
  - ii. Air filtering
  - iii. Cyclone separation
  - iv. Electrostatic precipitation
- b. List any five chemical methods of reducing air pollution. Explain any two methods briefly.
4. Explain the three major categories of sources of waste pollutants.
5. Plans and methods for treatment of effluents are primary responsibility of the process industries. Enumerate any three of these plans and methods usually applied by the industries.
6. Pollutants are resource materials in some industrial processes. Explain with examples.
7. Explain with the aid of relevant chemical equations how the oxides of nitrogen ( $\text{NO}_x$ ) could be eliminated in the chemical industry
8. Explain with diagrams, methods normally applied in the chemical industry for the removal of sulphur compounds from flue gases.
9. What are the major sources of nuclear waste?
10. Explain how you would remove the following types of waste.
  - i. Gaseous waste
  - ii. Liquid waste
  - iii. Solid waste
11. Explain what you understand by the following phenomena
  - i. Ozone layer depletion
  - ii. Greenhouse effect
  - iii. Acid rain
  - iv. Photochemical smog

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