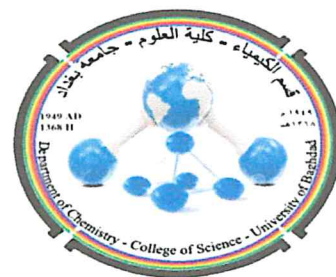


University of Baghdad
College of science
Department of chemistry.



Industrial chemistry

For Third Year Chemistry

First Semester

Translated and revised by

Assistant Professor Huda N.A. AL-Ani

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industrial chemistry

Physical processes used in chemical industries

Physical processes are all processes in which there are no changes in chemical structures of used materials for examples:

- 1- Transporting processes they are the first physical process, ship transporters used for solid and liquid materials, pipes are used to transport gas and liquid.
- 2- Grinding and crushing processes which are used to increase the surface area of solid substances like (red beet, sugarcanes, rocks and minerals).
- 3- Dissolution (dissolving solid in liquid), melting (conversion of solid to liquid) or called diffusion and evaporating ((conversion of liquid to gas) processes.
- 4- Mixing processes which are used in chemical processes to increase the rate of reactions mixing two immiscible liquid (emulsion; water with fat (natural butter) and for mixing dyes...
- 5- All separation methods:
 - A- Mechanical separation methods.
 - B- Electrostatic and magnetic separation methods.
 - C- Thermal separation methods:-
 - Distillation processes
 - Evaporation processes
 - D- Physicochemical separation methods:-
 - Extraction
 - Crystallization
 - Adsorption
 - Absorption

The common aspect of all separation methods is the need for two phases. The desired substance will partition or distribute between the two phases in a definite manner, and the separation is completed by physically separating the two phases. The ratio of the concentrations of a substance in the two phases is called its partition or distribution coefficient.

Based on the nature of the second phase the more commonly used methods of separation are classified as follows:-

1-methods involving a solid second phase include precipitation, electrodeposition, adsorption, ion exchange and crystallization.

2-method involving a liquid second phase is solvent extraction, in which the original solution is placed in contact with another liquid phase immiscible with the first.

3-method involving a gaseous second phase include gas evolution, distillation, sublimation and gas chromatography mixture of volatile substances can often be separated by fractional distillation.

A-mechanical separation methods:-

All mechanical separation methods are based on differences in Phase density, Phase fluidity, Mechanical properties of particles as size shape and density and on such particle characteristics as wettability, surface charge and magnetic susceptibility.

1-**classification**: (solid from solid by size and floating) using air classifiers as floating in air process like (separation of rice from its shells). Also floating on water which used to separate mixed raw minerals with water using air bubbles which pumped into the mixture [like separation of cupric sulfide from its mixture with quartz], the water layer surrounding mixture can be replaced by another substitute which stick to the air bubbles and float out these substance called collectors like R_2COH , RSH and amines.

2-**Centrifugation** (solid from liquid) is used for the separation of solids from liquids using centrifugal force for the separation of mixtures the solid have low weights (like suspensions) the particles settling velocity in centrifugation is a function of their size and shape, the density by difference between the particles and the viscosity of liquid.

quartz
side 2

For example:

It is used in chemical food industries.

Centrifugation is the most common method for uranium enrichment, relying on slight mass difference between atoms of U238 and U235 in uranium hexafluoride gas.

3-Filteration (solid from liquid and gas) is used to separate particles and fluid in a suspension where the fluid can be a liquid or a gas by interposing a medium through which only fluid can pass using filters (paper filters and sandy filters).

Commercially the term filter is applied to membranes where separation lattice so thin. Furnaces use filtration to prevent the furnace element from fouling with particulates.

4-pressing (liquid from solid) is used to separate liquids from solid having spongy nature (for agriculture substances like separating oils from fruit and water from red beet).

B- Electrostatic and magnetic separation methods:

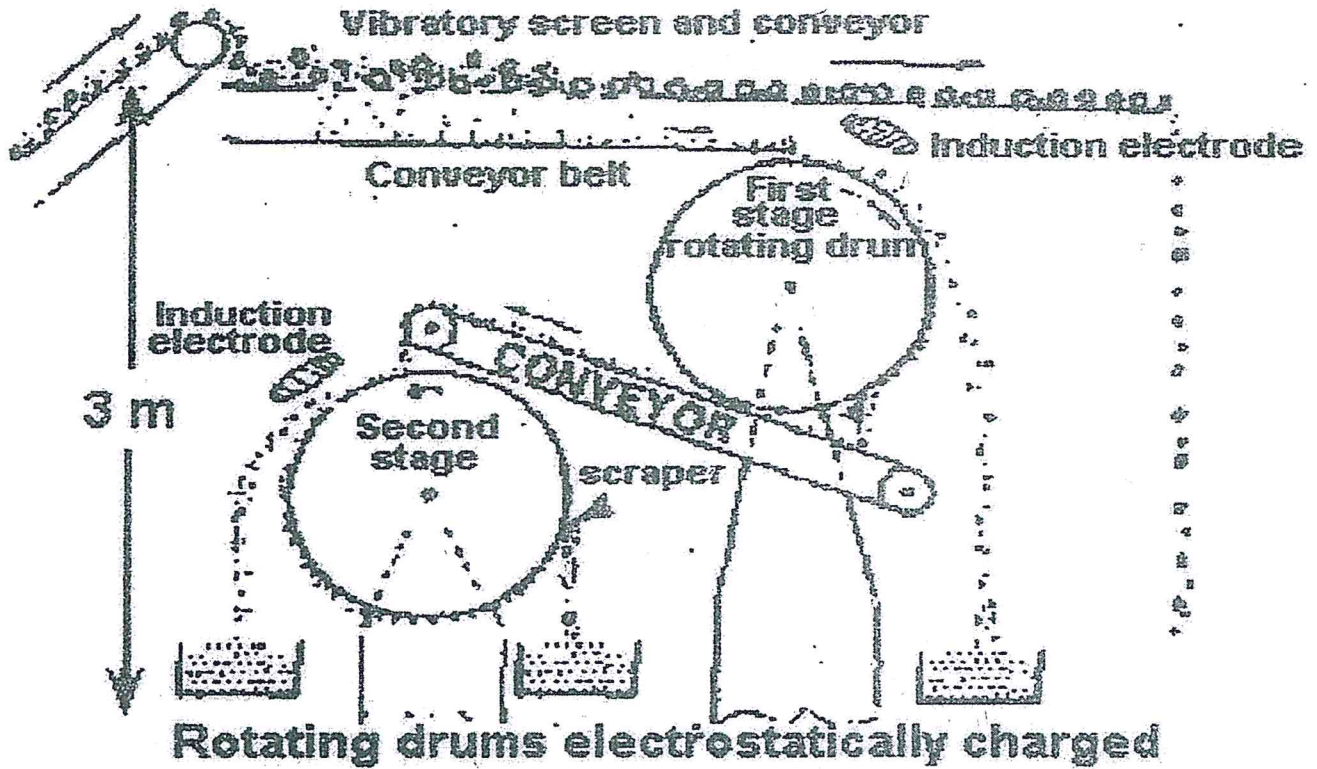
Electrostatic beneficiation is used for separating (mineral grains) Solid from gas according to their electrostatic affinity and it means charging with static electricity and separating them by passing them through an electric field. Different minerals have different electrostatic affinities will absorb different amounts of charge depending upon their composition, and hence are deflected different amounts by electric field After grains are sieved by size, they are placed through a beneficiator .

Beneficiators typically use free-fall of grains through electric fields. The grains of certain affinity will stick to the drum and others will fall to the ground.

beneficiators

This method is important in industry it is used for:

1. Purification of atmosphere air from lead dust (harmful)
2. Decreasing dust effecting on metals surfaces (cause corrosion).
3. Economic importance (expensive mineral dust).

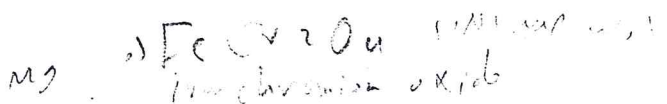
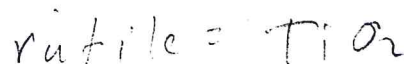


Magnetic separation is a process in which magnetically susceptible material is extracted from a mixture using magnetic force.

When minerals are placed in a magnetic field there are two classifications of magnetic particles,

Strongly magnetic particles (Ferromagnetic) such as [iron Co, Ni] and weakly magnetic particles (paramagnetic) such as rutile, ilmenite and chromite, particles that are repulsed by magnetic field called diamagnetic (Asbestos, limestone and quartz).

Using a similar principle (in electrostatic method) passing an eddy current through material can cause a conductive material to be separated from the non-conductive material. One of the largest uses currently is in the recycling industry, where wire and material made from copper and aluminum are separated from plastics. Product such as plastic, glass simply fall off the end of the separator.



C-Thermal of separation methods:

1-Distillation process is the process of heating a liquid until it boils, Capturing and cooling the result hot vapors, and collecting the condensed vapors .

Arab chemist used distillation to isolate perfumes

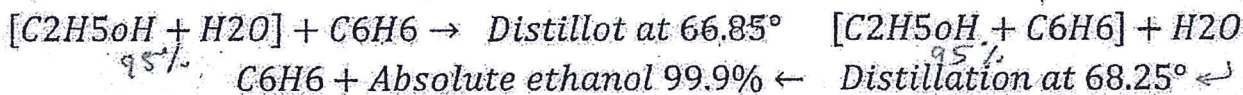
Distillation is used both for identification and purification of liquid organic compounds .
Distillation is used to purify a compound by separating it form a non-volatile material .

a-Simple distillation: is important for purification and identification (determine of boiling point of liquid).

b-Fractional distillation: used when mixture of liquids whose boiling point are similar (can't be separated by a simple distillation, separated by less than 25°). Using fractional column (packed, or trayed column) .

c-Vacuum distillation: is distillation at a reduced pressure. It is used to distill compounds that have a high b.p. or any compound which might undergo decomposition on heating at atmospheric pressure. The vacuum is provided by a mechanical pump. [since the boiling point of a compound is lower at low pressure].

d- Azotropic distillation: The behavior of lower constant b.p. mixture simulates that of a pure compound becomes the composition of the liquid phase is identical to that of vapor phase (this mixture is called azotropic mixture). The method depend on the components of the binary azotropic mixture and include distillation with third substance. This method is very important in industry for promotion of absolute ethanol from azotropic



2-Evaporation process : It is a type of phase transition by which molecules in liquid state (e.g. water) spontaneously become gaseous (e.g. water vapor) it is used to increase the centration of solution by vaporization of water from it. (Suger and sodium hydroxide manufactures.

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The factors influencing the rate of vaporization:

- a- Concentration of the substance evaporating in air (high concentration causes low evaporation) .
- b- Pressure: At less pressure evaporation happens faster .
- c- Surface area: A substance has larger surface area will evaporate faster.
- d- Temperature: If the substance is hotter, evaporation will be faster.
- e- Density: The higher density the slower liquid evaporation .

It is used also in a cloth dryer (hot air is blown through the clothes allowing water to evaporate rapidly).

It is used also in combustion vaporization.

D- Chemophysical separation methods:

Extraction:-

A separation of an organic compound from a solution or suspension in a liquid by shaking with second solvent in which organic compound is soluble and which is immiscible with liquid containing the substance. Diethyl ether is very widely used owing to its powerful solvent properties and its low b.p.

(35°). [liquid-liquid extraction or solvent extraction]

An industrial process will use an extraction step in which solutes are transferred from aqueous phase to the organic phase this is often followed by scrubbing stage in which unwanted solutes are removed from the organic phase, Then a stripping stage in which the organic phase must be then treated to purify its in a cleaning step to remove any degradation products, for example in PUREX process [it is an acronym standing for Plutonium Uranium Extraction].

It is based on liquid-liquid extraction ion-exchange standard nuclear reprocessing method for recovery of U and Pu from used nuclear fuel based on following the dissolution of the irradiated fuel aqueous nitric acid U and Pu are transferred to an organic phase by intensive mixing with an organic solvent [30% Tributyl phosphate (TBP) in kerosene. Further process steps enable the substance separation of U and Pu from one on other by ion-exchange method.

irradiated

To increase the efficiency of extraction,

a-Increase the surface area of used substance.

b-Increase the temperature using in the process.

c-Evaporate the solvent to get the solute by crystallization or precipitation.

2-Crystallization:

Is a chemical solid, liquid separated technique in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs.

Crystallization process consists of two major events, nucleation and crystal growth the solution must be supersaturated.

This can be achieved by :

a-solution cooling

b-addition of a second solvent to reduce solubility of the solute (antisolvent technique) .

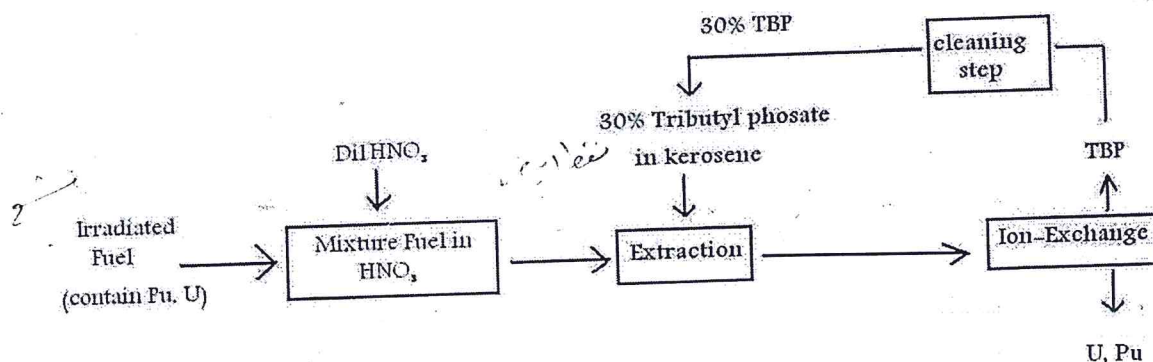
c-chemical reaction (precipitation) .

d-change in pH

e-solvent evaporation

for example:-

"powder salt for food" industry, silicon crystal water production and production of sucrose from sugar beet



3-Adsorption:

The adsorption is a process that occurs when a gas or a liquid solute accumulates (collects) on the surface of a solid (adsorbent), forming a molecular or atomic film (adsorbate) the binding to the surface is usually weak and reversible unless a chemical bond is formed.

For Example :-

Adsorption is used for removing a soluble substances from water by activated carbon (solid), It has a very big internal surface area (between 500-1500m²/g). Active carbon comes in two variations, powder Activated carbon (PAC) and Granular Activated Carbon (GAC).

The (GAC) version is mostly used in water treatment. It can adsorb the following soluble substance:

Mineral oil, poly aromatic hydrocarbons, phenol, halogenated substance, odor, taste, yeasts and non-polar substance.

The desorption is the reverse process [the isolation of adsorbate from surface of adsorbent].

This can be achieved by various methods,

- Increase the temperature to separate the adsorption.
- Using of another substance which more adsorption force than the adsorbate.
- By passing a water vapor on the surface of adsorbate [or N₂, CO₂ gases] to separate the adsorbate.

*Adsorbate

المادة التي يحدث لها الامتزاز على السطح

*Adsorbent

السطح الذي يحدث عليه الامتزاز

4- Absorption:

It is a process when a gas is taken in a solution the substance (gas) diffuses into liquid.

Sometimes a chemical bond is formed between the gas and the liquid like absorption of CO₂ in NaOH solution (stable)



Or an stable like absorption of CO by Cu₂Cl₂.

The process is usually carried out by solid packed column (Ceramic) (Coal).

Absorption includes both processes (adsorption and absorption).

Chemical Processes Technology

Technical processes (or industrial chemical process) deals with conversion of raw materials (naturally occurring) into industrial processes. The operations processing are number of processes, physical, chemical and mechanical that occur on the raw material (feed or feedstock) to covert them into desired product or range of products. Those processes were done in specific equipments called reactors.

The chemical processes include three stages:

- 1- Transfer the reaction components (feed) into the reaction place (reactor).
[the feed must be purified if necessary].
- 2- The chemical reaction which occur in the reactor.
- 3- Removing the products separate and purified them.

Types of chemical operation processes [industrial chemical processes]

There are two types of systems in the chemical operation processes:

- 1- Batch system
 - 2- Continuous system
-
- 1- The Batch system in which specific quantity of raw materials are introduced into the reactor, then number of changes are occur then the products are withdrawn, after completion for 2nd stage like purification or crystallization
 - After withdraw the products the processes are repeated again and so on.
 - In this system there is a determined time between introducing the raw material and removing the products.

The disadvantages of this system are:

- a- The equipments are complex.
- b- It needs a lot of workers.
- c- Controlling on this system is difficult because it depends on many factors for each batch like skill of workers and conditions of reactions or processes.
- d- It needs long time.

This system is used for small scale products or in some cases depends on the physical properties of the reactants.

Example for Batch industries:

Soap, pharmaceuticals products suspension, and polymerization.

- 2- Continuous system in which the materials are introduced continuously into the reactor or subsequently with removing the products also continuously as shown in figure (1).

Advantages of this system:

- Large production
- Accurate control on the conditions of reaction
- Mechanical controlling is easy
- Controlling on the quality standard because of the automatic controlling on the processes
- Many consumers prefer this system this system because it is more economic and does not need many workers and need less time
- But it is more expensive.

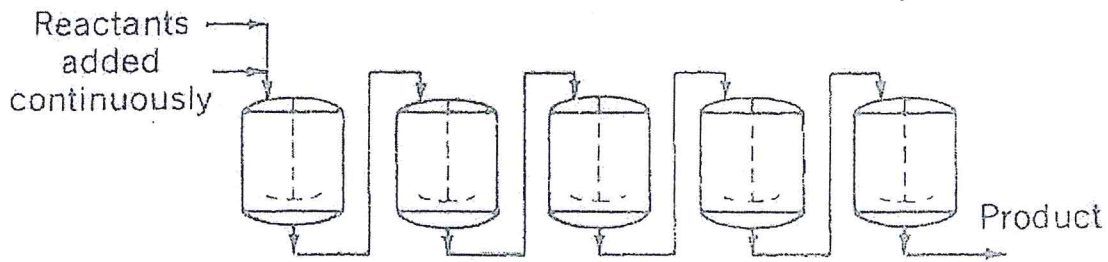


Figure 1

Reactors used in chemical operations

Reactors are the most important part in technological design, because in which most chemical reactions take place. These reactors take different shapes like:

- Furnaces
- Towers
- Tubular

They should contain mixture, Jacket for cooling, equipment for catalysts and heating or cooling system. However, there are many features or standard qualities should be provided in reactors:-

- 1- High production capacity and operation intensity.
- 2- High product yield and maximum process conditions.
- 3- Minimum power consumption.
- 4- Easy control and operations.
- 5- Low cost and maintenance.

However, many types of reactors are produced in industry depending on the system of operation (Batch or continuous) and on the raw materials, products and physical properties of them and on the catalysts using in the operations:-

1- The Stirred Reactor

This is the most common laboratory technique and widely used in industry as shown in figure (2). The vessel may be a laboratory flask plus stirrer, an autoclave or a large industrial container.

The reactor is used by mixing (0.1-5%) catalyst with liquid, bringing the mixture to the temperature and pressure of reaction conditions until the reaction is complete. The stirred reactor need not be used as batch reactor because the product will always be mixed with reactant and the catalyst may be recovered for reuse but it loses activity as a number of subsequent batches increase, where greater conversion of the reactant is desired, two or three stirred, continuous reactors are used in series and the product withdrawn from the last reactor.

2- The Fixed Bed Reactor

This apparatus is also common in both laboratory and industry. It comprises a column or (bed) of catalyst granules in a confined space and a liquid, gas, or vapor passed through the bed as shown in figure (2). In the plant the reactor is most often adiabatic with the fixed bed reactor; the reactant can be passed through the catalyst fast or slowly. All catalysts lose activity with use, the loss may be fast, in a matter of minute (as in the catalytic cracking of petroleum) or may be slow, in years (as with iron synthetic NH_3 catalysts). There is a problem with this type which is the regenerator of catalyst, and the volume of catalyst granules [pressure drop problem]. As the catalyst was pressed still harder, more active surface went into the reactor, however high pressure on the granules crushed many of the pores and the active surface (surface area) will decrease.

When catalyst rapidly lose activity, it is difficult to use fixed bed reactor in a continuous process.

3- The Fluidized Bed reactor

In this type it continuous a powdered catalyst and the air passed upward through catalyst, it behaves like a liquid or fluid with the gas or vapor reactant as shown in figure (3). It has advantages:

- a- Since a powdered catalyst is used, the surface area is larger.
- b- The catalyst is easy to move in and out of the reactor or regenerator. This type is used for strongly exothermic, oxidations and for catalytic process cracking of petroleum.
- c- The reactor is useful because the rapidly moving catalyst dissipates local hot spots [the temperature through the catalyst will be constant].

4- Slurry reactor [moving fluid – bed reactor]

In slurry reactor the catalyst is very finely divided and is carried through the reactor with the liquid fraction (reactants) as shown in figure (4). The reactors are usually mechanically stirred the [liquid / solid] slurry behaves as a homogenous phase.

In slurry reactor the particle size is even smaller than in fluidized, so the separation of catalyst from product is a problem and so the recovery of catalyst in residue processing is not practical so it is discarded with unconverted residue.

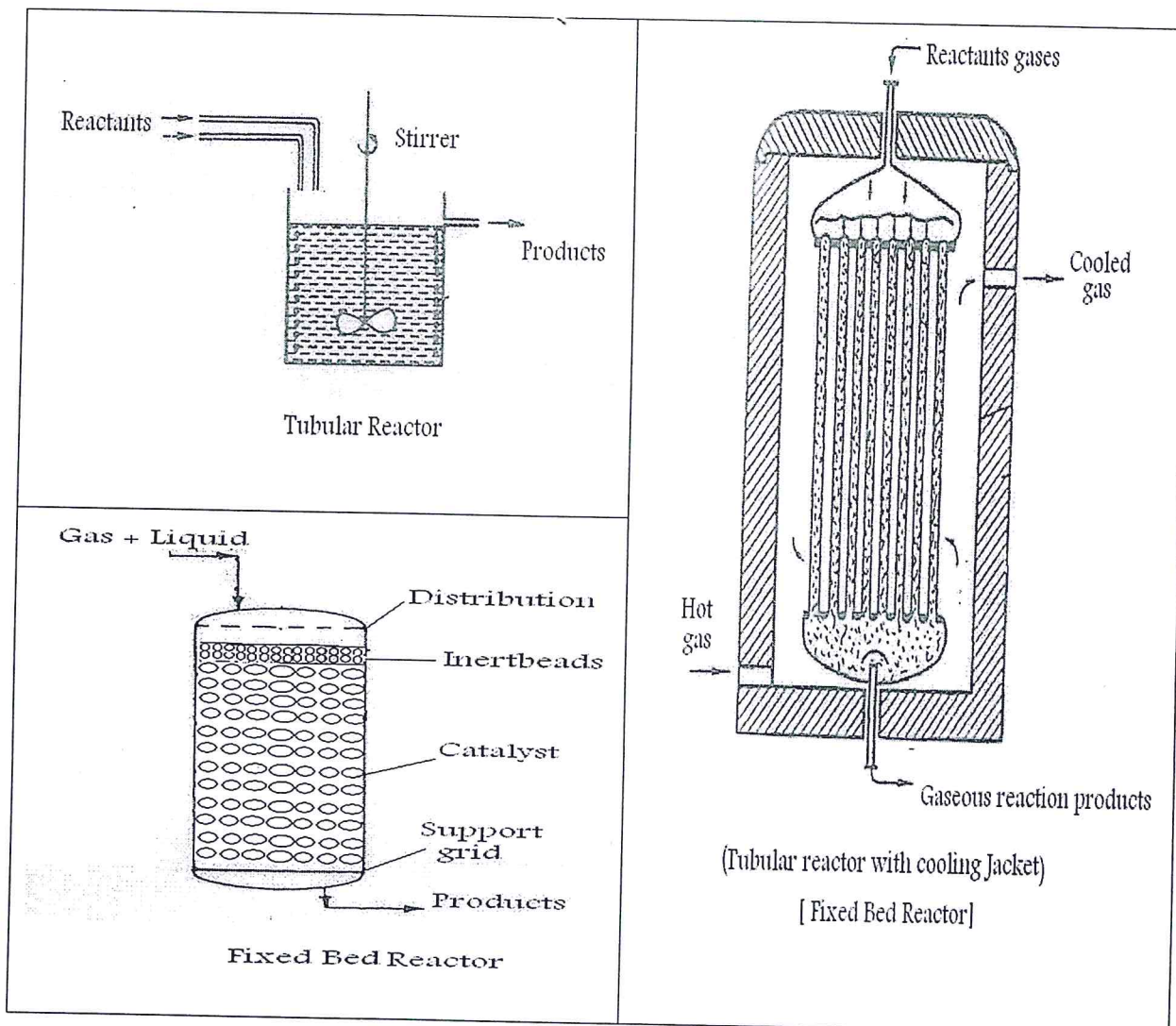


Figure 2

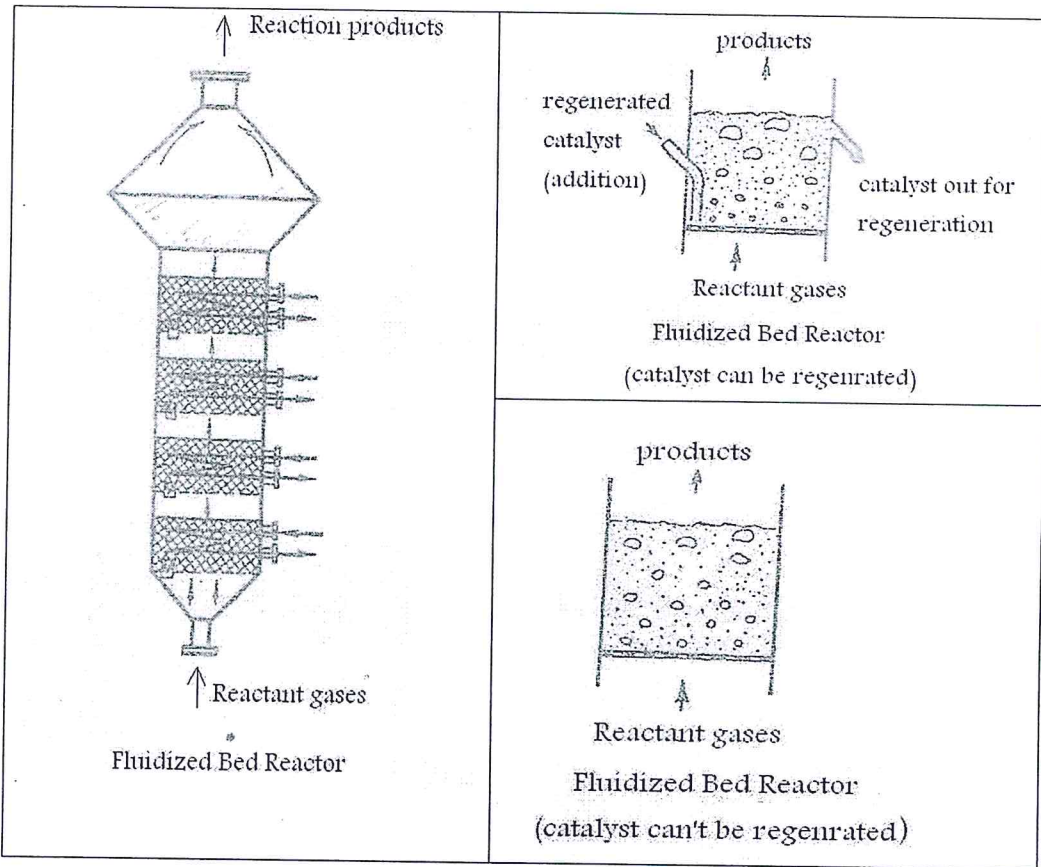


Figure 3

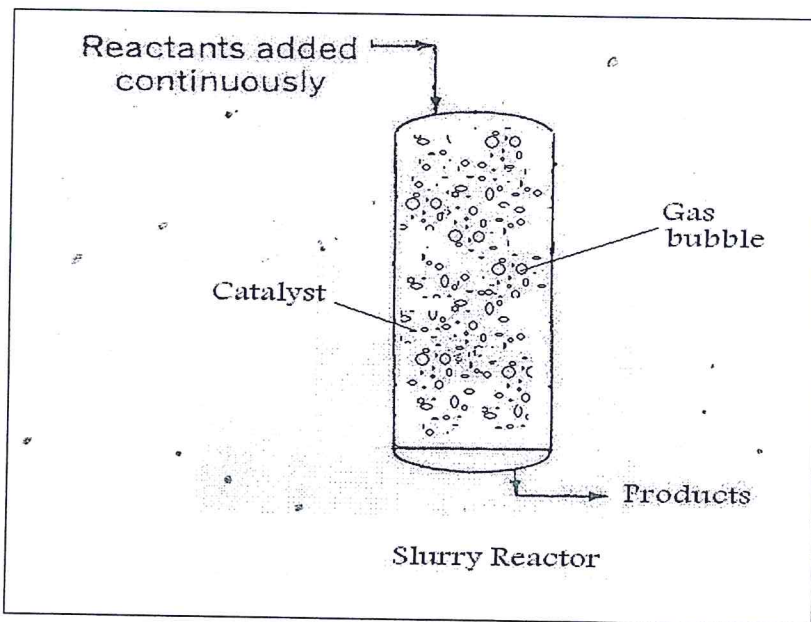


Figure 4

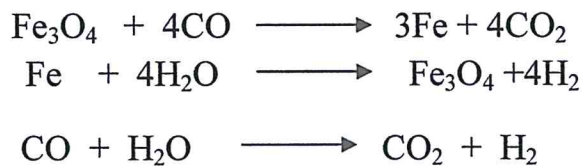
Catalysts

Catalysts a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. Catalysts can be divided into two main types - heterogeneous and homogeneous. In a heterogeneous reaction, the catalyst is in a different phase from the reactants. In a homogeneous reaction, the catalyst is in the same phase as the reactants.

There are general principles for catalytic action:

- 1- A catalyst is a chemical and the substance being catalyzed forms an intermediate chemical compound with catalyst. This intermediate reacts to give product or with second reactant to give product.
- 2- A catalyst possesses chemical or physical affinity for one or more reactants or products for example:

The catalytic interaction of steam with carbon monoxide by iron oxide:



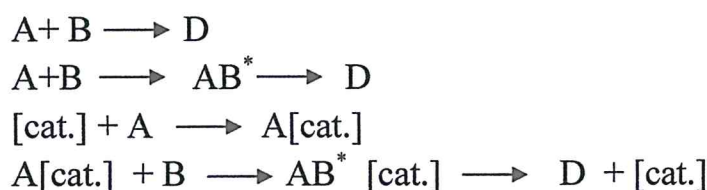
The reaction may be catalysed by platinum which don't enter to chemical cycle but which form adsorption complexes with reaction gases.

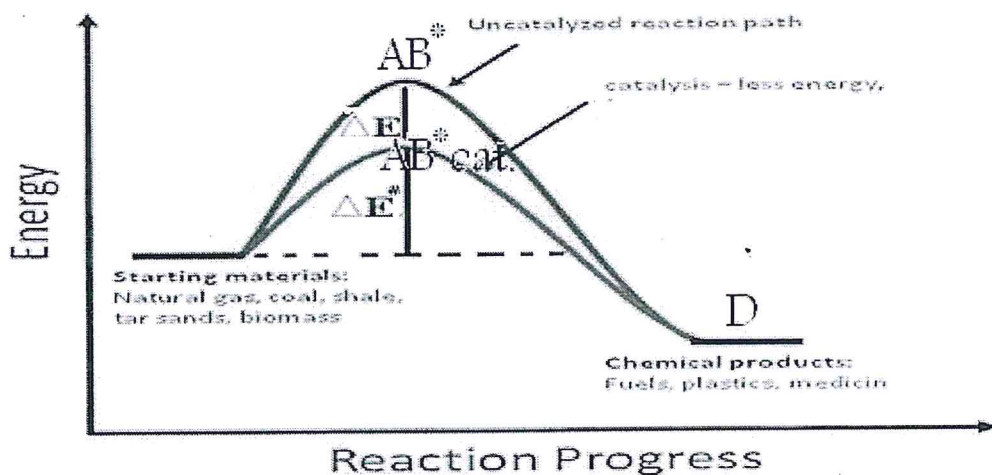
- 3- In the presence of catalyst the activation energy is less than along non-catalyst reaction.

Activation energy from Arrhenius Equation equal:

$$K = A e^{-E/RT}$$

Example



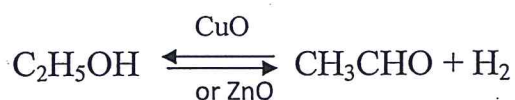


- 4-The catalyst causes no changes in the normal state of equilibrium.
- 5- The degree of acceleration is, under similar conditions, usually proportional to concentration of catalyst.
- 6- Whether liquid or gas (vapor), a reactant must get to the catalyst before it can react with catalyst (chemisorptions) and product must get away from catalyst (desorption).

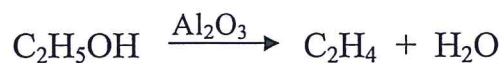
The characteristics of catalyst:

- 1- Selectivity of catalyst must be high toward the main product, for example:

- Dehydrogenation of ethanol in the presence of CuO or ZnO

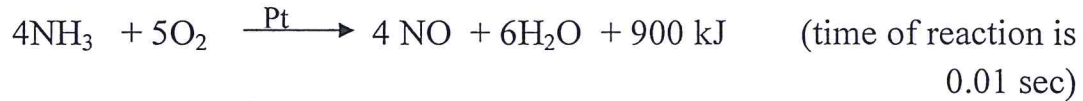


- Where with the presence of Al_2O_3 :



Another example:

The oxidation of ammonia on :



When reaction without Pt (preferable thermodynamic)



2- Stability toward high temperatures and poisoning which occur when there are impurities in feed.

3- Reactivity which depend on:

- a- Chemical composition of catalyst.
- b- Specific surface area of catalyst.
- c- Porosity and pores types of catalyst.
- d- Concentration and distribution of catalyst.

Role of Catalyst Deactivation

Deactivation is the loss of catalyst activity with time and can be either thermal (loss of surface area due to sintering) or chemical (poisoning or fouling).

Sintering can occur when temperature becomes too high and incomplete wetting of the catalysts particles (maldistribution), so the heat is not removed efficiently leading to hot spots. Sintering can be limited by heating the catalyst to high temperature.

Poisoning

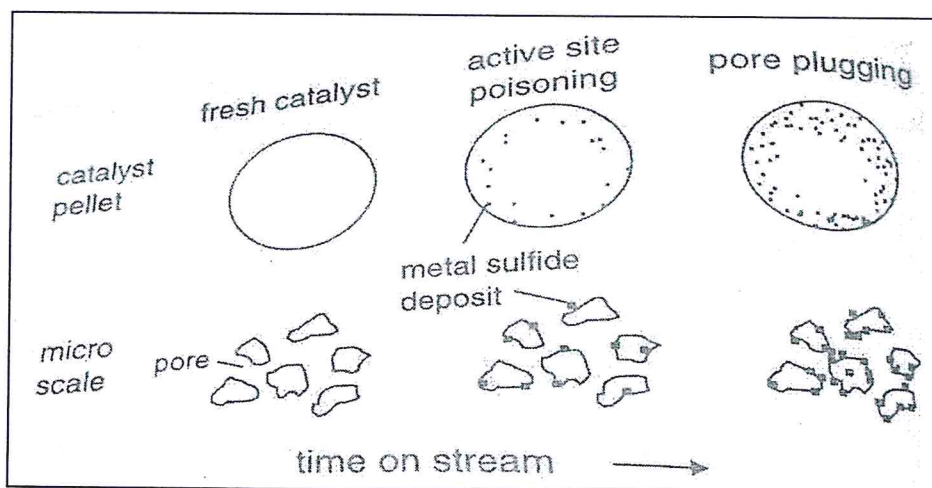
Poisoning of the catalyst occurs by adsorption impurities in the feed on specific catalytic sites, common poisons are sulfur (Pt catalyst), CO and CO₂ in ammonia synthesis, iron catalyst). Water can be also have a negative effect because it accelerates sintering.

Example on catalyst deactivation

The deactivation of catalyst by deposition of metals, all metals are present in crude oil, but the major ones are Ni and V. At the applied reaction conditions H₂S is present, and as a consequence, metal sulfides rather than metals are formed.



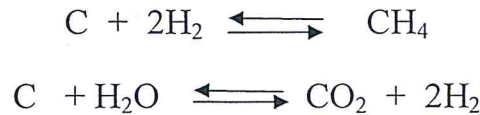
The catalyst is poisoned by this process, because of a large part of deposition occurs in the outer shell of catalyst particles.



Fouling

The most common cause of catalyst deactivation is fouling due to the occurrence of secondary reactions of reactants or products on the catalyst surface. The main example of this type of deactivation is coke formation.

Coke formation occurs by condensation reactions (cycloaddition, dehydrogenation) of aromatic compounds on the catalyst surface to form large structure of low hydrogen content. Coke is often simply indicated as carbon, C, optimal condition for coke formation are a reducing environment, high temperature, and low hydrogen pressure. Coke formation can be limited by addition of hydrogen, either as H₂ or as H₂O:



congr

Measurement of surface area

The surface area can be measured by equipment called [Gravimat] which depends on the small changes in weight.

The capacity of the mono layer of the catalyst [m_m] can be measured from the equation:

$$\frac{p/p_o}{m_a(1 - \frac{p}{p_o})} = \frac{1}{m_m c} + \frac{c - 1}{m_m c} \times \frac{p}{p_o}$$

p: vapor pressure which equal to every installment of N₂.

p_o: saturated vapor pressure of N₂ [77] torr.

m_a: adsorption quantity.

c : constant.

Methods of preparation of catalysts

- 1- Precipitation in which the active substance is precipitation on the carrier.

- 2- Impregnation in which the active substance (liquid) sorbed by the carrier.
- 3- Suspension technique in which the carrier is suspended in a solution of transition metal organic salts then the mixture is heated to convert the salts to metal oxide.

Composition of catalyst

Catalysts may be metals (Ni, Pb, Ag, Pd, Pt) or transition metal oxide, they have different shapes, they are pure or support on carrier, they may be metal wire or powder or crystals (pellets).

Most of solid catalysts consist of three components:

- 1- Active material of the catalyst (as salt's solutions), or as a liquid.
- 2- Carrier (support): it is an inert substance or has low activity like aluminum oxide (alumina) or silicon oxide (silica) e.g precipitation of nickel on Al_2O_3 or SiO_2 . The carrier must have large surface area, high porosity, high stability toward high temperature and not expensive.
- 3- Activator : the activity of catalyst can be increased by addition of another oxide e. g. $\text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$ gives 32.7% of dimethyl terephthalate in oxidation of p-xylene, but when Cr_2O_3 is added to the catalyst ($\text{Cr}_2\text{O}_3 : \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$) (2:1) gives 65% and where B_2O_3 is added ($\text{B}_2\text{O}_3 : \text{Cr}_2\text{O}_3 : \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$) the percentage increase to 89%.

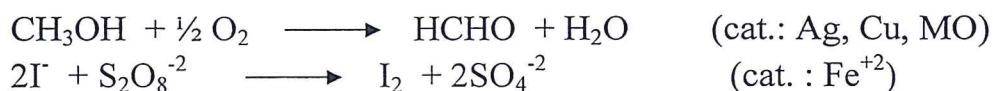
Activated Reactions

All the activated reactions (homogeneous or heterogeneous) are divided into two types:

1- Oxidation – Reduction reaction

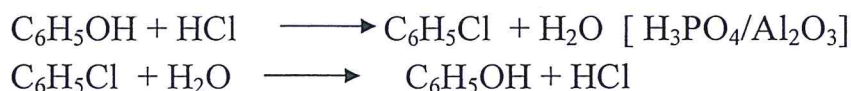
The addition of electrons or hydrogen or removal of O_2 is called reduction and removal of electrons or hydrogen or addition of O_2 is called oxidation.





2- Acid –Base reaction:

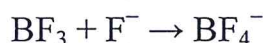
a- Arrhenius definition: acid dissociation in water releasing H_3O^+ ions, bases dissociation in water releasing OH^- ions.



b- Bronsted – lowry definition: acids are proton (H^+) donor, bases are proton acceptors.

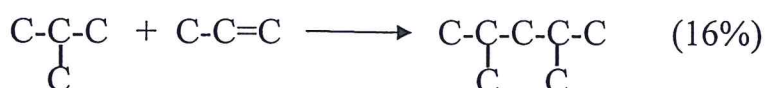
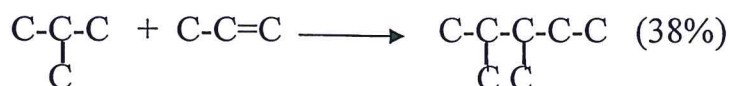


c- Lewis definition: acids are electron acceptors, bases are electron donor.



Comparison between homogeneous and heterogeneous catalysis

In homogeneous catalysis soluble catalysts are applied, in contrast with heterogeneous catalysis, where solid catalysts are used. One example of homogeneous catalysis is alkylation of isobutene with alkenes, with acids such as HF and H_2SO_4 as catalyst.



The homogeneous catalysts based on transition metals, and applied in essentially all sectors of the chemical process industry, in particular in polymerization, in the synthesis bulk chemicals (solvents, detergents, plasticizers), and in fine chemistry.

It is useful to compare homogeneous and heterogeneous transition metals based catalysis. In homogeneous catalysis the reaction mixture contains the catalyst complex in solution. This means that all of the metal is exposed to the reaction mixture. In heterogeneous catalysis on the other hand, the metal is typically applied on a carrier material or as a porous metal sponge type material, and only the surface atoms are active as shown in figure (5).

Example :

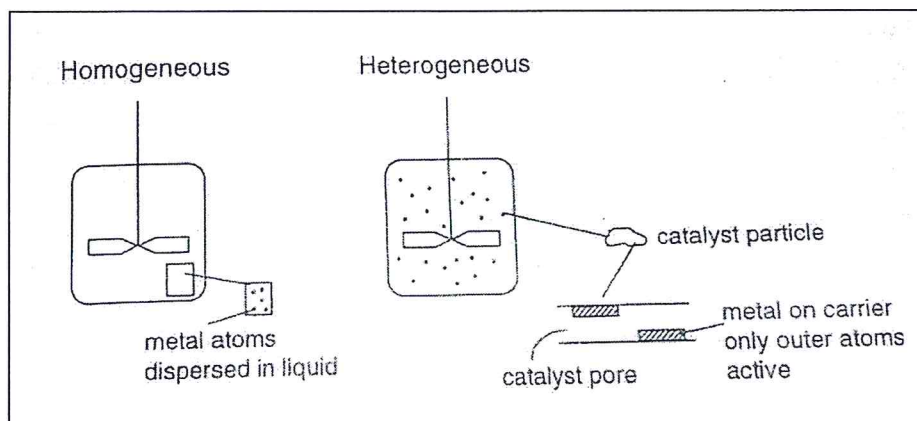
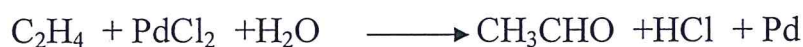


Figure 5

The homogeneous catalysts are more active (in terms of activity per metal center) in this type one poison molecule only deactivates one metal complex, whereas in heterogeneous catalysis a poison molecule can block a pore containing many active sites.

Homogeneous catalysis are more selective because there is only one type of active site, whereas heterogeneous catalyst often contain many different types of active sites, some of which could even catalyze undesired reactions.

Homogeneous catalysis has disadvantages:

- 1- The main problem is the separation of catalyst and product.
- 2- The use of solvents adds an additional separation step.
- 3- Their limited stability at high temperature so they are not suitable for strongly endothermic reaction such as cracking of C-C bond in Fluid Catalytic Cracking (FCC).
- 4- It is expensive.

There are types of reaction used in homogeneous catalysis.

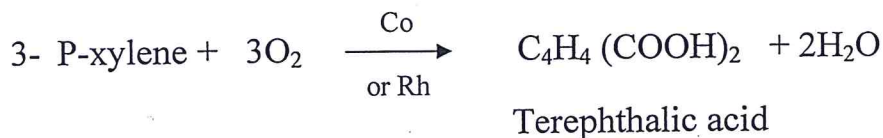
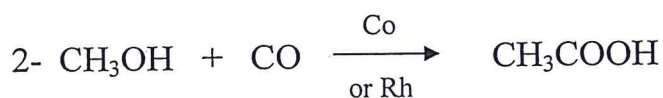
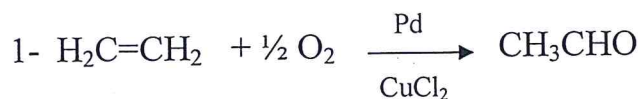
The main advantages of heterogeneous catalysis compared to homogeneous catalysis are:

- 1- Easy catalyst separation.
- 2- Flexibility in catalyst regeneration.
- 3- Less expensive.

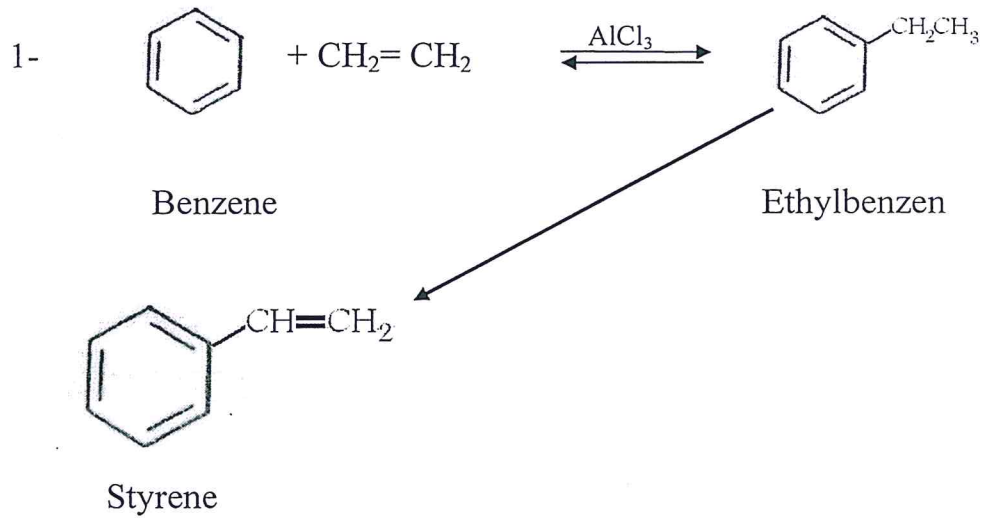
In industrial catalysis heterogeneous catalysis is generally preferable to use in continuous processes.

Selected examples of homogeneous catalysis

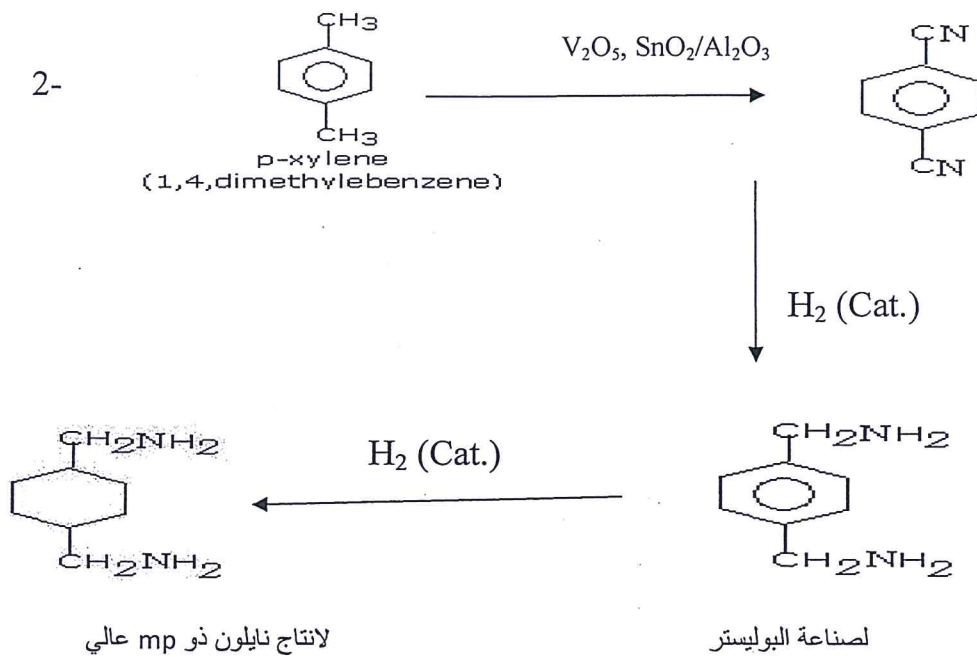
Reaction of industrial importance catalyzed by transition metals



Selected examples of heterogeneous catalysis



Styrene is monomer for polystyrene, which is used in the manufacture of all sorts of packaging materials.



Conversion, Efficiency, and Yield

Many reactions do not go to completion within a reasonable period of time. Frequently one reactant is charged to the reactor in greater than the stoichiometric amount in order to improve the reaction rate, or to shift the equilibrium in a favorable direction, or to limit by-product formation. For these reasons unchanged reactants frequently appear in the reaction mixture or in the product stream. These unconverted reactants may be disposed of as waste or, as is most often the case, they may be separated from the product and recycled to the process.

These alternatives have a profound effect upon the economics of the process. The terms “conversion,” “efficiency,” and “yield” are used to describe the amount of reactant consumed and the amount of product formed in a process. Conversion is expressed as a percentage and relates the amount of reactant that is chemically converted to another substance or substances to the amount of reactant initially charged to the process. Efficiency is also expressed as a percentage and relates the amount of reactant that has been converted to the desired product to the amount that has been chemically converted. The term “selectivity” may be used in place of “efficiency,” particularly when discussing catalytic reactions. Unfortunately, the term “yield” can cause some confusion. Yield may refer to the amount of product formed with relation to the amount of reactant consumed; or it may refer to the amount of product formed with relation to the amount of reactant charged to the reaction. In the latter usage the yield is equal to the product of conversion times efficiency. In order to avoid this ambiguity, the basis should be noted.

$$1- \text{Yield} = \frac{\text{Product (desired)}}{\text{Converted}} \times 100$$

$$\text{Converted} = \text{Feed (main reactant)} - \text{unreacted}$$

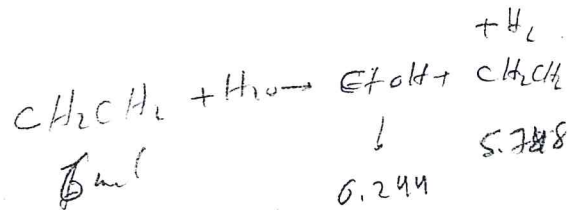
$$2- \text{Conversion \%} = \frac{\text{Converted}}{\text{Feed (main reactant)}} \times 100$$

$$3- \text{Efficiency \%} = \frac{\text{Products}}{\text{Converted}} \times 100$$

If there is an catalyst in the processes then

$$\text{Selectivity} = \frac{\text{Main product}}{\text{All products}} \times 100$$

$$\text{selectivity} = \frac{\text{product}}{\text{converted}} = \frac{0.244}{6-5.748}$$

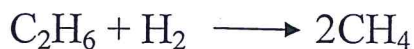


$$\text{Yield\%} = \frac{0.244}{6-5.748} \times 100 =$$

$$\text{Conversion} = \frac{6-5.748}{\text{Feed (6)}} \times 100$$

Examples:

- 1- To produce ethanol from adding water to ethylene. The percentage used as follows: 6 mole ethylene and 10 moles H₂O, after reaction had completed the yield contains: 0.244 mole ethanol, 9.75 mole H₂O, and 5.748 mole ethylene. Calculate yield%, conversion% and selectivity.
- 2- The following two reactions happened when removed hydrogen from ethane:



The results showed the following values:

Substance	%
C ₂ H ₆	35
C ₂ H ₄	30
H ₂	28
CH ₄	7

Calculate yield %, conversion % and selectivity % for ethane. *proportion*

to the CH₄

- 3- To produce ethylene glycol using catalyst 10 mole of water were added to ethylene oxide at acidic medium. The yield analysis shows the results: 3.8 mole ethylene glycol, 1.75 mole ethylene oxide and 3.8 mole water. Calculate yield % and conversion %.

Representation of material flow in a chemical process

A chemical process consists of an integrated series of reactions and associated operating steps, such as mixing, separation by distillation, and the like, whereby available raw materials are converted into a desired product. The process is carried out in an assembly of equipment through which material and energy travel batchwise or continuously. This equipment may consist of heat exchangers; material handling devices like pumps, compressors and conveyors; in addition to equipment used for materials mixing, reaction, or separation. Even the simpler processes involve several pieces of equipment. The movement of material through the various pieces of equipment is most often represented by a flow sheet.

A flow sheet is usually presented in the form of a line and block diagram, as illustrated in Fig. 6. Sometimes quantities of material and energy in the various streams are shown. Within the chemical industry there has been little success in developing a standard set of symbols for general use on flow sheets representing different types of equipment, and usual practice still involves indicating each equipment stage by a square, a rectangle, or a circle suitably labeled.

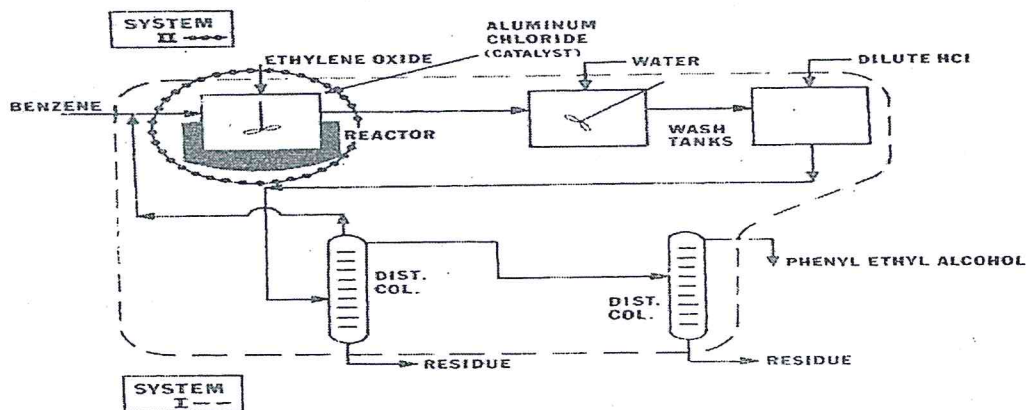
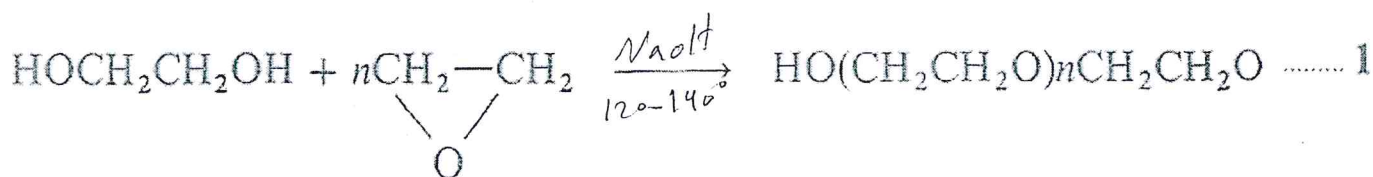


Figure 6 Flow sheet for the production of phenylethyl alcohol by Friedel-Crafts reaction.

Flow sheets of processes involving a single chemical reactor can normally be classified into one of the five categories described below. For more complex processes involving two or more reactors the flow sheet may be constructed by using combinations of these five basic types.

Type 1. Single Reactor Product Stream without Separation. Some chemical manufacturing processes, for which a typical flow sheet is shown in Fig. 7, involve no equipment other than a reactor to which reactants are fed directly without purification, and from which the product stream exits as a single phase, ready for use. Energy may also be added or removed from the reactor as needed.

An example of a process that can be represented by a Type 1 flow sheet is the production of polyethylene glycol by the reaction shown in Eq. 1



where $n = 6 - 9$. The reaction is run in the liquid phase in the presence of a sodium hydroxide catalyst at temperatures in the region of 120–140°C. With some formulations, the cooled product is ready for use in the manufacture of stearate emulsifiers for the food, drug, and cosmetic industries.

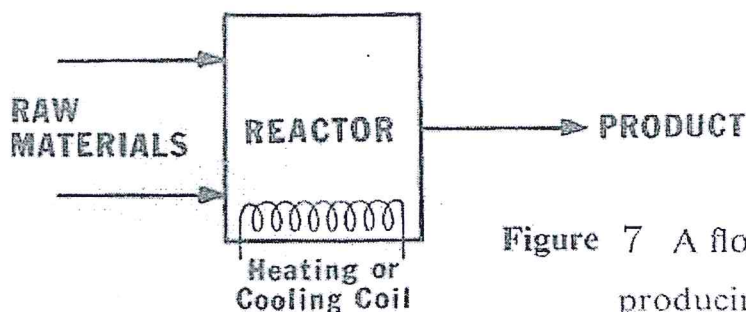


Figure 7 A flow sheet for a single reactor producing two product streams.

Type 2. Multiple Reactor Product Streams without Separation. This process is obtained when the reactants and products remain in different phases as shown in Fig. 8. Unreacted feed materials may leave in either one or both phases. An example of a process that can be represented by this type of flow sheet is as follows:

Aniline can be produced from chlorobenzene according to Eq. 2

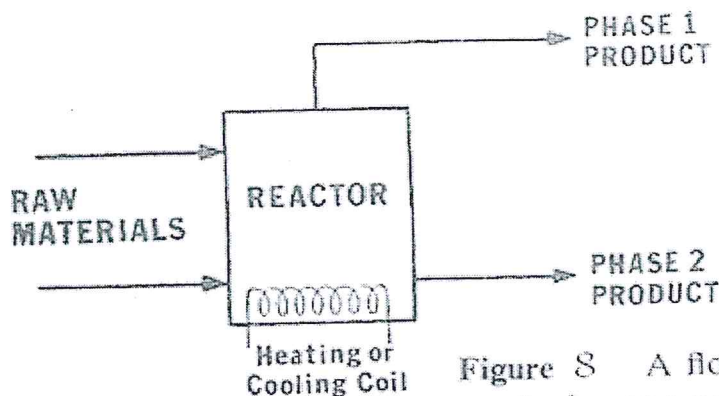
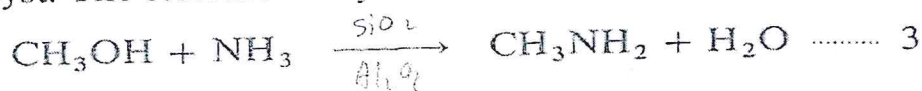


Figure 8 A flow sheet for a single reactor producing two product streams.

Ammonia is added in the form of a 28% solution where it reacts with the chlorobenzene in the presence of a cuprous oxide catalyst in a mild carbon steel reactor at temperatures between 220 and 250°C and pressures in the region of 2000 psi. The aniline and any unreacted chlorobenzene leave the reactor as an organic layer, and the coproduct ammonium chloride and any unreacted ammonia leave in the aqueous layer. The aniline produced is used as an intermediate in the manufacture of rubber chemicals and dyes.

Type 3. Single Reactor Product Stream with Separation. In many chemical processes the desired product must be separated and recovered from the mixture leaving the reactor. Many different separation schemes are used. Some of the more common separation techniques used are crystallization, distillation, solvent extraction, absorption, adsorption, filtration, and ion exchange. In the flow sheet of Fig. 9, recovery is by absorption in a suitable solvent followed by stripping in a distillation column. The unconverted reactants may leave in the tail gas, one of the product streams, or a combination of both product streams plus tail gas. An example of a process that can be represented by this flow sheet is as follows:

Methylamine is made by reacting methanol and ammonia over a silica-alumina catalyst. The stoichiometry of the reaction is given in Eq. 3.



The reaction takes place in the vapor phase at 350 to 450°C and 200 psi pressure. The methylamine vapor leaving the reactor is recovered as shown in Fig. 9 by water scrubbing and purification by stripping and distillation in the still. The methylamine produced is used in surfactants, photographic developers, rubber accelerators, drugs, and agricultural chemicals.

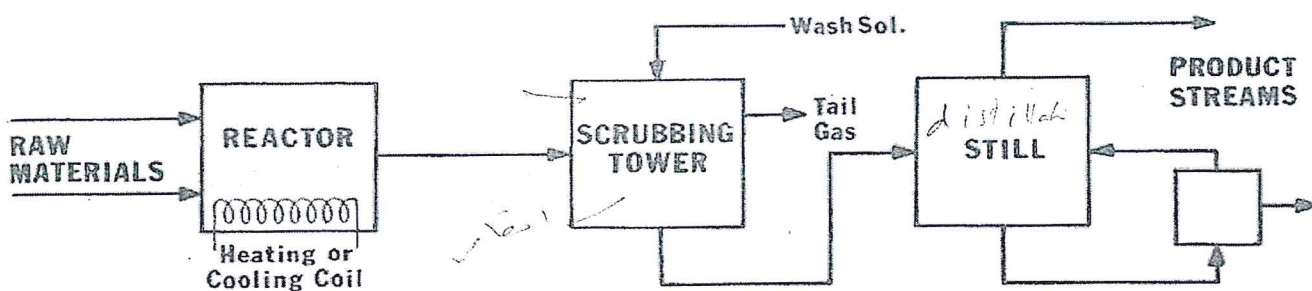
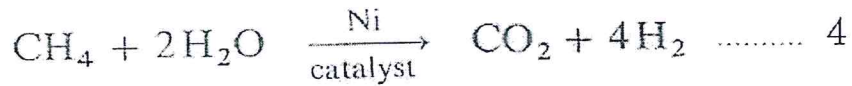


Figure 9 A flow sheet for a single reactor product stream with separation.

Type 4. Multiple Separations Involving Reactor Feed and Product Streams. This flow sheet represents an extension of Type 3, in that separations are also performed on the raw materials. In the illustrative flow sheet for this case, shown in Fig.10, raw material purification is by adsorption and product purification by absorption and stripping. Any other means of separation would involve the same type of block diagram. An example of a process that is represented by this flow sheet is the manufacture of H₂ by steam reforming of methane. The reaction is represented in Eq. 4.



As indicated, the reaction is carried out over a nickel catalyst. In order to prevent the deactivation of the catalyst, the methane obtained from natural gas is desulfurized by contact with activated carbon. The CO₂ is removed from the product H₂ by scrubbing with a monoethanolamine solution.

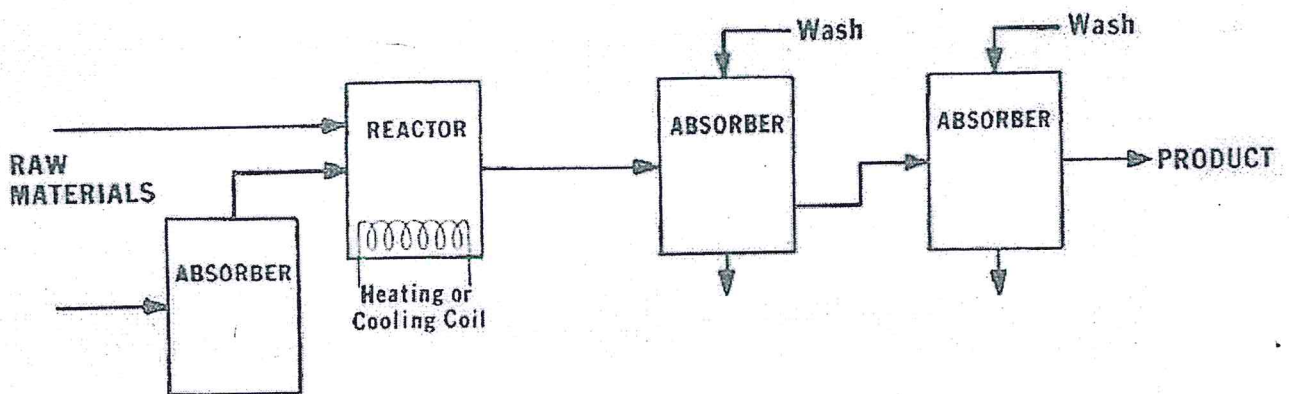


Figure 10 A flow sheet with multiple separations of reactor feed and product streams.

Type 5. Reactor with Recycle. This flow representation is very common, for a large number of chemical processes contain some form of recycle

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stream. Recycle as shown in Fig.11 involves the return of part or all of a process stream from a later to an earlier stage in the process. The general object of recycle in a chemical process is to minimize materials consumption per unit of product produced. Thus, when a reaction does not go to completion because of unfavorable kinetics or equilibrium, the unconsumed material is separated from the product stream. When material is recycled in this fashion, a purge must be provided, as shown, to prevent accumulation of impurities. The Haber process for producing ammonia is an example of a recycle system that can be represented by the flow sheet shown in Fig. 11.

27.21
27.5

Ammonia is made by passing a hydrogen-nitrogen mixture over a promoted iron catalyst at elevated pressure. The ammonia is recovered from the reactor off-gases by cooling and condensation or by water scrubbing. However, because of equilibrium limitations encountered at the operating conditions usually used, only a small amount of the hydrogen and nitrogen reacts to form ammonia. The economics of the process require that the gases be recycled. A purge is required to eliminate the buildup of any undesirable gases such as argon or methane in the reactor.

The stoichiometry of the reaction is shown in Eq. 5 .

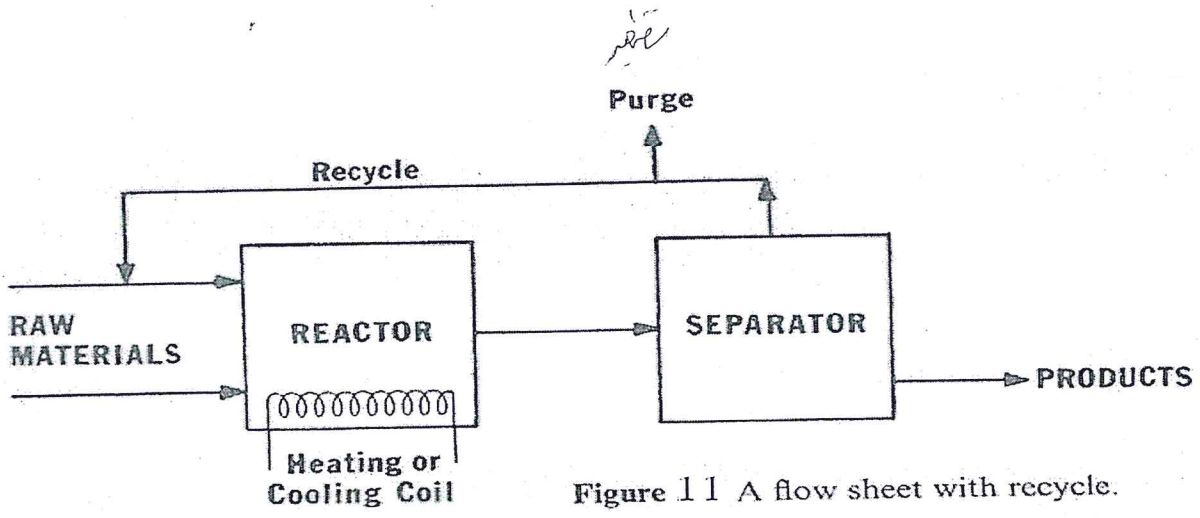
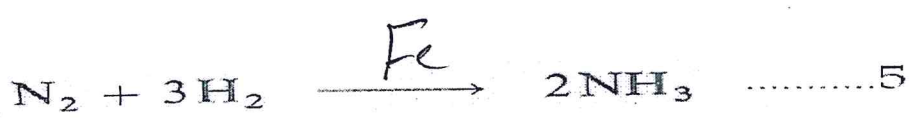


Figure 11 A flow sheet with recycle.

Complex Flow Sheet. As indicated earlier, most complex flow sheets may be considered as combinations of the five types just discussed. There are a number of reasons why such combinations occur. One of the most common is due to the need for multiple product separations. For example, suppose that a product stream containing a number of components is produced in

some process, and recovery of the individual components in relatively pure form requires many steps. The separation of crude oil into its useful products is a very complex process that results from the need to separate a mixture containing many components into mixtures containing fewer components. However, the entire refining process of crude oil can be represented by a flow sheet made up of a composite of the five types discussed above.

Another common reason for the occurrence of complex flow sheets is that frequently a process requires a number of reactions to be carried out in series. Such reactions often cannot be made to occur in a single reaction vessel, since the conditions favoring one reaction may not favor the others. A flow sheet of such a process might look like that shown in Fig. 12. The flow sheet as depicted is a combination of Types 1 and 4. The heat exchangers between the reactors allow for the reactors to be operated at different temperatures. This would be necessary if the temperature dependency of the stagewise reactions are different.

In all of the flow sheets that we have presented thus far, no information as to quantities of material flow has been recorded on the flow sheet. A complete representation of the process, of course, requires that this information be presented. It is at this point that we must rely on the material balance to give a complete description of the process.

In reviewing detailed process flow sheets where the material balance information has been recorded, the chemist soon learns that the units representing material flow and process conditions are not the same as those commonly used in the laboratory. The next section deals with the units problem that the chemist must confront in handling material flow and balance problems.

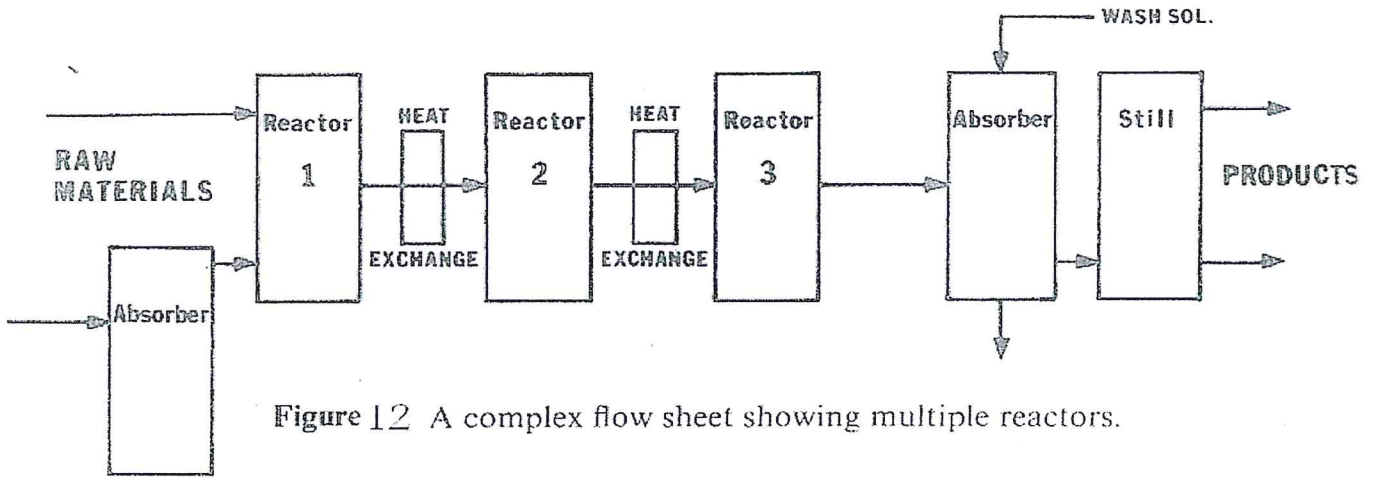


Figure 12 A complex flow sheet showing multiple reactors.

Conversion of a Laboratory Process to a Pilot Plant and Then to a Plant Procedure

سرفه
This chapter shows how a process has to be modified when large-scale production is contemplated. So far in this book we have looked at many processes run on large scale, and the reader should be somewhat aware of how different large-scale work is from preparations on a laboratory scale. We now discuss "scale-up," a phrase that refers to conversion of a laboratory process to the manufacturing stage.

5.1 SCALE-UP OF A LABORATORY PROCESS FOR COMMERCIAL PRODUCTION

In order to give the proper perspective on how research and development is carried out, we first discuss the way that an industrial research and development operation is organized. A chemical company needs to have products to sell. These products must be needed by society. The last 50 years have shown that these products are often on the market for a relatively few years. They are then displaced by other products, which either perform better or are less expensive. We now show what a company has to go through to have a flow of products for market.

سرفه 5.1.1 How a Company Is Organized to Bring Products from the Laboratory to the Commercial Stage

Management must have the means to learn about needs of consumers that can be met by products the company can supply. The author is most familiar with companies in which essentially all the aspects of this procedure are within the corporation. Some companies purchase technology necessary for a new product, (e.g., the licensing of the patent for a product). This chapter will be concerned

with the research, development, sales, production, patent, and other branches that get in the picture when new products are being created.

5.1.2 Stage I: Management Defines Project and Approves the Working Plan of Attack

Industrial research chemists do not usually define their own projects, as those working in an academic environment do. The research staff is hired because of its expertise as inorganic or organic chemists, biochemists, and so on. The direction of research takes into account available raw materials and proprietary knowledge of general groups of compounds obtained by the company over many years. Examples of this would be Dow Chemical Company's association with organic and inorganic bromine and chlorine compounds and Merck's association with pharmaceuticals. Both companies have prepared and tested substances within their area of knowledge for many years and have a great many successful compounds on the market. Within the limitations described, the research group endeavors to discover a useful product to fulfill a certain function within the aims of corporate research and development. These objectives are continually modified and refined by published data in technical journals and by input from sales, technical service, and ideas from the research staff. (See pages 1-2 for a general list of product groups included in the areas covered by all branches of the chemical industry.) Substances are prepared by the research people and are examined to see if they are of interest to management. Often many thousands of products are prepared, only a few of which may eventually be of interest. The direction of this synthesis work is restricted only by the background of the scientific staff, the company's patent situation, and the availability of certain raw materials and equipment. The chemist synthesizes products whose structure is considered to have the desired properties and submits the product for screening tests. The compound is carefully purified to ensure that the test results have not been affected by by-products.

5.1.3 Stage 2: Preliminary Cost Calculation

The products that pass preliminary screening are submitted for cost calculation. Two calculations are prepared (see Chapter 6).

Calculation 1. For the first computation, the chemist assumes that a commercial-sized vessel is available (e.g., 2000 L). It is assumed that the lab process is carried out in the filled reactor to give the same yield, using the same solvents and mole ratios of reagents and commercial costs for the raw materials, if available. The only thing changed would be a bigger batch resulting in a larger quantity of material prepared in essentially the same reaction time. This means

that, for the same man-hours, more product would be prepared, so the product would be significantly less expensive than the lab preparation. Loading and unloading the reactor will clearly take longer than in the lab and give a slight cost increase.

Calculation 2. For the second calculation, the chemist is asked to make a reasonable estimate, if additional laboratory work were carried out, of how high a yield figure might be reached, whether the time cycle might be shortened, and whether other simplifications might be achieved. The cost calculation is then repeated to see whether the cost would drop to an interesting value if the chemical predictions proved successful. Management then makes a considered judgment as to whether the product would fit into its product line at the optimistic price. If so, it authorizes laboratory process development work.

5.1.4 Stage 3: Laboratory Process Development

This work consists of the following stages:

1. Raw materials are tested in the lab process using samples of material available in commercial quantities. This is because if raw material is sold in commercial quantities only in purity requiring extensive purification before it can be used in this procedure, it will cause the estimate of cost to rise significantly. The same result might occur if the material had to be synthesized.

2. Solvents are to be used that are not severe fire, explosion, or toxicity hazards. Solvents that are dangerous to handle would likely require special safety equipment when used in large quantities. Usually, however, a substitute solvent can be found that has fewer problems.

3. All solvents used in large-scale work have to be recovered for reuse. The recovery process has to yield solvent of usable quality. The solvent should be recovered in at least 85% yield. A loss of 15% is usual in this work. This loss, plus the recovery equipment needed and extra time to be spent, will increase the cost. (For background on distillation set-ups see Chapter 8.)

4. Yield improvement studies must be conducted. A higher yield means lower cost (less kilograms of raw material becoming waste). The process called statistical design is a method whereby a limited number of experiments can be used to identify the significant variables affecting the yield. The studies by Davies (1978) and Hunter (1974) (on the Plackett-Burman procedure) are appropriate in this matter. When these are known, the process can be adjusted chemically in a logical way.

5. Identify all significant by-products chemically. It is necessary to have samples of these materials to add to the product to see what tolerable limits of by-product are acceptable in the finished product in the application tests. The toxicity of the by-products must also be determined. This will prevent situations

where there is a highly toxic by-product in a relatively nontoxic product from going unnoticed. Analysis of the statistical experiments referred to previously for these contaminants shows how the process variables affect the quantity of by-product. For example, a product added to give color stability to plastics should not have any color-forming by-products. The plastic is prepared at high temperature, and since most substances discolor at raised heat, the prepared material would be spoiled.

6. For a particular time cycle and reaction vessel size it is important to prepare as much product as possible. Reactions run in solvent should be studied to have as little solvent as possible, with the vessel as full as possible with reaction mixture, so that the quantity of product in the vessel is as high as possible.

7. Crystallization for purification should be carried out only as a last step. The crystallization process gives a yield of about 90% at best. A 10% yield loss is quite high. Of course, the material in the mother liquor can be purified with additional processing. There are other purification methods that are much more quantitative (e.g., extraction or chromatography).

8. The following factors should be considered in order to have as short a time cycle as possible:

a. Filtration of a slurry has to be fast. This requires well-formed crystals. If a process involving a slow filtration is carried out on a large scale, liquid will stop flowing off when the cake is several inches thick. Studies on how to obtain well-formed crystals must be made. Reduction in the quantity of by-products present is one of many factors that affect the size and quality of crystals.

b. The most common purification method used in large-scale processing is extraction by partition between immiscible liquids. The separation of liquids often requires a long time because of the tendency for emulsification. Laboratory studies to improve the speed of separation should be carried out. Solvents used may have to be changed or temperature adjusted, or a preliminary purification may have to be carried out by another method.

c. To get a clear idea of how the lab process will behave in large scale, the procedure should be carried out using the time cycle estimated for the large-scale preparation. For example, heating up a 4000-L vessel full of reaction mixture may take one-half to three-quarters of an hour, as against five minutes for the corresponding lab run. This extended time may affect the result of the run. Filtering the laboratory batch may be complete in five minutes but may take 1-2 hours in the plant. Will the reaction product be stable under these conditions? If it is not, then process modifications will be necessary.

d. It is necessary to balance the economic need for a short time cycle against the ability to control the increased heat safely when reagents are mixed. An addition rate much slower than that used in the laboratory is often needed so that the cooling water can remove the heat generated in the vessel. As the batch

size increases, the cooling has to be more efficient. Equipment change may be necessary. This sort of situation will be discussed in Chapter 8.

e. The final process should be carried out at a temperature 10–20°C higher than the final lab process calls for. This is to see whether the process is close to the point where an uncontrollably fast reaction occurs.

f. Analyses should be developed for showing the rate of product and by-product formation and of disappearance of raw materials. These analyses have to be fast, so that what is happening in the large-scale batch is quickly known to the chemist.

g. All gas, liquid, and solid effluent has to be weighed and analyzed, and a decision on proper disposal must be made. It is often found that additional processing is necessary.

5.1.5 Stage 4: Preparation of Pilot Plant Process

Management continually reviews the data that have accumulated and at a certain time decides that pilot plant studies should be made. Before this decision is made final, there are two more steps.

A written pilot plant process is prepared that includes the large-scale time cycle deemed necessary and the choice of equipment needed.

A second pair of cost calculations is carried out, using the same approach as in Section 5.1.3.

Based on the results of these costs and on a review of the process as well as on safety considerations and availability of raw material and equipment, management makes a decision about whether to approve a pilot plant campaign.

5.1.6 Stage 5: Management Approves Pilot Plant Work

It should be kept in mind that the pilot plant batch is a small, commercial-sized batch and is being examined to see whether there are any obstacles to full-scale production. The process should be the one used for the cost calculation referred to earlier. Pilot plant batches should have many samples taken from the batch at various stages and the process completed in the laboratory. This will clearly show what to do if there are large-scale problems that require process modification. Problems seen only at the pilot stage are:

ا. As the vessel size increases, the surface-volume ratio changes significantly. Factors such as reaction rate of a surface-promoted reaction or crystallization rate may vary greatly.

ب. Filtrations may be unexpectedly slow. The effect of different filter media is hard to predict. Crystal size and rate of growth are likely to be different when large batches are prepared under different types of agitation conditions.

- ✓ c. The separation of layers may be slow because of the synthesis of emulsion-forming by-products.
- ✓ d. Samples of the final product mixture should be taken as the crystals form, and they should crystallize in the laboratory. Experience has shown that changes in conditions such as we have been talking about often result in a different polymorphic form being precipitated. This causes trouble in any product that is sold for use in solid form. For example, if a pharmaceutical active ingredient has been formulated into pills, using a large laboratory batch, and the pilot plant material then is crystallized in another form, it is likely that the new pills will have different characteristics and will not hold together. It may also be that the new active ingredient will have different physiological properties. The rate of solubility in body fluids could be different for the second crystal form.
- ✓ e. It is often necessary to transfer hot slurries of reaction mixture from one vessel to another. An example of this would be to go from a glass-lined reactor to a stainless steel one when the pH value changes from strongly acidic to strongly basic. It has to be decided at what temperature the transferred mixture should take place in order to prevent the mixture from crystallizing out.
- ✓ f. Studies to use automated heating and cooling equipment certainly should be made in the pilot plant. Before these devices can be used, the heat behavior should be studied with the manually controlled large-scale batch.
- ✓ g. The effluent data from the lab should be confirmed for the pilot process. Because of the various changes referred to earlier, extra washes are often necessary. Also a detailed review of the experiences as far as safety goes is essential.

5.1.7 Stage 6: Management Approves Commercial Production

2/12
The following is a list of what management will look for before approving commercial production:

- ✓ a. The pilot plant material from a few batches has to be analyzed and specifications must be agreed on. The figures on the maximum of by-products allowed and the minimum product purity acceptable should be similar to the lab material tested previously but may be slightly different if the data from (b) is satisfactory.
- ✓ b. The performance of pilot plant material in application tests has to be similar to previously tested lab material.
- ✓ c. The cost calculation using the pilot plant process rewritten to reflect the large vessel experience should be prepared. It should not be too different from previous values and should present a promising economic picture.
- ✓ d. A review of the pilot plant process should show it to be safe. A safety data sheet should be assembled for the process. An outline of this document is given in Section 5.1.7.A.

e. Adequate raw material and large-scale equipment has to be available to manufacture the quantity of material to meet expected demand.

A. Safety Data Sheet

The raw materials, intermediates, and products should be tested so that safety data will be available for various emergencies. This information should be on hand where the substances are handled.

Physical Properties. Liquid or solid, boiling point, solubility in water, density and flammability are obvious points a fire crew would need to know.

How to Extinguish the Burning Substances. This involves clear instructions on obvious factors such as, for example, not to extinguish burning toluene with water (fire would spread) and not to use water near substances highly reactive with water (e.g., metal hydrides).

First Aid to Lungs, Skin, and Eyes. Chemical and medical personnel have to work together on this. If a toxic substance comes in contact with the skin, it should be removed by dissolving or suspending it in a liquid that will not cause the substance to be more readily carried through the skin. Skin, eyes, and lungs have to be considered for each chemical. Water is used on the body exterior in most cases.

Chemical Reactivity. One must consider which substances should not be stored in the same area. For example, acids should not be stored with bases, nor oxidizing agents with reducing agents. The author was once called to the scene of a truck accident, where the driver heard a crash in the rear of his rig. He opened up the truck and was overcome by the fumes. Fortunately, this occurred in front of a fire station. Fireman flooded the truck with water. Inspection of the truck showed that it contained a large glass vessel of nitric acid that the driver had placed next to a metal container of sodium cyanide. Because of the hot summer day, the glass container of nitric acid broke. The container of sodium cyanide had not yet corroded through. If the fire department had not responded in a matter of minutes, the heavily built-up area would have been exposed to hydrogen cyanide fumes. Careful planning is needed to avoid problems in handling emergency spills of chemicals during transportation accidents and in emergencies in warehouses. Chemists and fire personnel have to work together in planning adequately for reasonable countermeasures.

Storage of Chemicals. The majority of chemicals have only limited stability. It is necessary to purchase only what will be used up before degradation sets

in. This involves arranging for a proper analysis schedule. If material becomes off-grade during storage, a difficult disposal problem can occur, as well as the loss of money.

Ecological Problems. Today the ecological problems of chemical companies are very serious. The treating of processes to reduce pollution will be discussed in Chapter 7, along with the results of air and water pollution.

MATERIAL ACCOUNTING

THE LAW OF CONSERVATION OF MASS REALLY WORKS

In attempting to carry out a reaction in the laboratory, every chemistry student has learned that a vital step in the procedure deals with the calculation of the amount of starting materials required and the amount of product that is expected to be produced. Such calculations are also required when chemical reactions are carried out on an industrial scale. However, the format of the calculations differs from those that the chemist normally utilizes in the laboratory. The calculations differ because chemists in the laboratory normally work with closed systems, whereas most industrial processes are invariably open systems. Open systems are those in which there is a flow of materials into and out of the process equipment. In such systems heat or work energy may be added to certain process units and may be removed from others not only to satisfy operational requirements, but also to operate most economically. The complete accounting of all mass and energy in such chemical processes is referred to as a material and energy balance.

The material balance is frequently referred to as a mass balance or weight balance in industrial chemistry practice. Therefore, these terms are used interchangeably throughout this book. A material balance can be effected without an energy balance, but an energy balance requires a knowledge of the mass and composition of all streams. This combination, the material and energy balance, is one of the most powerful tools used in the sequence of steps necessary to bring a chemical reaction from the idea stage to a viable large-scale commercial process. It is also an essential tool in the effective evaluation of the day-to-day operation of an existing chemical process. The concept of the material balance is so simple, however, that the student is prone to assume erroneously that he can apply these balances skillfully without much training in their application. Thus, it is the purpose of this

chapter to discuss the basic principles of material balances and how they can be applied to industrial problems.

3.1 THE MATERIAL BALANCE EQUATION

In general, there are two types of chemical processes with which the industrial chemist deals, the "batch process" and the "continuous process." In the batch process the chemicals are added to the processing vessel in one operation and then the process is carried out. In some cases the products are removed during this period, but in others they are removed after the processing is completed. In the continuous process the chemical charge and the products enter and leave continuously. The material balance can be applied to either a batch or a continuous process. The biggest difference in applying the material balance to these two processes involves the element of time. A material balance applied to a batch process usually does not include a time variable. The balance in such a case is generally made over a complete cycle, which involves merely the processing of a single charge. In the case of a continuous process, however, the time variable must enter the material balance. The balance must be made over a specified period of time.

The material balance is based upon the concept of the law of conservation of matter, which in effect says that, except for situations involving nuclear reactions, atoms are neither created or destroyed. Atoms that enter a system must either accumulate in the system or must leave. This observation leads to the balance expressed in Eq. 3.1, which is valid for all atomic species in the system.

$$\left\{ \begin{array}{l} \text{Accumulation of} \\ \text{atomic species } j \\ \text{within the system} \end{array} \right\} = \left\{ \begin{array}{l} \text{total atomic} \\ \text{species } j \text{ entering} \\ \text{system} \end{array} \right\} - \left\{ \begin{array}{l} \text{total atomic} \\ \text{species } j \\ \text{leaving system} \end{array} \right\} \quad (3.1)$$

By summing over all the atomic species entering and leaving a system, the total material balance is obtained:

$$\left\{ \begin{array}{l} \text{Total accumu-} \\ \text{lation within} \\ \text{the system} \end{array} \right\} = \left\{ \begin{array}{l} \text{total mass} \\ \text{entering system} \end{array} \right\} - \left\{ \begin{array}{l} \text{total mass} \\ \text{leaving system} \end{array} \right\} \quad (3.2)$$

When there is no accumulation within the system, Eq. 3.2 reduces to the following:

$$\left\{ \begin{array}{l} \text{Total mass} \\ \text{entering system} \end{array} \right\} = \left\{ \begin{array}{l} \text{total mass} \\ \text{leaving system} \end{array} \right\} \quad (3.3)$$

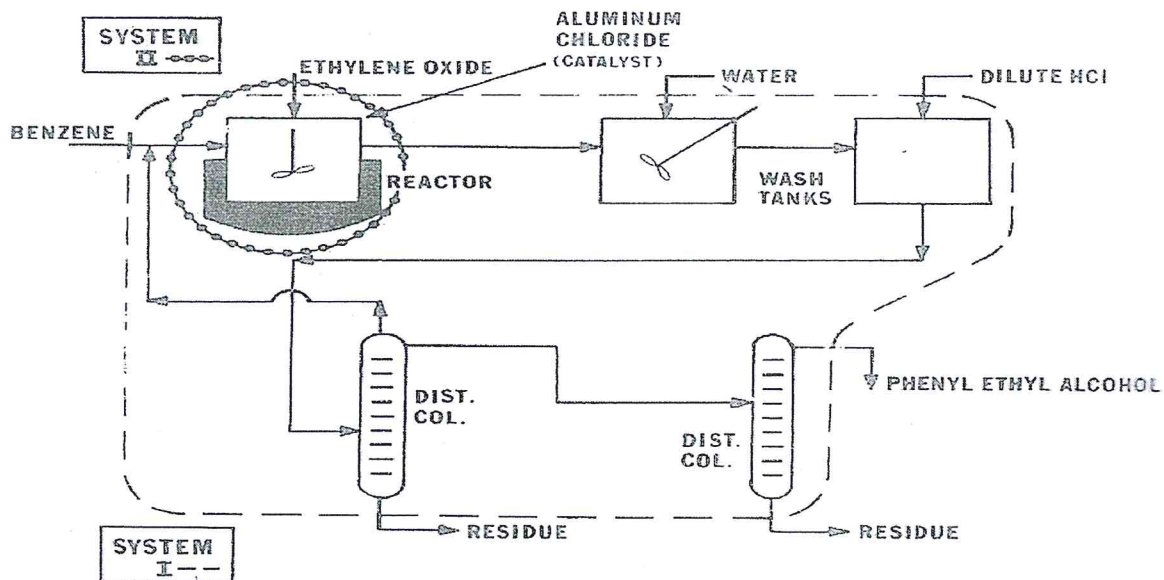


Figure 13 Flow sheet for the production of phenylethyl alcohol by Friedel-Crafts reaction.

Inherent in the formulation of each of the above balances is the concept of a system for which the balance is made. By system we mean any arbitrary portion or whole of a process as set out specifically by the chemist for analysis.

Figure 13 shows a process in which flow and reaction take place. We may be interested in performing a material balance on the entire process, in which case our system would be that enclosed by the boundary line for system I. On the other hand, our interest may only involve a material balance on the reactor, in which case our system would be that enclosed by the boundary line for system II.

In most continuous processes that the chemist encounters, the mass accumulation term will be zero; that is, the process is in a steady-state. In this book, we consider only steady-state processes. This eliminates the necessity for measuring the accumulation of material in the system so that input may be equated to output, and consequently we can say, "what goes in must come out."

One of the many useful applications of the material balance is during the pilot plant stage when the performance of a given process is being investigated. If each item of the input and output streams is measured, the material

3.3 UNITS OF MATERIAL FLOW AND BALANCING

The material balance principle may be applied either on the basis of units of weight, such as pounds or kilograms, or on the basis of gram-moles or pound-moles. Since the mole is merely a unit of mass that is numerically equal to the molecular weight, it is a very convenient unit to use in a material balance. If no chemical change takes place in the system on which a material balance is being made, the weight unit can ordinarily be used most conveniently. There are many applications, however, in which the mole unit is the most convenient even though no chemical change takes place. Of course, if a chemical change takes place then the mole unit is almost always the most convenient.

Within the chemical industry in the United States two systems of units are used, the metric system and the American engineering system. Table 3.1 compares the units of measurement in the two systems. The metric system is used primarily by chemists, while practicing engineers use the American engineering system. A major effort is currently underway to convert both scientific and engineering communities to the International System of Units (SI). The SI units may soon be predominant in our journals and eventually may be officially adopted for professional and lay usage. However, that day has not yet arrived. Practicality, therefore, dictates that an industrial chemist possess the ability to work and communicate effectively in both the metric and engineering systems. Accordingly, we use both systems in this book. For your convenience, a short set of essential conversion factors is given in Appendix A. At this point, we are now ready to take up the task of developing a method for solving material balance problems.

Table 3.1 Units of Measurement in Chemical Industry

System	<u>Length</u>	<u>Mass</u>	<u>Force</u>	<u>Energy</u>
Metric	cm	gram	dyne	erg, joule or calorie
Amer. Engr.	ft	pound (mass)	pound (force)	ft·lb _f , Btu or hp·hr

3.4 TECHNIQUES IN MATERIAL BALANCING

In this section we demonstrate the technique of setting up and solving problems that call for material balances. Most material balance problems contain the same basic elements, although the details of the application of the method of solution may be slightly different. Therefore first consider a generalized method for analyzing such problems that can be applied to the solution of almost any type of material balance problem. For some problems the method of approach is relatively simple, for others it will be more complicated; but the important point is to regard problems in chemical synthesis, distillation, crystallization, evaporation, mixing, gas absorption, or combustion not as being different from each other but as being related from the viewpoint of how to proceed to solve them.

The material balance may be applied to a process as an overall balance of the incoming mass with the outgoing mass. Or, it may be applied to intermediate parts of a continuous process. In general, for either of these systems, data dealing with two fundamental pieces of information is required. One of these is the mass in all streams of the material entering and leaving the system and present in the system. Information about the composition of all the streams entering and leaving the system and the composition of the material in the system must also be available. If a chemical reaction takes place inside the system, information about the reaction rate will be required.

In making a material balance there are a number of preliminary steps that are very helpful and desirable. The steps presented are flexible and can be modified as the chemist develops his own style.

1. Draw a simplified flow sheet of the process.
2. Place all the available data on the flow sheet using consistent units as discussed in Section 3.3.
3. Set down all chemical equations for the chemical reactions that occur in the process.
4. Select a convenient basis for the calculations.

Even in relatively simple problems it is worthwhile to draw a diagram, a schematic, or a flow sheet that depicts the problem at hand. A simplified flow sheet of the system that includes all the features pertinent to the material balance will help to keep careless errors to a minimum. It is well to develop the habit of always sketching a simplified flow sheet even for the simple problem. In complex problems, a flow sheet is essential.

All the data that will be used in the material balance can be located on the flow sheet.

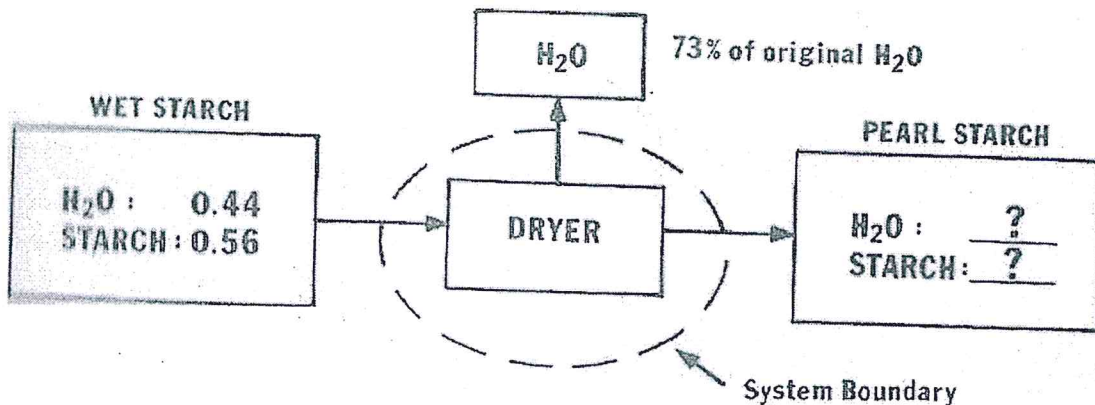
3.5 MATERIAL BALANCING BY USING A DIRECT APPROACH

Many material balance problems are encountered in which only one weight and one composition are unknown. Such problems can be solved by direct addition or subtraction as shown in the examples below.

Example 3.1 The Manufacture of Starch

One of the products obtained from the refining of corn is commercial starch. In the final stages of the refining process the starch contains 44% water. After drying, it is found that 73% of the original water has been removed. The resulting material is sold as pearl starch. Calculate:

- the weight of water removed per pound of wet starch,
- the composition of the pearl starch,



Example 3.2 Combustion of a Fuel Gas

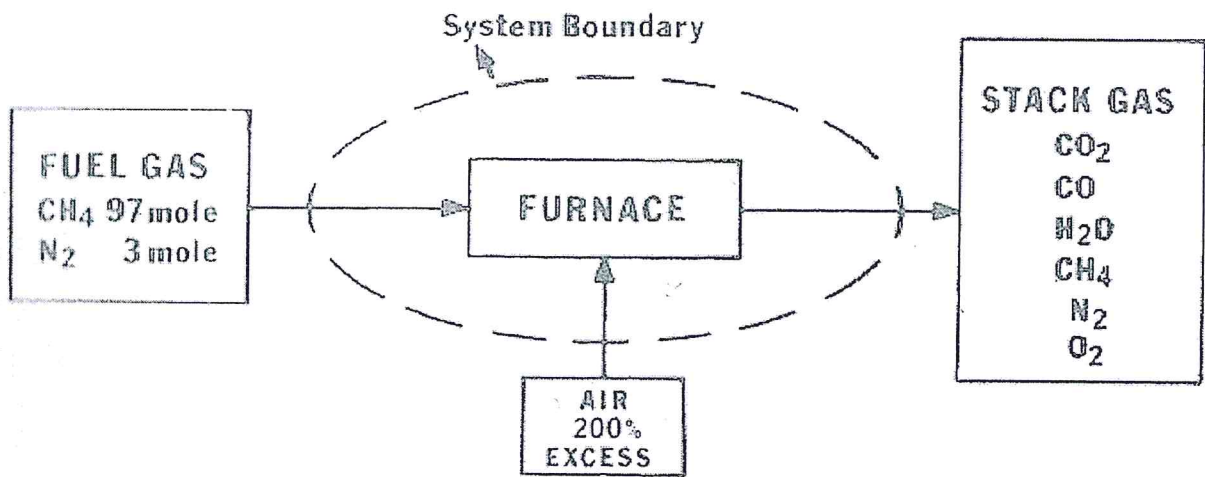
The combustion of fuel is the chief source of heat energy in the chemical process industries, and consequently material balancing of combustion processes is a common problem. In dealing with problems involving combustion, it is necessary that you become acquainted with a few special terms, such as:

- Stack gas**—consists of all gases resulting from a combustion process including the water vapor, sometimes known as combustion on a “wet basis.”
- Flue gas**—consists of all the gases resulting from the combustion process not including the water vapor. Sometimes known as combustion on a “dry basis.”

- (c) Theoretical air (or theoretical oxygen)—the amount of air (or oxygen) required for complete combustion.
- (d) Excess air (or excess oxygen)—the amount of air (or oxygen) in excess of that required for complete combustion as computed in (c).

The Problem

A fuel gas containing 97 vol % methane (CH_4) and 3 vol % N_2 is burned in a boiler furnace with 200% excess air. Eighty-five percent of the methane goes to CO_2 , 10% to CO , and 5% remains unburned. Calculate the composition of the stack gas.



3.6 MATERIAL BALANCING BY USING AN ALGEBRAIC TECHNIQUE

The problems in the previous section were rather easy to solve because the missing information pertained to a single stream. Therefore, only simple addition or subtraction was required to find the unknown quantities. When the missing information pertains to more than one stream, the method of solution becomes somewhat more complicated. Such problems are generally solved by assigning a letter to replace the unknown value in the total material balance or the component material balance, as the case may be. Then an independent material balance is written for each unknown so that the set of resulting equations will have a unique solution.

In solving problems with multiple streams, the calculations are often made easier by splitting a big problem into smaller parts. This splitting is often accomplished by making a material balance around a "mixing point." As illustrated in Fig. 14 a mixing point is a junction of three or more streams and can be designated as a system in exactly the same manner as any other piece of process equipment. You should remember that in splitting the larger problems into smaller parts, material balances can be

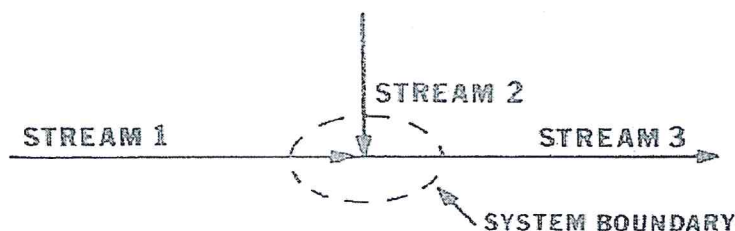


Figure 14 A mixing point.

written for each piece of equipment and each mixing point as well as a balance around the whole process. However, since the overall balance is nothing more than the sum of the balances about each piece of equipment, not all of the balances will be independent.

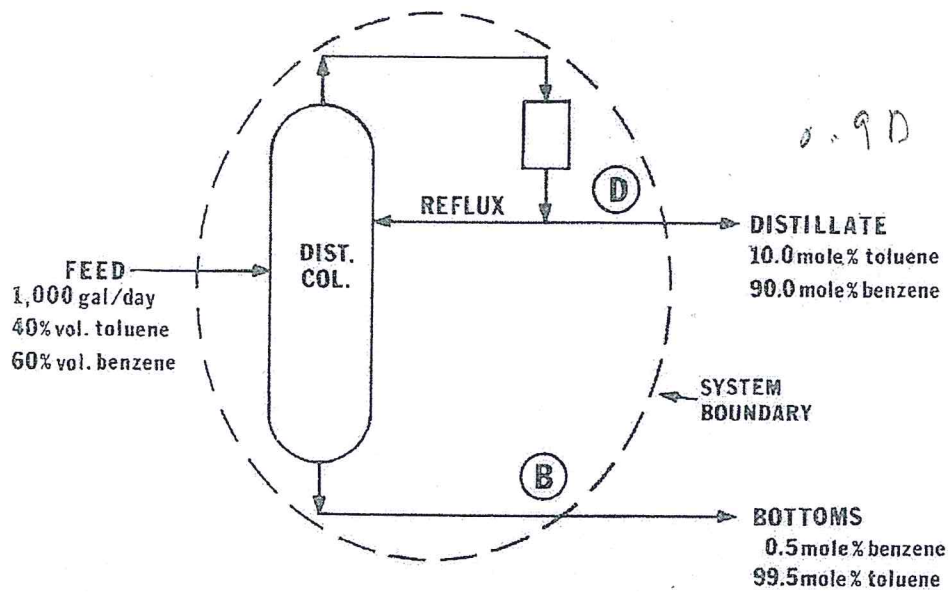
Illustrations of the use of the algebraic technique in solving material balance problems are given in the following problem set.

Example 3.3 Distribution of a Benzene-Toluene Mixture

A blend of 40 liquid vol % toluene and 60 liquid vol % benzene is separated by distillation in a solvent recovery plant. The overhead distillate product contains 10.0 mole % toluene and the bottoms product contains 0.5 mole % benzene. The blend is fed to the distillation column at 20°C and at a rate of 1000 gal/day. How many gallons of distillate and bottoms are produced?

Solution

Step 1. A flow sheet for this process is diagrammed below:



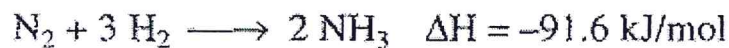
Industrial Products

1- Ammonia

Ammonia is an important primary inorganic material. 85% of the worldwide production is utilized in the manufacture of synthetic fertilizers. Ammonia production therefore represents an indicator of the size of the fertilizer industry in a particular country.

1-1 Ammonia Manufacture

Large scale manufacture of synthetic ammonia is exclusively carried out with "synthesis gas" ($\text{N}_2 + 3\text{H}_2$)



which is based on the investigations of Haber in 1904 into the equilibrium between nitrogen, hydrogen and ammonia. The exothermic reaction between nitrogen and hydrogen occurs in the presence of suitable catalysts and results in volume reduction, the highest ammonia concentrations being obtained at the highest possible pressure and the lowest possible temperature. All ammonia production plants in the world operate according to the same basic principles i.e. reaction of nitrogen and hydrogen in a catalyst-filled pressure reactor at temperatures between 400 and 500 °C, pressures between 100 and 1000 bar (depending upon the plant) and removal of the ammonia formed from the reaction gas. The plants differ in their design, catalyst composition and production and purification of the synthesis gas.

1-2 Ammonia Synthesis Catalysts

Ammonia synthesis catalysts consist of α -iron with small quantities of different oxides, so-called promoters, which increase the activity of the catalyst, increase its lifetime and decrease its susceptibility to poisoning.

The starting material for α -iron is magnetite, Fe_3O_4 , which is mixed with the promoter substances, which are essentially:

- 1- potassium carbonate, which in the presence of acidic and amphoteric oxides such as silicon dioxide or aluminum oxide increase the catalytic activity, but decreases the temperature stability.
- 2- aluminum oxide, silicon dioxide and calcium oxide which under the catalyst production conditions form aluminosilicates which protect the catalyst particles from pre sintering and thereby increase the temperature stability of the catalyst.

1-3 Raw Materials

The production of one ton of ammonia requires a mixture of 2400 m^3 of highly purified hydrogen and 800 m^3 of highly purified nitrogen (at 0°C and 1000 mbar). It is produced using different processes depending upon the raw materials utilized.

Nitrogen is taken from air or from the nitrogen content of natural gas. This is carried out by low temperature fractionation of air, which is preferred when pure oxygen is required as an oxidizing agent in the production of

synthesis gas. Hydrogen is produced from hydrocarbons or coal and water:

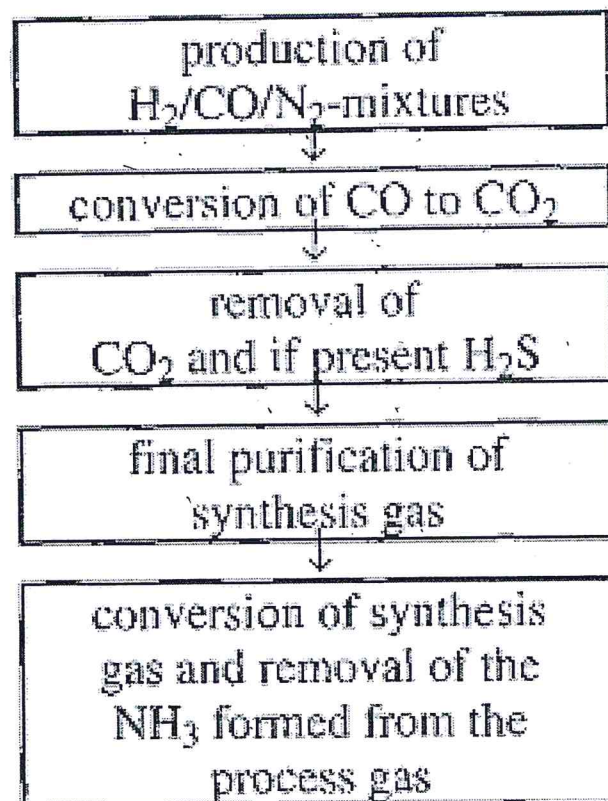
- from natural gas (methane) and naphtha (raw gasoline)
- from crude oil products (e.g. heavy heating oil)

- from coal (coal gasification) by partial oxidation using the steam-reforming process

1-4 Conversion of Synthesis Gas to Ammonia

The industrial scale reaction of synthesis gas to ammonia in pressure reactors takes place in a cyclic process in which the ammonia formed is removed from the reaction gas and the unreacted synthesis gas returned to the reactor. In addition to the ammonia formed, inert gases and the liberated reaction heat have to be continuously removed from the cyclic process. The excess heat of the product gas is used to heat the feed synthesis gas to the reaction temperature in a heat exchanger integrated into the reactor.

NH₃-synthesis consists of the following process steps:



1.5 Ammonia Applications

Ammonia is the starting material for the manufacture of nitric acid, urea and ammonium phosphate, as well as for the production of precursors for fibers, plastics, pesticides. By far the most important consumer of ammonia is the fertilizer sector.

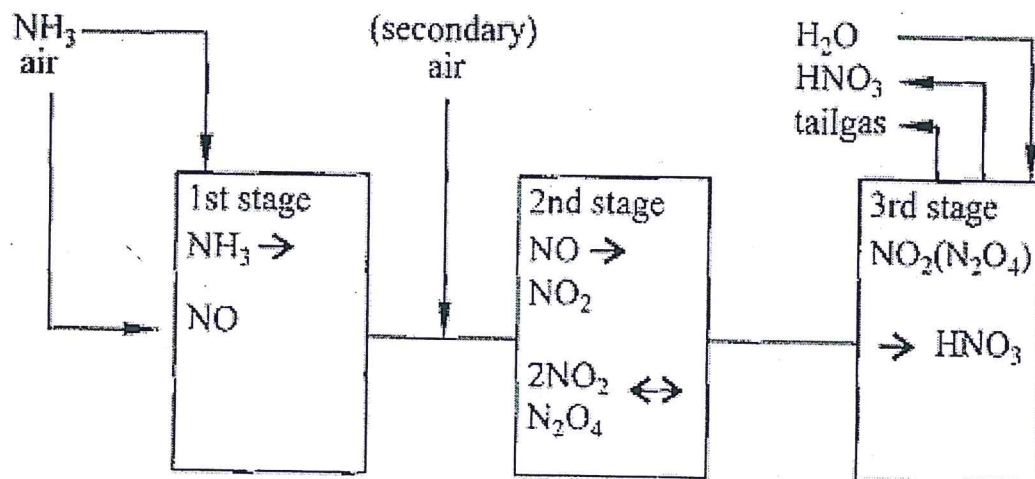
2- Nitric Acid

Nitric acid is one of the most important inorganic chemicals. Quantity wise it is one of the top ten industrial chemicals.

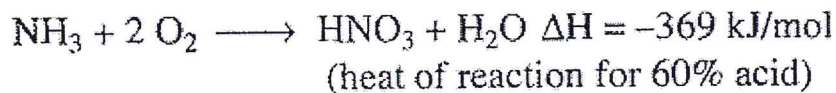
The nitric acid production in North America, Japan and Western Europe (as 100 % acid) amounted to 27.7×10^6 t in 1992. These regions account for about half of the world-wide production

2-1 Fundamentals of Nitric Acid Manufacture

The process for nitric acid manufacture from ammonia consists of three exothermic reaction steps as shown schematically in down Figure.



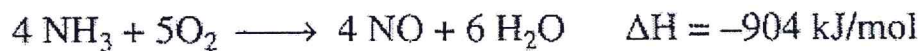
he overall reaction corresponds to:



The three reaction steps are based on very different physical chemical relationships which appreciably influence the operation of the process. The third step normally followed by tail gas purification, to prevent the emission of nitrous gases.

Three exothermic reaction steps are:

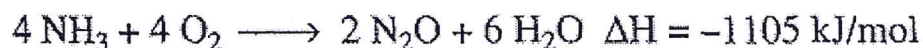
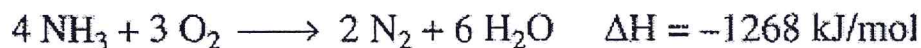
1- Catalytic Combustion of ammonia to Nitrogen(II)oxide:



[a catalyst at 820 to 950°C either at atmospheric pressure or at pressures up to 12 bar].

This reaction is one of the most efficient catalytic processes in industrial chemistry, having an extremely short reaction time (10^{-11} s) and a high selectivity.

The oxidation of ammonia benefits slightly from pressure reduction, since less nitrogen and dinitrogen(I) oxide (N_2O) is then produced in side reactions:



The ammonia oxidation catalyst is usually a platinum alloy gauze containing 5 to 10% rhodium, or additionally with 5% palladium,

2- Oxidation of Nitrogen(II) Oxide to Nitrogen(IV) Oxide and Dinitrogen(IV) Oxide:

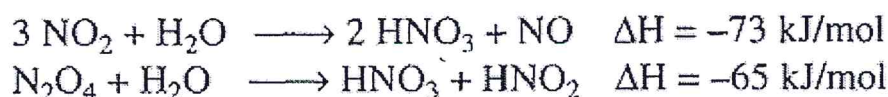


This reaction is favored by low temperatures. Dimerization to dinitrogen(IV) oxide is also promoted by low temperatures and high pressures.



3- Conversion of Nitrogen (IV) Oxide into Nitric Acid:

The gas mixture obtained by oxidation of nitrogen(II) oxide, containing nitrogen(IV) oxide and dinitrogen (IV) oxide (so-called nitrous gases), is reacted in the third reaction step with water as follows:



To nitric acid, nitrogen (II) oxide and nitrous acid. The nitrous acid is further oxidized to nitric acid by the (atmospheric) oxygen present, either in the liquid or vapor phase.

2-2 Nitric Acid Applications

Most of the nitric acid is utilized in the form of 50 to 70% acid for the manufacture of nitrogen-containing fertilizer, particularly ammonium nitrate. Ammonium nitrate is also used as an explosive

e.g. in mining, due to its low explosion temperature (safety explosive). Other industrially important nitrates are sodium nitrate, a speciality fertilizer and oxidizing agent in the glass and enamel industries, and calcium and potassium nitrates, which are also used as fertilizers

3-Urea

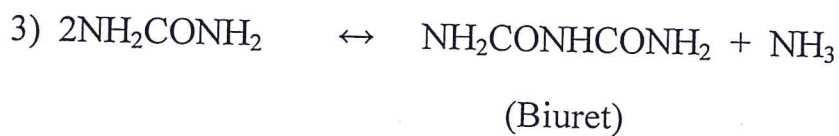
Urea is an important nitrogenous fertilizer. Its utilization is increasing steadily, it being the preferred nitrogen fertilizer worldwide. It is used in solid fertilizer, liquid fertilizer, formaldehyde resins and adhesives.

3-1 Process Technology

Although there are several processes currently used for the manufacture of urea, the underlying principle for all the processes is same. The two main reactions involved are:



Undesirable side reaction taking place is:



Both 1st & 2nd reactions are equilibrium reactions. The 1st reaction almost goes to completion at 185-190 °C & 180-200 atms. The 2nd

reaction (decomposition reaction) is slow and determines the rate of the reaction. Unconverted CO_2 & NH_3 , along with undecomposed carbamate, must be recovered and re-used. The synthesis is further complicated by the formation of a dimer called biuret, $\text{NH}_2\text{CONHCONH}_2$, which must be kept low because it adversely affects the growth of some plants.

3-2 Uses of Urea:

- About 56 % of Urea manufactured is used in solid fertilizer.
- About 31 % of Urea manufactured is used in liquid fertilizer.
- Urea-formaldehyde resins have large use as a plywood adhesive.
- Melamine-formaldehyde resins are used as dinnerware & for making extra hard surfaces.