SIMONA POPA

SPECIFIC PLANT IN ORGANIC CHEMICAL INDUSTRY

Manualul Studentului

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SPECIFIC PLANT
IN ORGANIC CHEMICAL INDUSTRY

The chemical industry uses a diverse range of machinery to produce a wide variety of products. The organic chemical industry requires special materials to meet the growing needs of consumers. The handbook presenting the machinery in the organic chemical industry and is very useful for foreign students who want to improve their knowledge in Romanian educational institutions, future engineers who will work in this field.

Referent ştiinţific: Prof. dr. ing. Gheorghe ILIA

The manual covers a topic of general and special interest for all those involved in the pedagogical and / or training activity at all levels of the profile education system: teachers, students, pupils. The paper is in line with the concerns related to the knowledge of variations and changes that can be found in the entire chemical manufacturing, organized in technological processes. The information and construction diagrams of the devices presented in this manual allow the student to become familiar with the most common equipment in the chemical industry and help to form an applied thinking mind, necessary for any technologist.

Referent ştiinţific: CS II. Nicoleta PLEŞU

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CONTENT

FOREWORD

This textbook is intended to be a useful book for students of the Faculty of Industrial Chemistry and Environmental Engineering and all those interested in the basic introductory theoretical aspects of machinery used in synthetic chemical engineering.

The manual is divided into 13 chapters. The first one presents the main materials used in the manufacture of machinery, apparatus and installations in the organic chemical industry, and also discusses some general aspects of corrosion. Chapter 2 deals with how technologies are organised. Chapter 3 deals with the raw material preparation operations and Chapter 4 with the operations for ensuring reaction conditions. Chapter 5 presents the apparatus used for transporting fluids, Chapters 6 to 9 the operations and machinery for separating the useful product, and Chapter 10 describes the operations for purifying the product.

It is very useful for a chemical engineer's handbook to also deal with aspects of the location of a chemical platform where aspects of infrastructure, availability of raw materials needed for the process, availability of personnel, ensuring safe conditions around the platform are specified (Chapter 11). It is also necessary to know the organisational structure of a chemical platform and the role and responsibilities of the technologist engineer. As this manual is for the use of students, who also aim to carry out a technological project, Chapter 12 presents general concepts for the design of such a project. It is mandatory for the technologist to be familiar with all the rules concerning safety and protection at work and the legislation in force, which are briefly dealt with in Chapter 13.

I would like to take this opportunity to thank the ladies Eng. Gizella Simo and Eng. Andreea-Maria Vagner for their help with the figures.

I am deeply grateful to Dr. Eng. Nicoleta Pleșu, CSII - from the Institute of Chemistry Timișoara of the Romanian Academy and Prof.dr.eng. Gheorghe Ilia - from the University of West Timisoara, who appreciated the work done in order to produce this material.

The Author

1. MATERIALS USED IN THE MANUFACTURE OF MACHINERY, APPARATUS AND INSTALLATIONS IN THE ORGANIC CHEMICAL INDUSTRY

1.1. Introduction

The chemical industry uses a wide range of manufacture materials determined by the operating conditions of technological processes (temperature, pressure and corrosive environment).

The wrong choice of manufacture material leads to wear and tear and to the installation being taken out of service. The amount of material loss caused by this exceeds the cost of the corroded equipment.

The organic industry uses a variety of manufacture materials, taking into account the demands of temperature, pressure and the action of corrosive environments.

Equipment used in the chemical industry is subject to mechanical, technical and chemical corrosion stresses that require consideration of the following characteristics:

1. Mechanical properties - important when we have static stresses, when studying yield strength, wear at break.
2. Physical properties.
3. Corrosion resistance.
4. Technological properties
5. Chemical properties - the property of a material to play a catalytic role.
6. Economic aspects - cost price of the material.

Manufacture materials can be:

A. Metallic materials:
1. ferrous materials
2. non-ferrous materials.

B. Non-metallic materials:
1. of an inorganic nature
2. of an organic nature.

1.2. Notions regarding corrosion

The major difficulties that arise in the operation and manufacture of chemical machinery are caused by corrosion phenomena. Corrosion consists of the storage of metal supports by chemicals. It is caused by chemical and electrochemical phenomena. Both phenomena are present in combination. The mechanism of chemical corrosion involves the dissolution of the manufacture material at the point of contact with the aggressive environment, resulting in the formation of corrosion compounds.

In the thermodynamic study of chemical corrosion the dissociation voltage of the corrosion products is important. The mechanism of electrochemical corrosion is due to anodic oxidation and cathodic reduction processes. The explanation of the phenomenon by the appearance of local stacks is outdated, the process being more complex.

Factors influencing the corrosion process are:

1. **Nature of the metal.** Although there is no perfect parallelism between the position of the metal in the standard potential series and its place in the periodic system on the one hand and its corrosion behaviour on the other, there is nevertheless a concordance between the corrosion stability of the metal and its position in the two systems mentioned above.
2. **Structure and condition of the metal surface.** In general, the purer and more homogeneous a metal is, with a better finished surface, the better it resists corrosion.
3. **Machine operating time.** The evolution of corrosion over time can be represented by diagrams resulting from empirical observations. They are constructed by plotting weight loss versus time, i.e. expressed as corrosion rate versus time.

The first category includes machines where corrosion changes over time, the aggressiveness of the environment is variable and the resulting products are not protective (Fig. 1.1 - a).

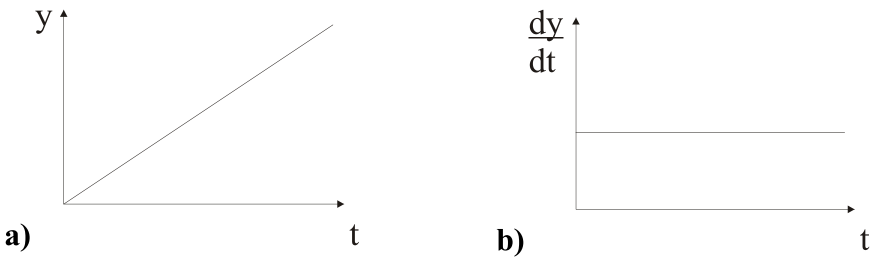


Fig. 1.1. Corrosion variation with machine operating time in aggressive environments **a**-corrosion changes over time; **b**-corrosion does not change over time

In the second category of metals there is an attenuation of corrosion due to the protective film that is formed, i.e. due to the depletion over time of the aggressive solution (Fig. 1.2. - b).

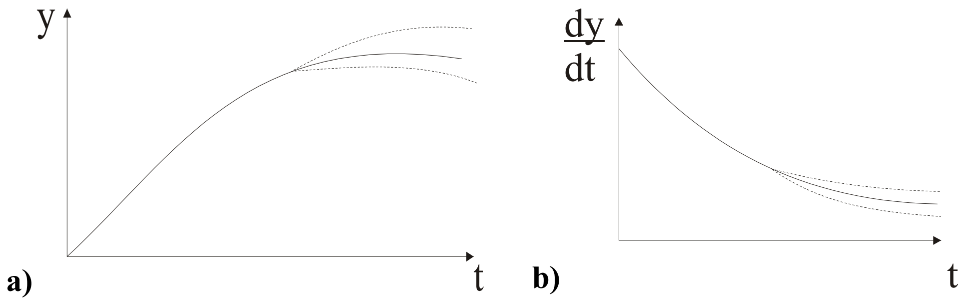


Fig. 1.2. Corrosion variation with machine operating time
in protective environments
a- formation of protective film; b-decrease of corrosion over time

The formation of the protective film leads to a decrease in corrosion over time (Fig. 1.2.2. - a, b).

The third category includes corrosion processes of metals under the influence of acids or alkalis (Fig. 1.2.3.- a,b).

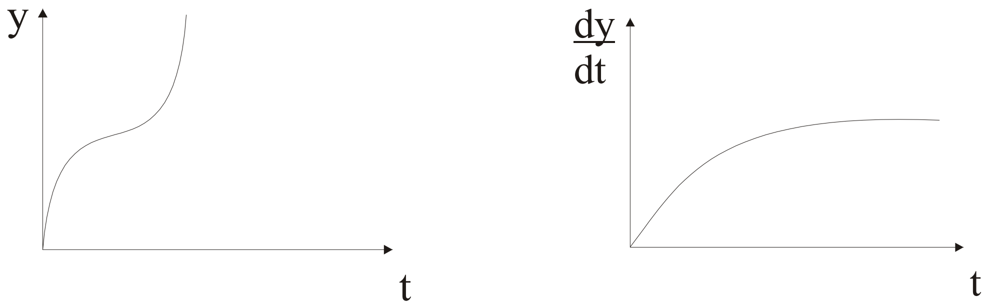


Fig. 1.2.3. Corrosion variation with machine operating time
under the influence of acids or alkalis
a- corrosion increases; b- corrosion increases

Corrosion increases with time after which it shows an inflection due to a phenomenon that occurs during the conduct of the process and finally results in an increase in corrosion. The phenomenon is caused either by a destruction of the protective film or by an increase in corrosion due to the temperature.

4. **Concentration and composition of the aggressive environment.** Corrosion is influenced by the concentration and nature of the corrosive medium, in particular it is influenced by the pH and oxygen content of the medium. Dissolved oxygen in the corrosive medium acts as a cathodic corrosion accelerator. Acidity and acid concentration favourably influence corrosion.

5. **Temperature.** Increasing temperature favours diffusion processes, accelerating corrosion, and is reversed at higher temperatures, as it favours the desorption of oxygen from the corrosive environment.

6. **Speed of movement of aggressive solutions.** As the circulation speed of the solutions increases, the corrosion speed also increases due to the increase of oxygen on the metal surface, as the solution jet destroys the protective layer, promoting corrosion.

7. **Pressure and vacuum ahead.** Increased pressure causes increased corrosion due to increased gas solubilisation capacity, i.e. oxygen.

8. **The appearance of stray currents.** Due to insufficient insulation of DC installations, stray currents occur, leading to increased corrosion.

9. **Manufacture features and rules of use of the apparatus.** Design elements have a significant influence on the corrosion of chemical machinery.

Corrosion is prevented by protective measures that substantially reduce the destructive process. Machine protection is achieved in the following ways:

1. **Electrochemical protection measures**
    a) anodic
    b) cathodic

a) **Anodic protection.** The process consists of intensifying the state of passivation and is based on the processes of positively shifting the potential of the alloy or metal being protected, by feeding from an existing current source, or by alloying the system with elements having a more electropositive potential than the protected system.

b) **Cathodic protection.** The corrosion rate decreases by shifting the steady-state potential under the action of an external current to values more negative than the equilibrium potential.

2. **Protective measures through environmental treatment**

Corrosion reduction is achieved by adding substances called corrosion inhibitors to the corrosive environment.

The number of inhibitors (cathodic and anodic) is very large. The corrosion rate does not decrease but the number of aggressive attack centres decreases. A protective film is formed**.**

Organic inhibitors are: macromolecular substances, amide hydrazides, thioderivatives**.**

Inorganic inhibitors: alkali hydroxylates, carbonates, alkali phosphates and sulphites.

3. **Protective measures by coating with metallic or non-metallic layers**

Depending on the method of application and the nature of the material used, the following possibilities can be distinguished:

a) Electroplating - electrochemical deposition.
b) Spraying - application by metallization.
c) Diffusion - thermal.
d) Hot dipping.
e) Plating (rolling, coiling, hardening).
f) Protective action of films obtained by chemical reactions.

In order to ensure adequate protection it is necessary that the surfaces to be covered are subjected to a process of:

- - abrasive grinding;
- - polishing;
- - degreasing;
- - pickling.

a) Galvanization is a high process and consists of coating with metals more stable to corrosive environment, by galvanizing, nickel plating, chromium plating from baths of metal salts.
b) Metallisation consists of spraying metal surfaces with a stream of metal particles obtained by dispersing molten metal with compressed air. The method is applicable to arc-melting metals: Al, Zn, Cd, Sn, Pb, Cu, Ni, Fe, etc.

Has the disadvantage of porous deposits and high metal consumption.

c) Thermal diffusion - is a process by which steel parts contract with metal vapours at high temperatures (Zn, Al, Cr, Ni).
d) Hot dipping consists of placing assemblies in molten metal baths followed by cooling. It is applied for Zn, Sn, Pb.
e) Plating consists of hot rolling and pressing the two by means of valves. Protect the steel with: Ni, Cr, Cu or stainless OL.
f) Protective action of films obtained by chemical or electrochemical reactions (oxides, phosphates)

Se aplică ca şi structuri înainte de aplicarea unor lacuri şi vopsele.

Oxidation is also called brumation and is achieved by artificially thickening the oxide layer. Phosphating is applied to steel and cast iron and consists of immersion in a solution of Mn and Fe phosphate, resulting in a uniform protective layer.

1.3. Ferrous metal materials

One of the most common ferrous materials is cast iron, which is noted for its mechanical properties and its ability to be machined by casting. Approximately 85 - 90% of chemical machinery is made of cast iron and steel. Cast iron accounts for 45% of materials used in the chemical industry.

Depending on the composition of the structural compounds we distinguish:

1. Grey cast iron (1.7 - 4.5%C) 1 - 3% Si.
2. White cast iron (2.5 - 3.5%C) ≥ 1%Si.
3. Malleable cast iron ≥ (2%C) ≥ 1%Si.
4. Modular cast iron ≥ %C (3.2 - 4.1% C).

Grey cast iron is the most commonly used. The main elements are Fe-C alloys, with Si, Mn, P, S, etc.

Average percentage limits are: C - 4%; Si - 1.6%; Mn - 1%; P - 0.8%; S - 0.12%.

The technology used to make cast iron machinery is casting. It is the process that has a low cost price. The symbols for grey cast iron are: FC - followed by two groups of numbers: FC-32-58. The first group represents the allowable tensile strength and the second refers to the corrosion resistance in kgf/mm^2. Sometimes tensile strength may be missing.

There is a direct correlation between the tensile strength value and the areas of use of the cast iron.

Cast iron is generally used in the manufacture of smaller diameter devices working at relatively low pressure – $p<6$ atm. Cast iron with superior properties is used for the manufacture of apparatus working under more demanding conditions.

Grey cast iron shows good chemical stability to concentrated H2SO4, but is vulnerable to dilute sulphuric acid and other agents. Increasing the phosphorus content of cast iron leads to increased stability against acids. The presence of sulphur above certain limits reduces chemical stability.

Cast iron is recommended for the manufacture of machinery processing alkaline melts. Stability against alkalis is considerably increased if grey cast iron is alloyed with Ni 0.3 - 0.5% or Cr 0.7 - 0.9%. The cast iron is used to make sulphonation reactors, various parts for pumps, pipes, valves, etc.

After each chemical operation, the machines are reconditioned by washing with dilute soda solutions, followed by drying.

By carburising cast iron with Ni and Cr, materials resistant to oxidising acids are obtained, without satisfying the processing requirements of reducing acids. Alkaline smelters are made from Ni-alloyed cast iron. Cast irons are not used for autoclaves (pressure reactors) (thickening the walls would be uneconomical).

Cast iron with a higher silicon content is much more resistant to high temperatures and the corrosive action of sulphonic and nitric acids of any concentration.

Silicon cast irons with a silicon content of up to 18% can be alloyed with Cr, Ni, Al and Cu. The resistance of silicon cast iron to acids increases with increasing silicon content in the material structure. Silicon castings have poor mechanical properties; they have a low coefficient of thermal conductivity, and as the Si content increases, it makes the material brittle and mechanical processing more difficult.

Centrifuges, reactors, columns with trays, coolers, etc. are made from silicon cast iron. Its low thermal conductivity does not allow thermal stress through reheating, overheating or sudden cooling.

The manufacture of machinery in the chemical industry requiring mechanical and physical properties superior to cast iron, coupled with advanced chemical stability, is achieved by using steels.

Depending on the composition and alloying ratio, we distinguish:

1. Carbon steels of ordinary OLC characteristics.
2. Alloyed steels with special properties.

Carbon steels are materials with outstanding mechanical, physical and technological properties, providing increased resistance to static and dynamic stresses.

In addition to mechanical strength, special alloys provide superior physical properties and chemical stability that varies with their structure.

The amount of carbon in steels is up to 1.5%, but for machine tool steels a low carbon content of no more than 0.7% is preferred. As the carbon content increases the mechanical strength improves, but the plasticity of the steel and its weldability decreases. Good quality steels have a carbon content of 0.1 - 0.2%.

Chromium alloyed steels are resistant to the action of nitric and sulphonic acids and are not resistant to the action of hydrochloric acid because no protective film is formed on the surface of the material. Chromium steels are also not resistant to organic and inorganic salts with reducing properties. Nickel-alloyed steels have increased mechanical strength and chemical stability, coupled with increased plasticity. The most suitable are chromium-nickel steels - called austenitic steels - which maintain the γ structure - of the iron-carbon alloy - even at high temperatures.

The content of alloying metals is variable, the most common special steel has 18% Cr and 8% Ni.

Cr-Ni steels are resistant to high concentration acids, alkali hydroxides, organic acids and alkali salts.

The mark of high-alloy steels with elements ensuring high stability is recognized by the indication of the percentage of carbon before the initial letter, after each symbol giving the percentage composition of the steel element: 15% Cr 18% Ni 2% Ti.

Mechanical strength is also increased by adding copper.

Nickel steels are mainly used in the processing of alkaline solutions.

Special steels include those alloyed with Cr, Ni, No. Molybdenum improves the mechanical properties, uniforms the structure and ensures a smooth surface when machined. Steels alloyed with these elements are widely used in the processing of hot acid and alkali solutions, salt solutions, organic acids, etc.

Other alloying elements are: Mn, which in quantities greater than 1% increases toughness and resistance to erosion and shock. Titanium prevents intercrystalline corrosion. Wolfranium increases hardness and Vanadin ensures uniform structure, increases conductivity and corrosion resistance. From the diaphragm, the strength of cast iron comparable to steels stands out.

Refractory steels are manufacture materials for technologies using very high temperatures specific to the organic industry. They are characterised by high mechanical strength under the action of static loads at high temperatures, while showing stability against corrosion by aggressive agents.

Table 1.1. shows various steel compositions and the environment for which they can be used.

Table 1.1. Steel compositions and the environment for which they can be used

		Cr	18	18	16	-	-	-	18	18	16	-		
		Ni	8	8	14	40	Cast iron	70	8	8	14	40	Cast iron	70
		Mo		2	2	10	Si	30		2	2	10	Si	30
		Cu			2	2	18				2	2	18	
H_2SO_4	>5%		▨	▨	▨	▨	▨	▨			▨	▨	▨	▨
	5–10%			▨	▨	▨	▨	▨				▨	▨	▨
	96%		▨	▨	▨	▨	▨	▨					▨	
HCl	<1%			▨	▨	▨	▨	▨			▨	▨		▨
	1-10%				▨		▨	▨						
	36%						▦							
HNO_3	<10%		▨	▨	▨		▨		▨	▨	▦		▦	
	>10%		▨	▨	▨		▨		▨	▨			▦	
	Conc D=1,4		▨	▨	▨		▨		▨	▨			▦	

Caption:

▨ Rezident
▦ In use
□ Non-rezident

Iron-carbon alloys with additions of Cr, Si, Al, Ni

Corrosion stability is determined by the formation of a protective oxide layer on the surface of the alloy. The most commonly used steels are those alloyed with chromium.

The addition of aluminium increases the chemical resistance, but the mechanical properties become unsatisfactory, as they become plastic at high temperatures and brittle at lower temperatures. Depending on the corrosion conditions, the most suitable steels with Si, Cr, Al additions are chosen, called sychromal steels, resistant to high temperatures (1200 - 1300°C), to oxidative environments, but unsatisfactory for reducing environments.

Refractory steels are used to make cracking columns, distillation apparatus, boilers and apparatus working at very high temperature.

1.4. Non-ferrous metal materials

Copper and its alloys

Copper lends itself to the manufacture of machines with a specific character, requiring an advanced purity of the metal in the range 99.5 - 99.7%. Copper can be cold or hot worked. It is vulnerable to oxidising solutions, with the corrosive action of HNO3 and H2SO4 being particularly noticeable.

The presence of oxygen in acid solutions greatly accentuates the corrosion process. However, copper shows good resistance to alcoholic solutions. It is not recommended to use copper when processing solutions of ammonia, ammonium salts, hydrogen sulphide vapour and dilute HCl. It is used in the manufacture of machinery working at temperatures <250°C. With a very good thermal conductivity coefficient, it is used in the manufacture of evaporators, distillation bases, heat exchangers, dryers, centrifuges, etc.

The mechanical strength of copper is sufficiently low, it is preferred to be used in the form of alloys, of which we mention:

a) Bronzes;
b) Brass.

a) Bronze is the alloy of copper with tin in a proportion of 8 - 10%.

For homogenisation 2 - 4% Zn is added.

Aluminium bronze contains 10% Al and is used in the manufacture of equipment working under load and at high rotational speeds (gear wheels, helical gears, pump parts).

Silicon bronze contains 3 - 4% silicon and is used to manufacture parts working at high temperatures and pressures.

b) Brass is an alloy of copper with zinc (20 - 55%). Depending on the zinc content, there are several forms, which differ in a number of properties.

Zinc content up to 38% provides ductile properties to the characteristic shape of the alloy. In the range of zinc content between 38 - 55%, the β phase predominates, being hard, and at a content above 55% zinc, the materials are brittle, being reported the γ form. The instability of zinc in acidic solutions limits the use of the alloys.

Nickel and its alloys

Nickel exhibits good mechanical strength and passivity to aggressive environments. It is particularly stable to alkalis of any concentration at high temperatures. Thus, machinery in the phenol industry is made of nickel and its alloys.

Nickel is passive to ammonia and aluminium salts, but is less resistant to nitric acid in the presence of oxygen. It is fairly resistant to sulphuric acid, but more sensitive to sulphurous acid. Nickel is used in the manufacture of machinery in which iron has an anti-catalytic effect. It is used in the manufacture of antiseptic machinery in the pharmaceutical and food industries.

Nickel forms many alloys with metals that are passive to aggressive environments, especially acids.

Ni-Mo alloys (65 - 30%) resist well to 60% sulphuric acid even at boiling. Similarly Ni-Cr alloys (60 - 80%; 13 - 20% Si) called "INCONEL" resist well to phosphoric acid..

The passivity effect is increased by using alloys with polymetallic structure. Ni-Cr-Mo-Cu alloys - called "ILIUM" - resistant to sulphuric acid of any concentration have been prepared. Some nickel alloys are found in nature. Ni-Cu alloy with good resistance to corrosive environments is found in Canada. Alloys also contain other elements: 67% Ni; 29% Cu; 1.9% Mn; 1.7% Fe; 0.4% C; 0.2% Si "MONEL".

Processes well, resists well to various temperature solutions of ammonia, benzene, acetic acid, ethyl alcohol. It is less resistant to nitric acid. Can be used for processing alkaline solutions.

Lead

Lead's potential uses are limited, as it has low mechanical strength and a relatively low melting point and is used at temperatures <150°C. It also has a lower coefficient of thermal conductivity. Its predominant use is in the sulphuric acid, sulphates, chlorides and salts industry, which causes the formation of a compact film adhering to the metal surface. With increasing temperature the strength of the film decreases. Not resistant to alkaline solutions, nitric acid, hydrochloric acid, aldehyde phenols. Corrosion resistance is increased by passivation with concentrated acid solutions. Lead alloys with 10% Sb provide superior mechanical strength. Also known as hard lead. It is used in the manufacture of pumps, filter presses, pipes, valves, etc. It is common practice to coat appliances with lead; by homogeneous plating and electrochemical method.

Aluminium and its alloys

The metal is coated with a hard, adherent oxide coating that provides good corrosion protection. Impurities present in aluminium significantly reduce its resistance to corrosive environments. Aluminium has good physical, mechanical and technological properties. Its low density and very good thermal conductivity make it suitable for chemical machinery. It is used in the manufacture of heat exchangers, cathodic cracking apparatus, mounts, tanks, acid transport vessels.

It is resistant to oleum sulphuric acid, chlorosulphonic acid, nitric acid, but not to hydrochloric acid, alkali hydroxides and organic acids. Aluminium corrosion products are non-toxic and are recommended for use in the food and pharmaceutical industries..

It is recommended when making machinery for transporting coal tar. Aluminium alloys include:

1) Duralumin, Cu (3 - 5% Cu) has excellent mechanical properties.
2) Siluminium (containing 4 - 13% Si) is suitable for demanding technical processing. Aluminium is sensitive to moisture, as deformation processes of the protective layer occur.

Tin

Is used as a protective coating on the surface of Fe, Cu, Pb devices, providing advanced oxygen stability in the presence of acids. It is sensitive to alkalis.

Zinc

Is used to protect surfaces made of other metals, providing very good resistance to organic acids.

Noble metal

Gold, silver, platinum. They have good mechanical properties and superior anti-corrosion qualities, but come at a high cost. However, they are recommended for use in machines working in strong corrosive environments.

Silver is used in the manufacture of distillation and esterification equipment, in the phenol and urea industries, and to obtain pure products in the pharmaceutical industry. It resists alkalis well.

Platinum has excellent anti-corrosive properties and is resistant to nitric, sulphuric and hydrochloric acids up to 1200°C.

Platinum is used for piping, lining catalytic reactors, making autoclaves that work under special conditions.

Platinum plus 5% Radium is used to make catalytic sites.

Tantalum. It is a hard metal fusible to 3000oC. It exhibits outstanding chemical stability and superior mechanical strength even at high temperatures. It is used in the manufacture of autoclaves, heat exchangers subject to thermal stress, in the manufacture of pumps, coils. However, it is very expensive.

Titanium. It is highly resistant to nitric acid and inorganic salts. Expensive, it is used for lining appliances. It is also resistant to organic substances (urea industry).

1.5. Non-metallic materials

The class of materials of inorganic nature includes natural antacid materials, consisting mainly of quartz and feldspars. Chemically, these products are the salts of silicic and polysilicic acids from silica. According to the % silica content, we distinguish:

1. Ultraacidic rocks with a content > 75% SiO_2
2. Acidic rocks containing 65 - 75% SiO_2
3. Medium rocks containing 55 - 65% SiO_2
4. Basic rocks containing 40 - 55% SiO_2
5. Ultrabasic rocks containing < 40% SiO_2

These materials are used as regular shaped chipped stone which is fixed with acid-proof grouts for making with special machines as a filler for absorption columns.

Natural products include:

A. Granite, andesite and volcanic tuffs

Granite. It is the basis for making absorption columns in the nitric and hydrochloric acid industry. It is too hard to process. It does not have good resistance to high temperatures (contains quartz, feldspar and mica).

Andite. (Feldspar with harnblende interstices). It has a porous character. Resistant to acids with high thermal stability (900oC). It is used in the lining of absorption towers, drying towers, denitration towers of electric filters, collecting vessels, decanters.

Volcanic tuffs. These are porous rocks resulting from lava verification. They are used by melting and spraying at 1300 - 1400oC to obtain acid and high temperature resistant lining grouts. Due to its low thermal conductivity, it is also used as an insulation material.

Asbestos. The diversity of uses for asbestos is justified by the presence of flame retardant properties, complemented by resistance to acids and bases.

The appreciable strength of asbestos fibre makes it possible to process it into fabric. It has low thermal conductivity.

Seals are made from asbestos and can be:

1. dry gaskets $p < 250$ atm $t = 400 - 500^{o}C$
2. self-lubricating seals $p < 25$ atm $t < 300^{o}C$
3. Rubberised seals $p = 1$ atm, temp. $250^{o}C$

Asbestos is also used as a filler for insulating and heat-insulating plastic.

B. Acid-proof material

Antacid cements. The lining of reactors with antacid materials is achieved by using silicate-based cements. The binder used is a putty that is obtained by mixing inert fillers with admixture powder, quartzite, porcelain and soluble glass in the presence of a setting accelerator (SiF_6Na_2).

The strength of the material obtained is comparable to natural antacid products. Binders of this kind are used for lining reactors. The resistance of the putties is improved in the presence of acids but is not resistant to alkalis.

Apparatus lining with antacid materials must meet the conditions:

1. Rigid manufacture to have stability.
2. The surface to which it is applied must be uniform without protrusions.
3. The surface to be coated is cleaned prior to uniform drying.
4. Have stability of placement.

Litharge-, sulphur- and silica-based cement (58% S, 40% filler, thioalcohols and plasticisers) is also used.

Litharge-based cement (4-6 parts litharge and 1 part glycerine).

Acid-proof concrete. It is used in load-bearing manufactures with high mechanical strength (floors, floors, parapets). It is obtained by mixing an acid-proof material in a concrete mixer with soluble glass and a setting accelerator (Na_2SiF_6).

This concrete is used in the manufacture of drains, crystallisers, neutralisation tanks, drainage.

C. Ceramic products

They have a high chemical stability. They are divided into:

1. Simple ceramics
2. Fine ceramics

a) with compact structure
b) with porous structure

Plain ceramic bodies are used with tower fillers, for lining filters and waste solution channels.

Fine ceramic products are used in the manufacture of tubes with plates, drain taps, risers, pre-collection vessels and ceramic pumps.

The raw material for the manufacture of machines from ceramic products is clay, feldspar and silica.

In order to improve the characteristics of the external surfaces by reducing the permittivity, these products are coated with a thin layer of vitrified mass (glaze). The coating product is prepared using clay, iron ore and chalk by pouring and pouring in water, which can be applied by: brushing, spraying or inserting, followed by heating in kilns at high temperatures.

Porcelain. It is a product containing 25% feldspar, 50% kaolin and 25 quartz. Thermal and chemical stability are the essential characteristics of the product and it is used in chemical and pharmaceutical laboratories. It is not suitable for large apparatus due to uneven shrinkage on cooling.

It is recommended for the manufacture of fine apparatus in the pharmaceutical industry, nuce filters, vacuum apparatus, evaporating boilers, dyeing vats.

Quartz glass. Quartz is obtained by melting SiO_2, resulting in an amorphous mass. High purity SiO_2 (99.7%) is required for the manufacture of the devices.

Quartz glass withstands high temperatures (1000^oC) and is chemically and thermally stable and refractory. It is widely used in the laboratory and industry. Quartz is used to make coolers, absorbers, electrical insulators, vacuum tubes, etc.

Bar glass. It is characterised by high chemical resistance at high temperatures. It is used in the manufacture of small diameter appliances, chillers, pumps and coils. When making control windows.

Email. It is an opaque, sometimes coloured mass obtained by melting at high temperatures natural rocks consisting of feldspars and sand to which borax and alkali carbonates are added as flux. Depending on the use, dyes, opacifiers and oxidisers are added to these, which help to colour the mass and increase adhesion.

The enamel coating consists of:

1. The base coat (primer)
2. The top coat, which ensures chemical stability.

The first layer of enamel (primer) is applied directly to the metal, ensuring mechanical and thermal stress relief between the metal and the protective layer. In order to obtain the primer, the mixture of products mentioned above is melted at 1200 - 1300°C and then poured into water.

By wet grinding the product in ball mills, enamel slip is obtained. Further drying and fine grinding results in coating enamel.

Enamel application technology involves the perfect cleaning of metal surfaces by various processes (sandblasting) with a blasting gun or brush cleaning.

This is followed by thermal stress relieving by heating the machine to 600°C. A primer coat is then sprayed on, followed by the previous drying at 60 - 70°C and finally heating to 900°C. The application of the topcoat enamel is done by spraying the powder onto the surface of the machine brought to red, after which the machines are placed in the oven at temperatures that are 50°C lower than the adhesion temperature of the primer.

The steel appliances undergo the same treatments, except that the coating enamel is applied at lower temperatures and not at glowing.

In order to enamel, machines must meet certain conditions:

1. They must be spherical or cylindrical in shape.
2. They must have a rigid, non-deformable manufacture.
3. Have uniform wall thicknesses to ensure a uniform thermal regime.
4. The joints of the different parts in the surface to be enamelled shall be smooth and uniform.

Mounting and transporting enamelled appliances is difficult. As such, a number of precautions must be observed:

- Enamelled appliances must not be allowed to heat up or overheat suddenly.
- The use of heavy and stiff stirrers should be avoided.
- Enamelled appliances are not recommended for use at medium and high pressures (p = 5 - 6 atm.).

The machines undergo tests to check the characteristics of the email:

- The enamel is subjected to a wooden hammer blow to detect any air bubbles in the coating.

- The unevenness of the coating is (made) determined with a high frequency detector.
- Cracks not detected by the naked eye are determined using a coloured solution.
- Air inclusions can be identified by defectscopy.

Enamelled devices are used in the synthetic organic, pharmaceutical, dye and rubber industries. The enamel layer resists the action of mineral acids and organic compounds up to 300ºC.

1.6. Non-metallic materials of an organic nature

Organic building materials are mostly monomolecular compounds. The general characteristic of the products is poor resistance to oxidising media (H_2SO_4, HNO_3 acids) and low chemical stability to the action of organic solvents. They have good stability in non-acidic environments and are suitable for mechanical processing.

With low thermal stability and poor mechanical strength, the use of plastics in the manufacture of chemical machinery is limited. Among the manufacture materials of an organic nature, the following may be mentioned:

Plastics

Due to their plasticity they can be shaped at certain stages of the thermal regime and then given a finite shape. Depending on the raw material and the production process, a distinction is made between:

1. Plastics based on polycondensation resins.
2. Plastics based on polymerisation resins.
3. Plastics based on natural and synthetic bitumens.

Among the large number of polycondensation resins are phenolformaldehyde resins.

Bakelite varnishes resist HCl of any concentration, 50% H_2SO_4 at temperatures up to 120ºC, acetic acid up to 100ºC. However, they do not resist the action of nitric acid, oxidising solutions and alkalis. Formaldehyde resin lacquers are used for the interior lining of machinery. They are obtained by dissolving the resole resin in a solvent followed by fixing to the surface of the machine. The application of bakelite lacquer on the machine surface is conditioned by:

1. The existence of simple and easily accessible surfaces.
2. Presence of continuous and straight joints.
3. Lack of protrusions and recesses.

Prior to this, a good surface cleaning by sandblasting, sandblasting, wire brushing, pickling with acids if possible. After chemical cleaning treat with alkali and dry.

The bakelite coating is applied after the surface has been previously corrected by grouting and phosphating to increase the adhesion of the varnish. The varnish is applied by brushing, spraying or dipping. In order to ensure uniformity of the film, the process consists of applying successive coats of resin followed by drying. Drying is done uniformly using infrared rays.

The product with the widest range of uses is **phaolite**. Asbestos filler is added to the resin, ensuring acceptable mechanical strength and good processing technology. Depending on the composition, there are several types of phaolite. The thermal conductivity of phaolite resins is close to that of ferrous materials.

It is used in the manufacture of condensers, crystallization of washing towers.

Phaolite devices are obtained by moulding modified resin films onto patterns made of wood or metal. In order to increase the mechanical strength of the machines, they are reinforced with metal skeletons.

This process is used to make shells for reactors and absorption towers. Steel or cast-iron boilers are lined with tinplate.

They are applied by heating the machine to a temperature suitable for plasticizing, after which the material is shaped using rollers.

Textolite. It is a material made by pressing cotton fabric yarns with phenol-formaldehyde resin.

Glasstextolite. It is obtained by impregnating glass fabrics or inserts with phenol-formaldehyde resins.

Azbotextolite. Obtained by impregnating asbestos with polycondensation resins.

The products obtained by impregnating asbestos can be mechanically processed and are used in the manufacture of gear wheels, pumps, agitators and seals. To increase resistance to various corrosive environments, the outer surfaces of the parts are protected with bakelite varnish.

Silico-organic resins. High thermal stability and electro-insulating properties. It is resistant to nitric and sulphuric acid.

Plastics based on polymerisation resins

Polychlorinated vinyl resins

Polyvinyl chloride obtained by polymerisation is a fragile product. By plasticising and mixing with fillers, its mechanical properties are improved and it becomes more elastic. Polyvinyl chloride dissolves well in organic solvents, leading to polychlorinated vinyl varnishes after plasticization, which can be used to coat metal surfaces to protect them from the various environments to which this manufacture material is resistant.

By chlorinating resins of this class, perchlorvinyl products are obtained, with a much better adhesion to metal. Perchlorvinyl resins are used for the protective coating of reactors, absorption towers, tanks.

Durability is maximum 2 years.

Viniplast type twigs

Products in this category are obtained by thermal plasticizing polychlorinated vinyl resins. Viniplast resins are processed by welding under conditions known for metal.

They have good adhesive properties for metal. Viniplast is used to make: valves, taps, pipes, casings, foil linings for lining reactors.

To increase mechanical strength, the product is reinforced with metal skeleton. Resistant to acids and alkalis. Not resistant to oxidising environments. It is currently tending to replace non-ferrous metals in the organic and food industries.

Polyisobutylene.

It is a rubber-like plastic. Mechanical strength increases with increasing molecular weight, but is lower than that of rubber.

Polyisobutylene is soluble in hydrocarbons (benzene, toluene, xylene, mineral oils). The use of the product is limited to lining metal and concrete machinery. Isobutylene resins have a high water resistance and are used in pipes, waterproof coatings, floor coatings and lining of appliances operating at low temperatures (-80°C to 0°C).

Polyacrylic resins

Products in this category are obtained by polymerisation of methyl methacrylate. The resulting mass is transparent, with a low specific gravity and satisfactory mechanical strength. Acrylic resins do not show resistance to aromatic hydrocarbons and oxidising environments but behave satisfactorily in alkaline environments and in the presence of aliphatic hydrocarbons.

The possibilities of thermal plasticization at temperatures of 100°C, allows the processing of plexi-glass by appropriate heat treatment for anti-corrosion coating of chemical equipment.

Polystyrene

The product has thermoplastic properties, is transparent and has good adhesion. Polystyrene welds well. It is recommended for protective spray coating on heated surfaces of chemical machinery and is a good thermal insulator.

Polyethylene

Polyethylene materials are semi-transparent with good chemical resistance, and suitable for: piping, lining, tubing and gaskets.

Teflon

Teflon products have mechanical properties similar to ferrous metals and (comparable to platinum) excellent chemical resistance. It exhibits stability to sulphuric acid, nitric acid, oxidants. Molten alkalis corrode it. It is suitable for making pipes, fittings, for coating or lining reactors.

Resins based on natural and synthetic bitumens

The use of bitumens in chemical machine construction is limited by the moisture content of the material under the influence of temperature. Bitumen-based resins are used by mixing with a drying oil, which provides water-repellent properties. They are not recommended for the manufacturing of machinery that process solvents, compounds and acids with oxidising character.

Rubber

Vulcanised synthetic rubber is recommended for anti-corrosion coating. The fundamental properties of rubber are elasticity and chemical inertness. The first characteristic allows the absorption of the shocks to which the equipment is subjected in operation, and chemical stability recommends the use of rubber for lining equipment processing: H_2SO_4, HNO_3, HCl, hydrocarbons and various salts.

Protection is achieved by applying rubber to the smooth surface of the apparatus using the rubberising process. The application technology involves lining the surfaces with successive layers of rubber films, fixed with rubber or thermoplastic oil. After pressing the foils with wooden rollers, the rubber is vulcanised.

Vulcanisation is carried out in a closed system, which consists of introducing rubberised machines into a reactor under steam pressure of 3 - 4 atm., or in an open system by heating the machines to 100ºC after inorganic salts have been introduced. Rubberized equipment made of steel, Cr, Sn, Zn should be protected, equipment made of Pb, Cu, Al should not be coated. Appliances to be rubberised must meet a number of design conditions.

It is possible to protect machinery by using rubber-based varnishes. Rubber-based films are obtained by solubilising the product in organic solvents and mixing with drying oil. Application is by spraying, reversing or brushing. Chlorine rubber-based lacquer, resistant to mineral acids, is known.

Wood

It is a material with limited uses in the food and leather industries. It has good elasticity and satisfactory chemical stability. However, it has a low coefficient of thermal conductivity and is relatively expensive. It is readily degradable to moisture, flammable. It has high chemical resistance due to the resins it contains. To improve its physical and mechanical properties, the wood is impregnated with phenol-formaldehyde resins. The impregnated material is placed in an autoclave where it is first subjected to vacuum and then to 6 atm pressure. This ensures the penetration of the resin into the material, improving the characteristics of the wood.

2. HOW EACH TECHNOLOGY IS ORGANIZED

All chemical manufacturing is organised into technological processes. The technological process is a series of successive, parallel or cyclical operations of a mechanical, physical or chemical nature, carried out to produce a product.

Different types of operations are found in the technological processes of chemistry:

- mechanical: grinding, sieving;
- physical: heating-cooling, evaporation, crystallisation, melting, condensation;
- fundamental chemical processes: hydrogenation, nitration, halogenation, acidification, oxidation, etc;
- auxiliary operations: transport of materials, supply of utilities, measurement and adjustment of parameters, etc

The operations that aim to achieve a chemical reaction are called fundamental processes; they will make up most of the material in this course. The different types of non-chemical (mechanical, physical) operations are called unitary processes (unitary operations).

Technological processes in the chemical industry can be classified according to several criteria:

a) By the nature of the finished product:

- basic organic synthesis (obtaining alcohols, acids, esters, solvents, etc.);
- fine organic synthesis (production of dyes, medicines, pesticides, reagents, etc.).

b) According to the mode of supply and discharge of the plant:

b.1. continuous processes. An operation or process is continuous when the plant is continuously and uniformly supplied with raw materials, materials and utilities and continuously and uniformly discharges the product.

Any continuous operation is characterised by:

- feed flow rates and product flow rates;
- processing time (dwell time, contact time) = the time taken for the material to travel through the entire installation;
- the quantity of material in the plant at any one time (plant stock).

b.2. batch processes. These take place in streams. The plant is intermittently charged with a certain quantity of material, which is processed, then the product is discharged and the next stage is carried out. Batch processes are characterised by:

- the size of the batch (the amount of material that is loaded once into the reactor);
- the amount of product produced per batch;
- the duration of a processing cycle

When some operations are discontinuous and others continuous, it is called a mixed or combined process.

Continuous processes are characterised by a so-called steady state in which the amount of material in the plant is constant (inputs = outputs), energy is discharged at the rate at which it is produced, and the intensive parameters (temperature, pressure, concentration, flow rates) have stationary values at the same measuring points throughout the process. The non-stationary regime involves positive or negative accumulations of material or energy in the plant and is characteristic of batch processes.

With the elements presented above, the field of fine organic synthesis could be defined as having the following characteristics:

- production is mostly discontinuous, in shifts, characterised by a non-stationary regime of processes;
- production capacities are small and very small (in the order of 101-105 kg/year);
- raw materials, materials and finished products are characterised by a high degree of purity (95 - 99.999%);
- fine synthesis technologies are complicated, with a large number of steps, many of which are unitary separation and purification operations;
- low degree of automation;
- high manpower (physical work done by operators);
- very wide range of raw materials and materials required; very wide range of finished products;
- versatile installations (made up of units that are often even mobile and can take over similar phases of different technological processes).

Obviously, with these characteristics, the fine organic synthesis industry has a number of **disadvantages** compared to the basic organic industry, characterised by high production capacities (101-105 t/year), low labour, high degree of automation, constant product quality.

Given the specific nature of the course, the following will briefly define the essential elements of a technological process in order to create a basis for a technological language.

The raw material is the initial substance from which the synthesis process starts and which is found in whole or in part in the molecule of the final compound.

In most cases, the final product is the result of a series of transformations of the raw material, with the formation of intermediates.

Intermediate is the product resulting from a more or less advanced processing of the raw material and which requires one or more further processing in order to obtain the finished product (synonym: raw material which has reached a certain degree of processing).

Auxiliary materials are substances that participate in the reaction with the raw materials or intermediates, making the reactions possible but are not present in the final product (e.g. acids, bases, solvents, catalysts, drying agents, etc.).

In order to achieve the parameters necessary for a reaction or unit operation to take place, certain conditions (temperature, pressure, etc.) must be created. Achieving these requires the consumption of heating agents (hot water, steam, electricity), cooling agents (cold water, solids), compressed air or nitrogen, vacuum, etc. All these materials are known as ***utilities..***

The manufacturing phase is a component part of the process that comprises all the physical and chemical operations required to obtain, usually through a chemical reaction, an intermediate or finished product.

The division of a process into phases is a necessary and useful operation, as it allows the production of each intermediate product to be traced and at the same time helps to organise a manufacturing section by dividing it into sub-sections corresponding to the component manufacturing phases.

The technological flow is a schematic representation of the operations that raw materials, intermediates and auxiliary materials undergo during a manufacturing phase or technological process.

The representation of a technological flow is based on the following conditions:

- the fundamental processes and unit operations fall into rectangles;
- raw materials, intermediates and auxiliaries are written to the left of each operation, to the right of arrows pointing to rectangles, suggesting their introduction into the process;
- secondary products are written on the right side of the operations (the direction of the arrows is also from left to right), suggesting removal from the process;
- the link between processes and unit operations is made by vertical arrows from top to bottom;

- recirculation of some products is represented by dotted lines.

The process flow diagram is a schematic representation of the sequence of processes and operations involved in the production of an intermediate or finished product (in a manufacturing phase or for the entire technological process).

The diagram shows the machinery in which chemical transformations take place (reactors), as well as the other apparatus necessary for unit operations (filters, distillation columns, storage vessels, etc.), and the materials involved in the process and their flow.

Controlling the technological process. More than any other branch of the chemical industry, in the organic synthesis industry it is necessary to rigorously control the technological parameters at each stage of production, the quality of the raw material, the operating condition of the machinery and the quality of the finished product.

For the various fine synthetic products, the conditions of admissibility of the products on the national or international market are regulated by specialised bodies that control the pharmaceutical, cosmetic and food sectors.

The stringency of the admissibility criteria increases in series:

Technical substances < Chemical reagents < Cosmetics < Food < Pharmaceuticals

Even for a single field, e.g. pharmaceuticals, there are several quality grades, depending on how they are used, with increasingly stringent conditions being imposed for each grade.

Example: cutaneous < oral < injected

In order to meet these quality criteria, producers have to resort to a number of measures, some of them very costly: the use of raw materials of advanced purity; the use of special construction materials for the apparatus; rigorous interface control; the use of additional purification steps for the intermediates or the finished product; rigorous control of technological parameters; the recovery of shreds of inadequate quality by re-purification (an extremely costly and embarrassing operation for current production); rigorous checking of the quality parameters of the finished product from each shred.

Control of the parameters of the technological process and interface control (of raw materials, intermediates and the finished product) are part of the technological project; sometimes, in addition to these, industrial practice also introduces other parameters or control points, which lead to more reliable quality manufacturing, with advanced quality from one batch to another and products that meet the stringency of the required conditions.

A **unit operation** or **unit process** (as opposed to the notion of fundamental process) means any non-chemical (mechanical, physical) transformation, i.e. not involving chemical transformations of raw materials, intermediates or finished products.

The type and sequence of unit operations are rendered in the following steps of successive realization, namely:

Step I - Preparation of raw materials (RM) and auxiliary materials (Aux M.) involves:

Their storage in central warehouses;

Their transport from the warehouse to the plant and within the plant;

Storing them in the required quantities in the plant (own stores, day tanks, etc.);

Dissolving solids - which enter the process as solutions (e.g. Na_2CO_3, NaCl, etc.);

Grinding and sieving of solids (bringing to the desired particle size in the process).

Step II - RM and Aux M. are dosed according to their aggregation status:

Solids (if they do not have to be dissolved beforehand) are usually handled manually (bags, boxes, sacks), weighed on scales placed at the reactor inlet and, less frequently (when large quantities are involved or when continuous feed is used), dosing hoppers or scoop conveyors are used;

Liquids are pumped into measuring vessels fitted with level bottles graduated in units of volume; these measuring vessels are located at the top of the installations for free-fall use;

Gases are introduced into the reactors by bubbling through special devices, their metering being done by flow meters (rotameters) when coming from gas pipelines or by differential weighing of cylinders of compressed or liquefied gases.

Step III - Processing of RM and Aux M. is a complex step, which involves ensuring optimal conditions for one or more chemical reactions to take place, which transform RM into a finished product (FP). In this step, the following are carried out:

Intimate mixing of the reaction components (easier in homogeneous systems, harder in heterogeneous ones), applying according to the type of mixture (homogeneous or heterogeneous) the optimal mixing variant;
Heating/cooling the reaction mixture to the prescribed temperature or maintaining it at a given temperature;
Also in this step, the fundamental chemical processes take place.

Step IV **-** Separation of the useful product from the reaction mass is a decisive step, both for the quality of the finished product and for the overall yield of the process, and therefore its economics.

What should be noted about the separation of the useful product from its mixture with other components is that, whatever the separation method applied, the latter is based on finding and exploiting a physical (rarely chemical) property of the useful product that is sufficiently different from the same property of all the accompanying components.

For example: state of aggregation, solubility in a given solvent, density, miscibility with other liquids, melting point, boiling point, etc.

Finding and intelligently exploiting such differences allows extremely valuable separations and purifications (e.g. zonal melting, membrane diffusion, etc.).

Depending on the state of aggregation of the **useful product** in the reaction mass, one of the following separation options can be chosen:

a) The **U.P**. is in solid state in a liquid reaction medium. In this case it can be separated by:
    Decanting the supernatant liquid;
    Filtration;
    Extraction of the solid with a liquid in which it is slightly soluble, but which is immiscible and chemically inert to the reaction medium (solid-liquid extraction).

b) The **U.P**. is dissolved in the liquid reaction medium. In this case, the solution of the useful product is subtracted from the reaction mass by:
    Evaporation-concentration, followed by crystallisation of the U.P.;
    Precipitation of the U.P. by changing the polarity of the medium in which it is dissolved (e.g. precipitation of sulpho-chlorides when pouring sulpho-mass over ice, precipitation of azo dyes by salting, etc.);

Precipitation of U.P. by chemical transformation and poorly soluble compounds, from which the useful product can easily be obtained.

Note: It can be seen that, whichever route is followed, the problem boils down to separating the solid useful product from a liquid medium (case a).

c) The **U.P.** is immiscible liquid with liquid reaction mass - it forms a distinct liquid layer (top or bottom); in this case a simple separation of the liquid layers, based on gravity, is sufficient. The operation is carried out directly from the reactor by emptying the lower layer (e.g. U.P.) into another vessel.

In general, two immiscible liquids have different densities, separating gravitationally into two layers; in the case of large differences in density or small volumes of liquids, the most economically efficient separation is carried out using separating centrifuges. In these cases, however, the unpleasant effect of emulsion formation may occur, especially if compounds with surface-active (emulsifying) properties are present in the reaction mass; in this case, specific emulsion separation methods are used to achieve separation of the two liquid phases in layers.

d) The **U.P.** is an immiscible liquid with liquid reaction mass: it is the most difficult case of separation and unfortunately it is very common. For the separation of the useful product the following are used:

Extraction of the liquid product with a solvent immiscible with the reaction mass and chemically inert towards it (when the problem is reduced to case c), and the useful product is recovered from solution by simple distillation.

Distillation / rectification of the entire reaction mixture, an energy-intensive operation requiring special equipment, but which allows recovery of the other liquid components of the reaction mass with high purity grades in addition to the useful product.

A typical example is (in the petrochemical industry) the separation of the aromatic fraction (BTX) from the crude oil (de-aromatisation), which is also a reaction mixture, a process which first produces the BTX mixture and then, after further rectification, the 5 pure components, which are widely used as solvents and raw materials in various manufacturing processes..

The recovery of by-products that may exist in the reaction mass (secondary reaction products, solvents or catalysts introduced into the process, etc.) is carried out in order to make the technological process more cost-effective and is done exactly according to the separation scheme of the useful product, by processing the mixture remaining from the separation of the latter. When the mixture remaining after the separation of the useful product (and possibly by-products) is no longer of economic interest, it becomes a waste, whose destruction (ecological reintegration) is a problem specific to other industries.

Step V - Purification of the useful product is basically also an operation of separating the useful product from its companions, but under conditions where the concentration ratio of useful product to impurities is very high. Purification is therefore the operation of maximising (towards) this ratio.

In modern technology, very few fields of activity can be satisfied with technically pure organic products. In the catalogues of suppliers of fine synthesis chemicals, the grades are still found:

Usually above 99.5%; purum (p); purum pro analysi (p.a.); purissimum (puriss.) Usually above 99.99%. Detailed specification of the limiting concentration of a whole list of impurities: spectrometric grade; chromatographic (HPLC) grade; electronic grade.

Like separation operations, purification operations are chosen according to the state of aggregation of the product:

a) the product is **solid** - in this case the following are used:
   - recrystallisation from a suitable solvent, followed by removal by drying of the moisture (water or solvent) remaining after filtration / centrifugation;
   - sublimation (if the product has this property) without further drying.
b) the product is **liquid**, in which case careful distillation / rectification is carried out, removing more volatile or less volatile products than the useful product; drying of the liquid product is rarely necessary after distillation (if necessary, it is carried out with solid drying agents: $CaCl_2$, Na_2SO_4, $CuSO_4$, molecular site).

The separation and purification operations presented here represent the most common cases and common procedures. Depending on the specifics of the technological product and the useful product, sometimes special separation and/or purification methods are applied, such as:

- use of ion exchange (in streptomycin technology);
- use of membrane diffusion (ion separations);
- formation of adducts and supramolecular combinations (separation of iso-paraffins and paraffins by urea adduct);
- preparative chromatography (in the separation of very expensive biologically active products);
- molecular distillation (separation of highly valued f.p. products);

- formation of chelate combinations with metal ions for the purification of electronic grade solvents;
- enzymatic processes;
- cleavage of racemates with optically active acids/bases.

Step VI - Commercial packaging of the useful product.

Some products of fine organic synthesis (except those used as raw materials in other manufacturing, auxiliary materials, solvents, reagents, etc.) such as drugs, pesticides, dyes, explosives, surfactants, etc. are not supplied in pure form but in mixtures specially designed for the purpose of use. These mixtures contain, in addition to the active compound (the actual useful product), other compounds which give it or increase its value for use: solvents, fillers (diluents), additives to protect against degradation of the active substance (by oxidation in the air, by reaction with moisture in the air, by UV radiation in the solar spectrum), emulsifiers, plasticisers, colouring agents, etc. A general classification of conditioning products is practically impossible (there are thousands of them), because of their very wide variety of structures and functions.

Example: packaging of medicines (tablets, syrups, effervescent tablets, etc.); plastics + rubber; cosmetics (sprays, etc.).

Step VII - Packaging. The products thus packaged are packed appropriately for the purpose (type of packaging, quantity, foreseeable storage time, transport conditions, etc.).

3. RAW MATERIAL PREPARATION OPERATIONS

Grinding is the operation of dividing solids to the desired geometric mean dimensions. Grinding of solids is almost always followed by sorting (separation) of different sized grains. The purpose of these operations is to increase the specific surface area, to standardise the speed of processes characteristic of heterogeneous phases (dissolution, reaction, sedimentation, etc.) and to facilitate the transport: mechanical (flow from hoppers or screw conveyors) and pneumatic of the powders.

The grinding of solids is carried out in mills of various types: ball, bar, hammer and disc mills, which operate on the principle of impact or friction grinding. The type of mill is chosen according to the hardness of the solid material and the desired degree of comminution. The resulting powders are characterised by a certain particle size.

The duration and intensity of grinding are chosen to achieve the largest possible proportion of the desired diameter. The resulting powders are sorted by means of consecutive sieves with progressively smaller mesh sizes. The mesh size of the sieves (expressed as the mesh width in mm, as the number of meshes contained in cm2, or in other specific ways) defines the characteristics of the sieves. These are standard sizes in any country. The amount of material that passes through the sieves mesh (so of smaller diameter than the mesh size) is called **sieving (S)**, and the amount of material that does not pass (because of diameters larger than the mesh size) is called **sieving rejection (R).**

In a system of overlapping, mechanically operated (shaken) screens the passage of each upper screen represents ***the sorting material*** of the lower screen and the rejection of any given screen represents ***the grain size fraction*** having sizes between those of the given screen and the higher order screen. Thus, a powder can be classified into more or less tightly packed ***particle size classes*** (Figure 3.1.).

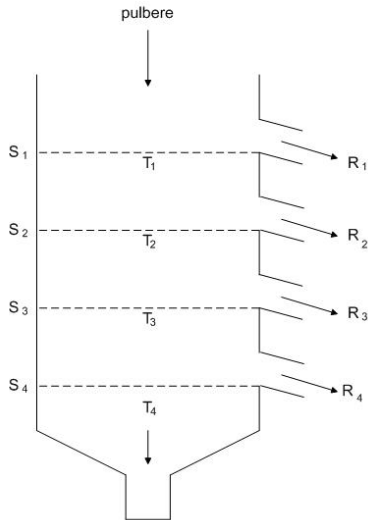


Fig. 3.1. Sorting of solids by particle size classes

Grinding and sorting of solid materials are important not only as preparatory operations for the raw material of a process, but can also be considered as physical conditioning operations of products. Thus, medicines intended for the production of classical or effervescent tablets must be brought to particle diameters that ensure optimal compression and disintegration. Some medicinal products (e.g. nystatin), which are injected i.m. as a suspension, are "micronised" to a size that ensures their resorption within 24 h (depot drug). If the dimensions achieved are less than optimal, the viscosity of the suspension is too high and it does not flow through the syringe needle. If the crystals are too large, they clog the needle, making administration impossible or insufficient (only the saline in which the crystals are suspended is injected).

Dissolving is another operation to prepare solid raw materials when they cannot be purchased in a dissolved state (example: NaOH 40-50% lye), but are introduced into the reaction in a dissolved state. Dissolution can be carried out directly in the reaction vessel or, if the technological procedure does not allow this, in special vessels, uncovered or closed, always provided with stirring and optionally heating/cooling to compensate for the thermal effect of the dissolution.

4. OPERATIONS TO ENSURE REACTION CONDITIONS

The following conditions are necessary for chemical reactions to take place under optimal conditions:

- bringing the reactants into intimate contact;
- ensuring the optimum temperature in the reaction mass, in order to achieve a high rate of the main reaction and avoid side reactions altogether;
- ensuring compositional and thermal homogeneity of the reaction mass (to avoid overloads and/or local reactions).

These conditions must also be ensured to a large extent for physical processes in which chemical processes are not (or should not be) involved: dissolution, evaporation, distillation/rectification, absorption, extraction, drying, crystallisation and recrystallisation, etc.

If during physical processes requiring external heat input, due to insufficient homogenisation, local areas of overheating may occur, favouring some undesirable reactions (e.g. accelerated hydrolysis, thermal decomposition, carbonisation) which may sometimes take on the character of damage (self-ignition, explosions).

4.1. Stirring in chemical plants

Stirring is one of the most commonly used operations in the chemical industry, both as a stand-alone operation to achieve homogeneity in a mixture and as a means of increasing the contact surface in other operations such as absorption, extraction, drying.

In general, stirring refers to the particular case of homogenisation of a mixture of two or more components of the same phase (gases, miscible liquids or powders).

By stirring, the masses to be processed have a homogeneous quality and it is possible to control the speed of physical (dissolving, flowing, boiling, etc.) or chemical processes. Stirring improves heat and mass transfer. Insufficient stirring can lead to undesirable local deposition, overheating or undesirable chemical reactions (secondary).

The parameters that determine the choice of types of stirring devices and ensure mixing efficiency are: the state of aggregation of the components, their density and viscosity.

A fundamental condition of stirring is the movement of the materials to be mixed. The way in which the materials are set in motion and maintained in this state is influenced by the properties of the materials, which largely determine the nature of the mixture. Therefore, stirring operations differ according to the properties of the mixture under consideration.

Stirring systems are either fluid or made of solid particles. Depending on their state, fluids are divided into gases and liquids. Two types of motion can occur in fluids: spontaneous and forced. It is known that fluids that are miscible with each other, introduced into a container undergo spontaneous mixing within a certain time. This stirring is achieved by the movement of fluid particles due to molecular diffusion or mass transfer by natural convection. This is caused by uneven densities of fluids or possibly uneven temperatures in different regions, or both processes at the same time.

Spontaneous mixing is not of much importance for practical purposes because it proceeds too slowly. Faster mixing requires mass or heat transfer by forced convection. Forced convection is achieved by an efficient movement of the fluid, e.g. by flowing.

The motion of the fluid is caused by the forces acting on it: pressure and mass forces. Resistance to fluid motion is due to internal friction, i.e. viscosity.

In stirring, the character of the flow is of great importance. It depends on the flow velocity, the viscosity and the geometrical configuration of the space through which the fluid passes.

There are two basic types of flow: ***laminar*** - in which the fluid particles move along streamlines parallel to the direction of flow; and ***turbulent*** - in which, through a hydrodynamic process, vortices are produced, the fluid elements move not only in parallel layers but also have irregular paths.

Molecular diffusion always achieves slow mixing. The speed of operations in the stirring technique is increased by the mutual penetration of elements from one fluid into another due to the action of turbulent diffusion. An efficient mixer provides the optimum conditions for this penetration.

Types of stirring

Stirring in a pipe

The simplest mixing process is that which takes place during the transport of miscible fluids through a pipe, in this case the mixing is carried out by turbulent diffusion, since in technical practice the liquid is pumped under turbulent conditions.

This stirring method is suitable for both gases and liquids in motion. It can be used in cases where the pipe through which the fluid passes is sufficiently long. The length of the pipe is of particular importance for liquids, as mixing is slower.

Stirring in a container

Liquids are more commonly mixed in containers than in pipes. Mixing vessels can be designed for either continuous or batch operation. In both cases the mixing is carried out by forced convection, which means that the movement of the liquid produced in the vessel must be strong enough to cause turbulence and thus generate turbulent diffusion.

It is never possible to ensure the same intensity of turbulence throughout the entire contents of the container. The turbulence is less intense especially at the walls. For this reason it is desirable to periodically pass the entire quantity of eliquid in the container through the regions where the turbulence is most intense. This is achieved by circulating the liquid in the container.

Jet mixing

Jet mixing is used for both gases and liquids and the principle is the same. Jets are usually used for mixing liquids in combination with a pump, which draws some of the liquid from the tank and recirculates it through a pipe which has a nozzle at the end of it that is immersed in the tank.

Fluid passing through a nozzle into a large space takes the form of a cone, dispersing as the distance from the orifice increases. This phenomenon, shown schematically in Fig. 4.1, is caused by the following causes.

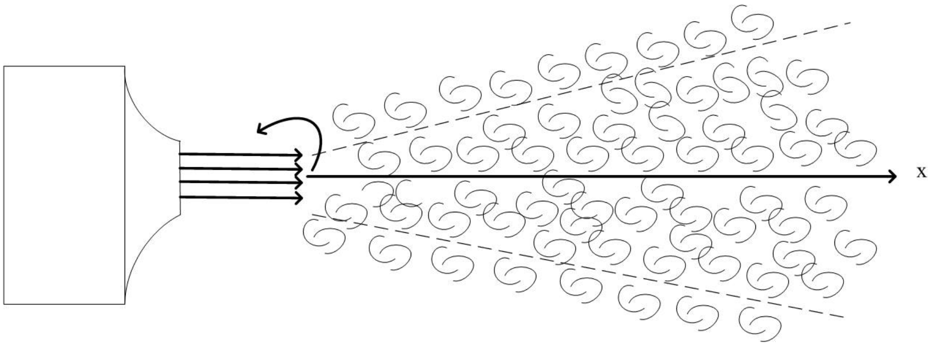


Fig. 4.1. Jet mixing scheme

1. Fluid coming out of the nozzle dislodges the fluid in the container in front of the orifice.

2. The fluid layers adjacent to the jet are entrained in a flow-parallel motion as a result of the transfer of part of the momentum of the fluid jet to the surrounding fluid by turbulent penetration of the fluid elements in the jet into the fluid in the container.

The velocity of the fluid entrained by the stream is slower than the velocity of this stream and each layer of fluid in motion entrains adjacent stagnant layers, the cross-section of the stream consequently becomes larger the further it is from the nozzle orifice.

3. When the surrounding fluid is entrained by the current, a pressure drop occurs at its original location, causing another amount of fluid to be rapidly sucked into this location and also set in motion as a result of momentum transfer from the jet. This cycle repeats itself continuously.

Entrainment of the flowing fluid leads to the formation of a turbulent boundary layer at the periphery of the cone, through which mixing takes place.

The thickness of the boundary layer increases in proportion to the distance from the orifice. Gradual increase of the boundary layer leads to an enlargement of the cone and a movement of the core which eventually disappears at a certain distance from the orifice.

Stirring liquids using a gas

In principle, mixing liquids with a gas can be done in a container in two ways:

- By free bubbling of the gas (air)
- By controlled bubbling through a draft tube

Stirring by free lift of air is similar to mixing by an immersed nozzle, as in Figure 4.2. A turbulent liquid cone rises vertically into the liquid, starting from the gas inlet of the container and resembling a jet caused by the immersed nozzle. In order to include a maximum volume of liquid in the cone, the air outlet connection is usually located at the bottom of the container. For the same reason, containers for mixing liquids by free bubbling are designed to contain a high column of liquid.

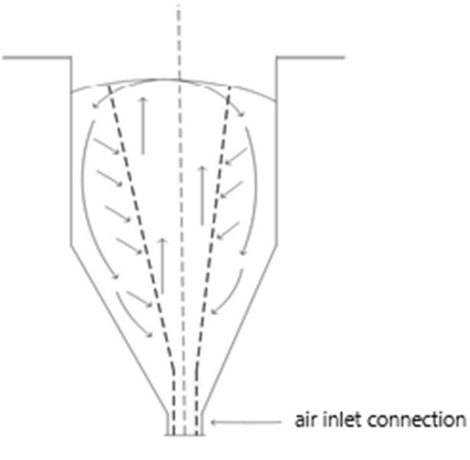


Fig. 4.2. Stirring by free lifting air through an immersed nozzle

The flow regime is generated as follows: gas enters the liquid in the form of bubbles, and these bubbles, in their upward movement, move the liquid to the top and to the sides.

A vortex is formed behind the bubble and the liquid in its immediate vicinity is entrained by the action of tangential tension between the bubble surface and the liquid. Behind the rising bubble there is a pressure drop, which is immediately equalised by entrainment of the surrounding liquid in this space.

The swirls caused by the expansion of the bubbles (the upward direction decreases the external hydrostatic pressure) and their collisions promote turbulent diffusion and mixing.

In the system with a draft tube (Figure 4.1.3), the tube prevents entrainment of liquid from the rest of the volume in the container, because liquid can only enter through the draft tube at the bottom.

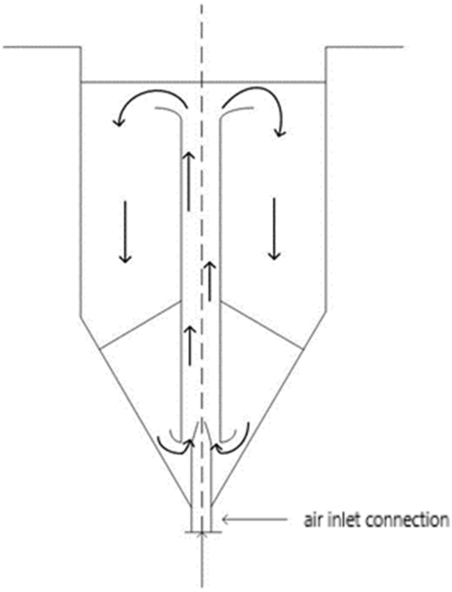


Fig. 4.3. Stirring using a draft tube

Consequently, the flow velocity in the draft tube is higher than in the turbulent cone produced by a free lift of air and even increases towards the surface under the influence of the energy released by bubble expansion.

As a result, the intensity of turbulence in the liquid flowing through the draft tube also increases towards the surface, which again is convex at the end of the draft tube. The liquid at the surface flows towards the walls of the container and down to the base, where it is drawn back up the draft tube. The velocity of liquid flow in the vessel depends on the diameter of the draft tube as well as the flow rate of the gas entering the vessel.

Mechanical stirring in a container

Mechanical mixers are used almost exclusively for liquids. They produce a certain flow regime in the liquid, and the devices used for this purpose are mostly rotary stirrers.

The liquid adheres to the surface of the rotating disc and as soon as the stirrer has started to rotate the liquid layer rotates with it. Due to the action of viscosity, other adjacent layers are set in motion until the flow extends into the entire contents of the container.

Some of the most commonly used types of mechanical mixers are shown in Fig. 4.4.

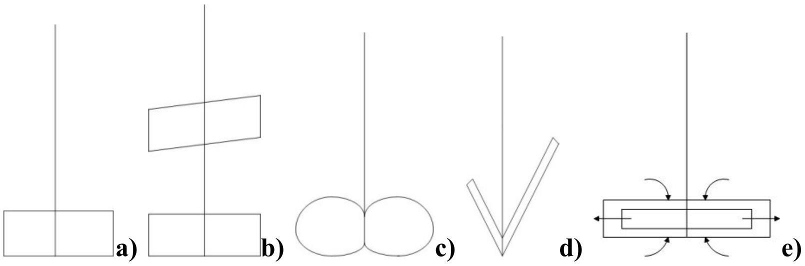


Fig.4.4. Types of mechanical mixers
a-single blade; b-double blade; c-screw; d-impeller; e-turbine

In the case of paddle, turbine and propeller stirrers, the rotating blades exert pressure on the liquid, displacing some of it into the surrounding medium and thus initiating the rotational movement in the liquid.

The pressure drop that occurs behind the vane entrains the liquid from the surrounding medium. The displacement and entrainment of the liquid causes turbulent currents around the vanes.

As the rotational speed increases, the liquid between the vanes is also subjected to centrifugal forces due to which it is radially displaced from the periphery of the rotor. This increases the flow velocity of the liquid into and out of the rotor. The liquid that is removed from the periphery, due to the action of centrifugal forces, permeates into the surrounding liquid in a similar way to the flow from an immersed nozzle. This means that here too there is a transfer of momentum to the surrounding medium, which manifests itself in an increase in the cross-section of the flow and a gradual loss of velocity with increasing distance from the rotor. The combination of these processes sets in motion the entire contents of the container.

The current path caused by the stirrer in the vessel can be represented by the flow spectra: tangential, radial and axial.

Predominantly tangential flow (Figure 4.1.5.) occurs in a paddle mixer, which rotates at a speed insufficient to produce a sensible centrifugal force action.

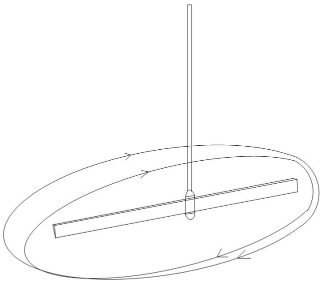


Fig. 4.5. Tangential flow

In radial flow (Fig. 4.6.) the liquid is removed from the rotor at right angles to its axis and along a radius. The viscosity of the liquid resists the flow in the surrounding medium, and overcoming this resistance requires a certain centrifugal force produced by the agitator depending on its diameter and speed. As soon as the centrifugal force overcomes the resistance of the medium, radial flow from the impeller to the medium begins.

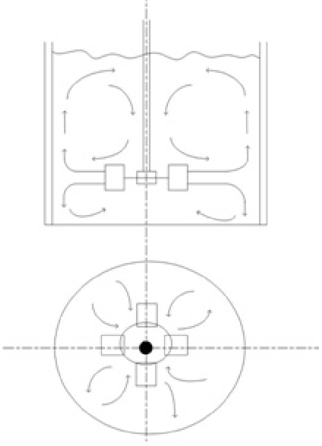


Fig. 4.6. Radial flow

So, all other conditions being maintained, it is possible to achieve a gradual transition from tangential to radial flow by varying the rotor speed.

The rotor generates two flow zones: at the bottom it entrains the liquid in an upward direction and displaces it at right angles to the rotor axis, and at the top it entrains the liquid in a downward direction, also moving it perpendicular to the rotor axis.

In axial flow (Fig. 4.7.), the liquid enters the rotor and leaves it in a direction parallel to its axis.

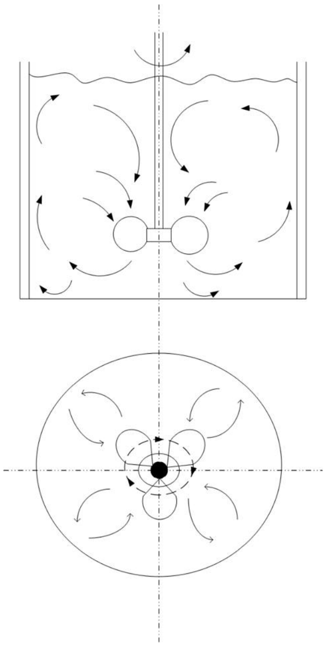


Fig. 4.7. Axial flow

Depending on the pitch of the impeller and the direction of rotation, the impeller can pump liquid from the bottom to the surface or vice versa.

In mixing vessels, combinations of the three main types of flow are usually found.

By fitting chicanes in the vessel or by using certain types of turbine mixers the rotation of the liquid parallel to the rotor axis is prevented. The change from axial to tangential flow is a feature of turbine mixers with inclined blades.

Heterogeneous fluid systems

In practice it is often the case that the resulting mixture is a heterogeneous system. In other cases, the substances being treated initially exist in two phases, which then gradually form a single phase (dissolving a solid in a liquid).

Gases as such are completely miscible. Dispersion of solids or liquids in gases leads to heterogeneous mixtures, fumes and mists respectively.

As far as liquids are concerned, there are three basic types of heterogeneous mixtures, namely: mixing a gas with a liquid, mixing immiscible liquids and mixing a solid with a liquid.

Mixtures of immiscible liquids like solids and liquids are mostly highly viscous.

Liquids dispersed in gases

Liquids are dispersed in gases by spraying the liquid phase into the gas phase, which is done using three types of equipment: nozzles, two-component nozzles and centrifugal atomisers.

In the case of nozzles, the energy required for dispersion is produced by exerting pressure on the liquid. Dispersion with two-component nozzles is achieved by a gas escaping from the nozzle at a very high velocity. In centrifugal atomisers, the liquid to be dispersed is accelerated by a rotating disc. Due to the specific weight, the droplets tend to fall towards the bottom, the smaller they are, the slower the fall and the longer the heterogeneous mixture is maintained. Sedimentation can be reversed by an upward flow of gas.

Solids dispersed in gases

Solid particles are most commonly dispersed in a gas by fluidization, which consists of passing a stream of gas at a sufficient velocity through a layer of finely divided solid particles so that the upward velocity of the gas is greater than the deposition velocity of the individual solid particles.

Gases dispersed in liquids

This is achieved by bubbling the gas into the liquid. In practice, three situations can occur:

1. The gas is insoluble in the liquid
2. The gas is physically dissolved in the liquid
3. The gas physically dissolves and chemically reacts with the liquid

If absorption of the gas into the liquid is desired, mechanical mixers can also be used to keep the diameter of the bubbles as small as possible so that the specific surface area is as large as possible

Nemiscible liquid

Mixing immiscible liquids is a common process encountered in practice in emulsion formation and extraction. The operation can be carried out in batches or continuously.

In batch mixing of two immiscible liquids the dispersion is achieved gradually. Before mixing, the liquids form two superimposed layers; if their densities differ, the dispersed liquid (the one distributed in fine droplets in the main liquid), due to the action of the mixer, is first divided into small cylinders, which expand to form thin strips. These emit globules which are further disintegrated to very fine droplets.

How this process unfolds depends on hydrodynamic conditions. In turbulent flow, droplets move in all directions and often collide, and in some cases two smaller droplets join to form a larger droplet. At a constant rotor speed, after a certain time, an equilibrium state is reached between the number of droplets combining and the number of droplets splitting.

In continuous mixing of two immiscible liquids, the machine is first charged with the continuous phase, after which the dispersing phase is introduced. If the continuous phase has a higher density, the dispersed phase is added at the bottom.

When the stirrer is at rest, the phase with lower density rises in droplets due to the influence of the upward force. When the stirrer is set in motion, the rising droplets enter the area exposed to mixing and are broken up into smaller particles.

If the density of the continuous phase is lower, the dispersed phase is introduced at the top and drops from the main phase to the bottom of the mixing vessel. In the stirred zone the droplets are divided. The higher the agitation intensity, the more effective the droplet division.

Solids suspended in a liquid

Suspension of a solid in a liquid is important in the processes of dissolution, extraction, in heterogeneous chemical reactors.

When the stirrer is at rest, all solid particles are deposited on the bottom of the container. Gradually increasing the stirrer speed leads to the following process:

1. The mixer rotates at low speed and the solid particles remain deposited at the bottom. The speed of the liquid is low and insufficient to bring the particles into suspension.
2. As the stirrer speed increases, the liquid stream first dislodges the particles along the bottom of the container towards the centre, where they accumulate under the impeller, forming a mound. Gradually, the driving action of the agitator begins to take effect. The particles first move in circular paths, parallel to the vessel wall, and rise to a height above the bottom. This height is given by the flow conditions of the liquid and the deposition velocity of the solid particles. After reaching this height, the particles move towards the agitator shaft where they are dragged downwards towards the agitator, the whole process repeating itself. In the course of time the agitator entrains more and more particles from the bottom into its rotation, until a steady state is reached, in which the

number of moving particles is constant, characteristic of a given rotor speed.

3. Further increase of the stirrer speed leads to a state in which all solid particles are dispersed in the liquid and centrifugal forces become evident. The particles will now rise in helical paths and be distributed throughout the contents of the container.

Increasing the length of the agitator blades (without changing their width) increases the surface area of the rotor, and if the diameter of the container remains unchanged, this leads to a greater suspension action. When an optimum length is reached at constant speed, the distribution of solid particles in the volume of the whole container is most uniform. Further elongation of the vanes leads to vortex formation and negatively influences the uniformity of the suspension.The same effect is obtained by increasing the width of the vane (at constant length), leading to an increase in the surface area of the rotor.

Of particular importance is the positioning of the rotor in relation to the bottom of the vessel. It is not advantageous to place it close to the surface, but the uniformity of the suspension increases as the rotor is placed deeper in the vessel. It is also not advisable to place the rotor at the very bottom of the vessel, but at a distance equal to 1/3 of the total height of the liquid, as otherwise it will only entrain the liquid above (Fig. 4.8.).

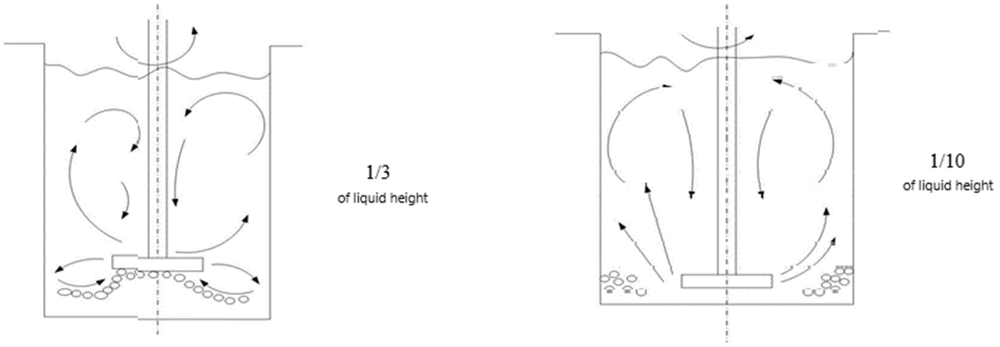


Fig. 4.8. Positioning the stirrer in the mixing vessel

Stirring highly viscous liquids and pastes

Pastes are viscous suspensions, emulsions or melts that are plastic and retain their shape through deformation. Pastes only start to flow when a sufficiently strong force acts on them.

When mixing high viscosity liquids and pastes, favourable flow spectra are achieved by large diameter and wide blades such as helical belt mixers or mixers.

In a belt mixer that rotates about its vertical axis so as to dislodge the liquid from the bottom to the surface. The liquid rises along the walls and returns to the bottom through the central part. The entire amount of liquid is in motion.

A mixer works like this: the snail pulls the liquid from the bottom of the container and brings it to the surface, where it returns to the bottom through the narrow space between the draft tube and the container wall.

Types of mixers

Mixers are divided into four main groups, depending on the state of aggregation of the materials being mixed.

1. Gas mixing machinery
2. Machinery for mixing mobile Newtonian liquids
3. Machinery for mixing pastes and other non-Newtonian substances
4. Machinery for mixing of airborne solids

Gas mixing equipment

If several gases or a gas and evaporated vapour are mixed in one gas, nozzles can be used. The diagram of a nozzle is shown in Fig. 4.9.

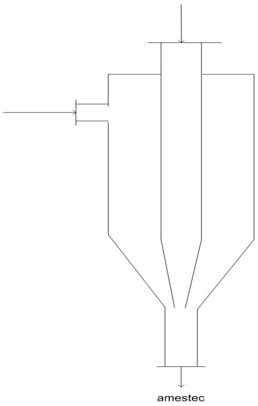


Fig.4.9. Scheme of a nozzle

If two gases are mixed, this can be done very easily in pipelines (Fig. 4.10). A necessary condition is that the length of the pipeline and the velocity of the gases are sufficiently large.

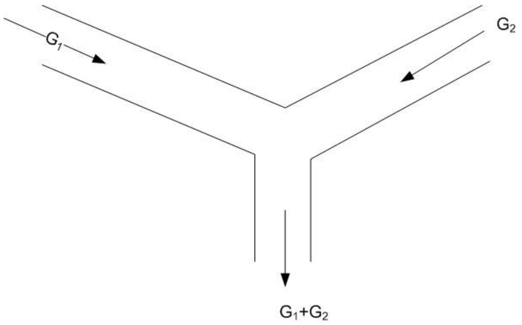


Fig. 4.10. Mixing of gases in pipelines

Centrifugal atomizers

This type of apparatus is mainly used for drying, and is shown schematically in Fig. 4.11.

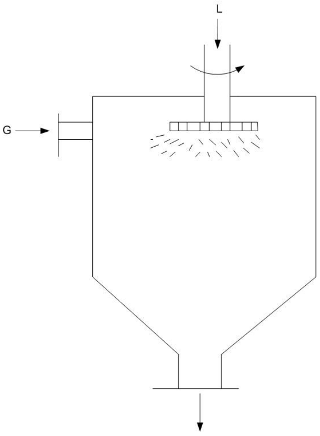


Fig. 4.11. Scheme of a centrifugal atomizer

The liquid flows through a rotating disc, which rotates at high speed and is fitted with grooves to disperse the liquid in droplet form. Discs with a large diameter require a slower rotational speed.

Liquid mixing equipment

The mixing of liquids can be done either directly in pipes with the help of turbulence caused by the flow of the liquid, or in special containers, with continuous or discontinuous operation.

There are the following types of mixers: piped, pumped, air or steam stirred, mechanically stirred.

When mixing in pipelines, the simplest equipment is to connect two Y-shaped pipelines. To improve the process, inner baffles can be fitted to increase turbulence.

Injectors work on the principle of nozzles. The scheme of a swirl injector is shown in the Fig. 4.12.

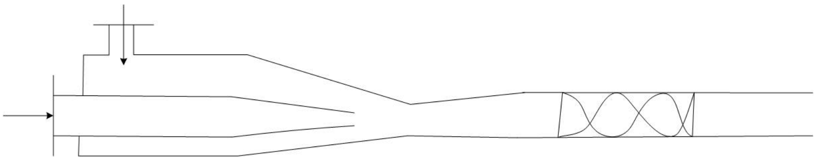


Fig. 4.12. Scheme of an injector with helical chicanes

The scheme of a Venturi tube mixer is shown in the Fig. 4.13.

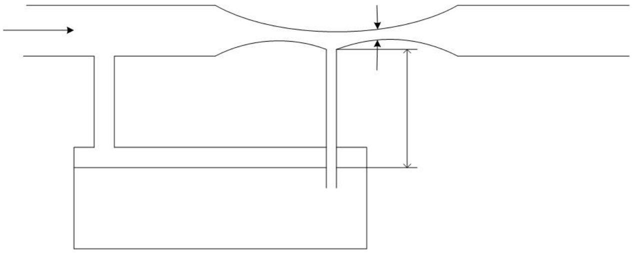


Fig. 4.13. Scheme of a Venturi tube mixer

Pumps that recirculate the liquid in the container can be used to increase the mixing intensity. The scheme of such a mixing type is shown in Fig. 4.14.

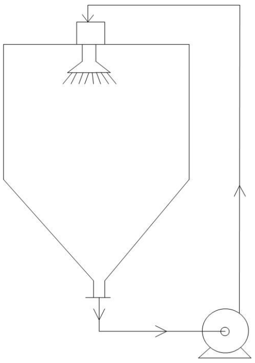
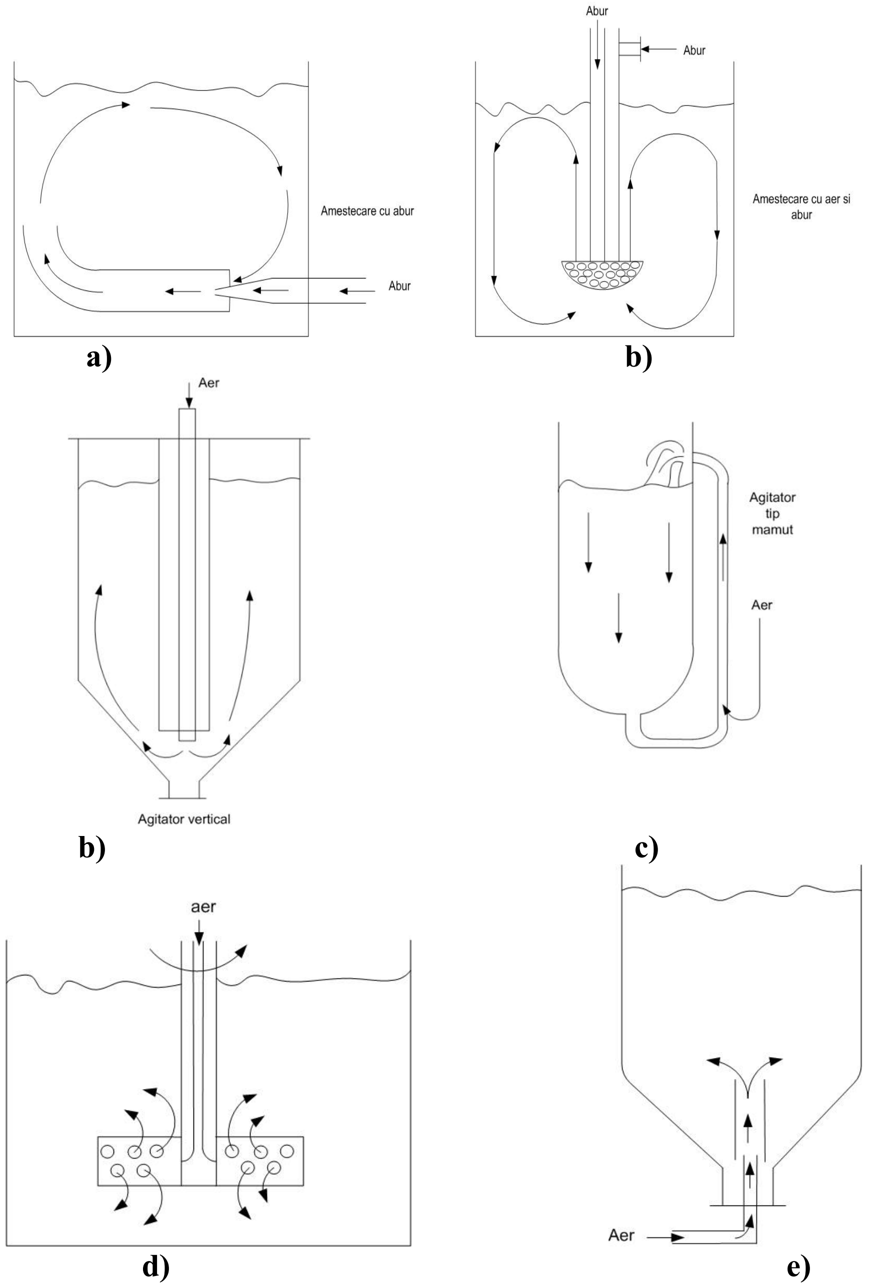


Fig. 4.14. Mixing in containers with pump circulation

Mixing by bubbling air or steam (in which case it is also combined with direct heating) is often used in industry. Some schemes in which this type of mixing is carried out are shown in the Fig. 4.15 (a-f).



a) b)

b) c)

d) e)

Fig. 4.15. Agitation by bubbling air and/or steam

Mechanical mixers are mixing elements mounted on a vertical, horizontal or inclined shaft and are driven by mechanical energy. They are suitable for mixing liquids and pastes.

Depending on their design, there are paddle, propeller, anchor, turbine and special mixers. They can be high or low speed.

Paddle mixers are centrally located, have large diameters and low speeds. There is no danger of vortexing. They are usually used without a paddle. If operating at higher speeds, horizontal or vertical chisels should be used because of the possibility of vortex formation (Fig. 4.16).

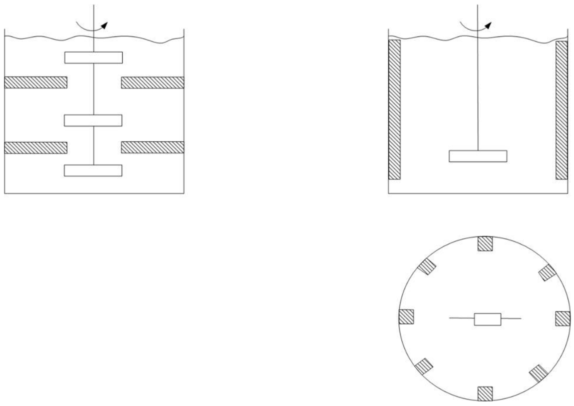


Fig. 4.16. Positioning of the chick inside the container

In order to achieve correct and economical operation in the stirring calculations, the viscosity of the mixture, the shape and size of the vessel, etc. are taken into account. For example, for viscosities up to 1000cP and a single paddle on the shaft, we will have, according to the notations in Fig. 4.17., the following dimensions:

d/D = 0,66 – 0,9 ; h/d = 0,1 – 0,2 ; A/d = 0 – 0,3 ; H/D = 0,8 – 1,3

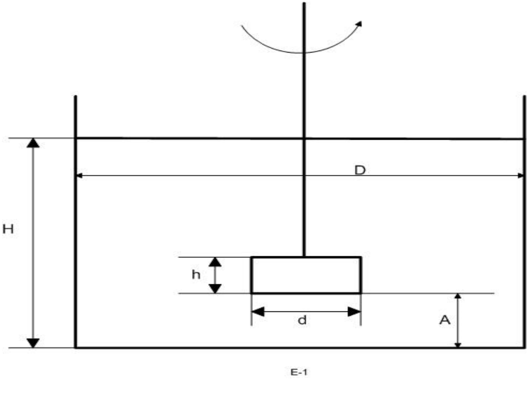


Fig.4.1.17. Notation for calculating agitation

In deeper vessels, the vanes are mounted on the shaft on top of each other (as in Figure 4.1.16.) so as to enhance turbulence. Usually the distance between the vanes is *0,3-0,8 d* and is chosen according to the viscosity of the mixture.

In heated jacketed vessels in which plastics are mixed, there is a danger that the mixture will adhere to the wall and bottom and that by-products may form or even explode on heating. In this case, the diameter of the mixer is as large as the inside diameter of the container, so that it can scrape the walls and bottom - making it easier to empty the bottom.

Machine manufacturers develop models that can be easily changed and modified, producing agitation according to specific orders.

The paddle blender has the paddles mounted on an arm mounted on a shaft, either vertically or horizontally, if the container is cylindrical, placed horizontally, as in the Fig. 4.18.

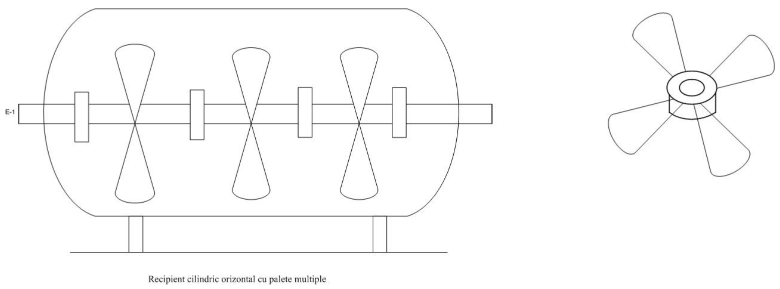


Fig. 4.18. Paddle stirrer in a horizontal container

Propeller mixers have a propeller attached to a vertical, horizontal or inclined rotating shaft (Fig. 4.19).

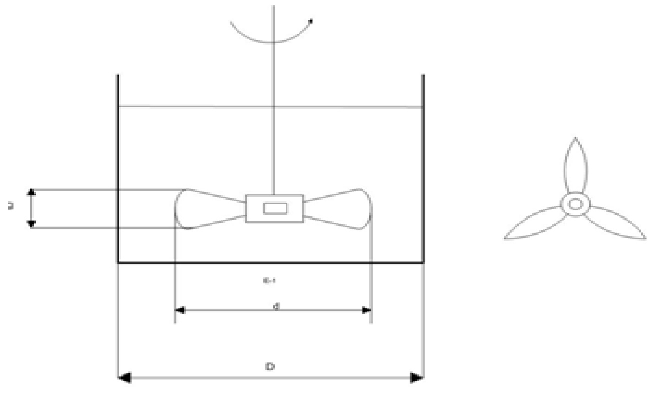


Fig.4.19. Propeller mixer

These mixers have high speed, short mixing times. They should only be fitted in convex containers. The pitch of the propeller is a very important size, and represents the distance between the neighbouring maxima of the spiral forming the propeller. The size is not directly measurable, but is calculated from the formula:

$$s = 2\Pi r \operatorname{tg}\varphi$$

where: r - radius of the propeller blade (radius of the cylinder formed in the liquid due to the movement of the mixer; φ - angle of inclination of the blade.

The maximum viscosity at which propeller mixers can still be used is 2000cP. They are used for rapid mixing or for the formation of low viscosity emulsions, for dissolution and for liquid phase chemical reactions up to a maximum volume of 7 m3. For suspensions, the upper particle size limit is 0.1-0.5 mm and the maximum proportion of dry residue is 10%. Not to be used for rapidly settling suspensions, dissolving of poorly soluble substances and gas absorption.

The most common stirrers of this type are 3-bladed. The main sizes commonly used are

$$d/D = 0{,}2\text{-}0{,}5\ ;\ \ s/d = 1\text{-}3\ ;\ \ A/D = 0{,}1\text{-}0{,}5\ ;\ A/d = 0{,}5\text{-}1\ ;$$

$$H/D = 0{,}8 - 1{,}2 \text{ (for a propeller) } ;\ H/D = 1\text{-}5 \text{ (for more propellers)}$$

The multiple propeller feeder has two or three propellers attached to a shaft, the number of propellers being limited by the mechanical strength of the shaft. Two mixers can be mounted on a common shaft, which can either move in the same direction or in opposite directions, creating intense agitation.

Propeller mixers in draft tubes are used for mixing low viscosity liquids.

Turbine mixers work similarly to a centrifugal pump, they operate in a vessel against negligible back pressure. Mixing is carried out by the turbine blades which drive and displace the liquid. Due to the predominantly radial flow of the liquid in the mixer, an important condition for the proper functioning of the turbine is an appropriate shape of the container. After being discharged from the mixer, the liquid collides with the wall, where it splits into two streams that cause mixing due to their energy. The suction takes place in the centre, as in centrifugal pumps, and the discharge on the circumference of the blades, as in the Fig. 4.20.

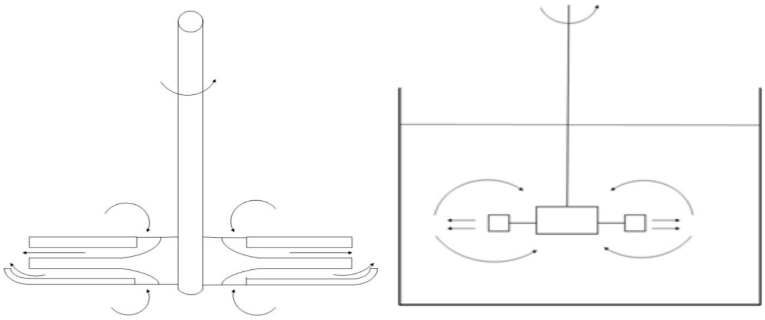


Fig. 4.20. Turbine mixer

In order to concentrate the drive action at the bottom, guide rings are sometimes fitted under the turbine, especially in the case of suspensions, when the solid substance settles directly in the centre of the container under the mixer.

The main advantage of these types of mixers is the wide range of application in terms of viscosity and density in which they can be used. The speed of these mixers is 1200 rpm and the peripheral speed 200-500 m/min.

The mixing of pastes and plastics has a wide application, being used in rubber products, plastics, medicines, soap, as well as in the food industry.

It is used in the following cases:

1. The mechanical mixing of a liquid with solid products to form a paste or plastic mass.
2. A paste or plastic mass may originate from a mixture of two or more initially liquid components during the mixing process either due to a physical process or a chemical reaction.
3. During mixing the solid powdery substances are transformed upon heating into a paste or a plastic mass or vice versa, the molten solids are mixed and a paste is formed inside by cooling.

Mixers for pastes and plastics must meet the following main requirements:

1. Have the required capacity and the container must be of suitable shape and sufficient strength.
2. Ensure that the material is fed into an effectively agitated area.
3. The mixing paddles or arms must process the mixed substances in the active zone so as to achieve the desired degree of mixing.
4. The mixing equipment must be easy to empty and clean.

There is a gradual transition between highly viscous liquids and pastes or plastics, and the mixing equipment is similar to that used for mixing liquids. Depending on the increase in consistency, the mixers can be classified and arranged in the following order: paddle, turbine, ball mill, moving vane and stationary paddle, moving vane and vertical shaft paddle, belt, frame and anchor, scraper, double motion paddle, planetary mixing paddle, valve mill, mixer.

Depending on the shape of the container, the following machines for mixing pastes are distinguished: vertical tank, horizontal tank, vat or tub, mills, valves, emulsifying and homogenizing machines.

The chemical reactor can be likened to a vertical tank. Most of the devices for mixing pastes in vertical tanks use the principle of paddle mixers, adapted in construction to ensure movement in mixtures of a fairly high consistency. In the vast majority, in addition to the horizontal arms, these mixers also have vertical arms to intensify the vertical movement, which is difficult to transmit especially in a dense environment. The shape of the mixer often corresponds to the shape of the container.

The simplest mixer of this type is the anchor stirrer. It consists of a curved arm corresponding to the concave bottom of the container and is mounted on a vertical shaft, as shown in the figure 4.21.

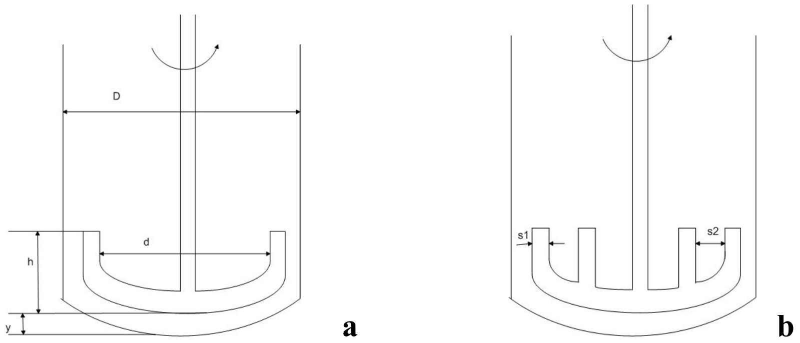


Fig. 4.21. Anchor stirrer
a – simple anchor, b – double anchor

For the simple anchor stirrer, the dimensions are:

$$d = 0{,}9\text{-}0{,}98\ D\ ;\ h = 0{,}4\text{-}0{,}8\ D\ ;\ y = 0{,}05\text{-}0{,}1\ D\ ;\ v_p = 0{,}5\text{-}1{,}5\ \text{m/s}$$

For the double anchor agitator, the values are as follows:

$$d = 0{,}9\text{-}0{,}98\ D\ ;\ h = 0{,}4\text{-}0{,}7\ D\ ;\ y = 0{,}05\text{-}0{,}1\ D;$$
$$s_1 = 0{,}08\ D\ ;\ s_2 = 0{,}15\ D\ ;\ v_p = 0{,}5\text{-}1{,}5\ \text{m/s}.$$

Anchor stirrers are mostly used in containers heated at the bottom with a mantle, and their task is to scrape the bottom. That is why they are always located directly above the bottom.

Vertical stirrers can also be fitted in vertical containers with anchor stirrers, as shown in the Fig. 4.22.

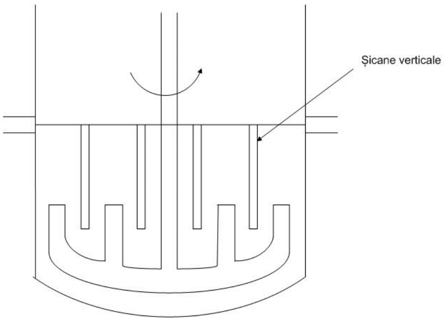


Fig.4.22. Mounting an anchor stirrer with vertical chicanes in the container

Scraper mixers are another type of mixer with horizontal and vertical elements. The purpose of this construction is to prevent turbidity of the entire mixing mass.

Although of relatively simple construction (as in Fig. 4.23), they are satisfactory during operation.

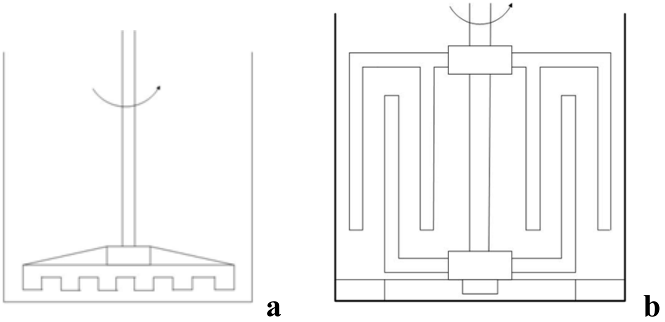


Fig. 4.23. Mixers with scraper
a – simple mixer; b – double mixer

On the double mixer, the top branch is fixed and the bottom branch rotates. The two scrapers intermesh, shearing the mixing material and increasing the intensity of agitation.

The *soap mixer* consists of a continuous propeller mounted in a draft tube, which fits tightly around the propeller (Fig. 4.24).

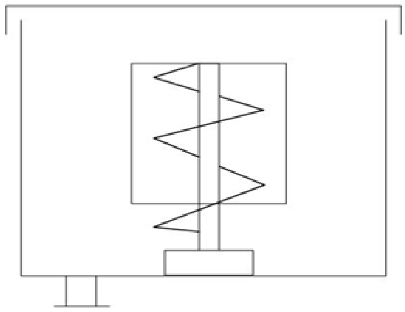


Fig. 4.24. The soap mixer

The helix lifts the material into the draft tube, from where it spreads around the circumference. The mixer is suitable for pastes of small to medium consistency, but has the disadvantage that the movement of the material along the walls is not intensive. Adding arms that move in the opposite direction at a lower speed (15 rpm) than the propeller (100-125 rpm) eliminates this disadvantage.

The following considerations concerning agitation can be mentioned, namely:

Gas mixing is the simplest case, due to the high diffusion coefficients: gases mix spontaneously on contact, and the mixing rate can be increased by increasing the flow rate of the mixture, placing baffles in the flow path, flow diversions, etc. Gas mixing is seldom necessary in the fine organic synthesis industry, being rather characteristic of the large tonnage industry (NH_3 synthesis, CH_3OH, oxosynthesis, etc.).

Mixing in liquid media is the most common and is a more difficult case than the previous one due to the higher viscosity of liquid media and sometimes due to large differences in density between the components of the mixture (e.g. gas-liquid, liquid-solid). The devices used for mixing liquids can be ***static*** (without moving elements) or dynamic (with rotating elements, rarely translational). The former are characteristic of gas-liquid and liquid-liquid mixing and may be: ***packed columns*** (a), columns with baffles (b), gas bubblers (c) or ***static mixers*** (Fig. 4.25).

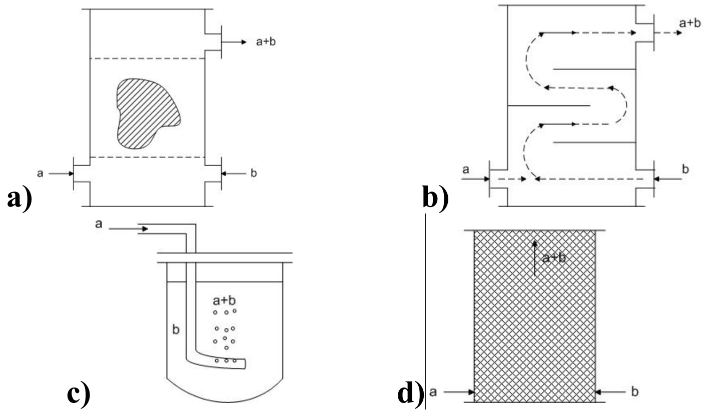


Fig. 4.25. Column types: a) column with filler; b) column with chicanes; (c) gas bubbler; (d) static mixing section

Of these devices, the most modern and efficient are static mixers. These are, in fact, specially shaped surcharges, regularly placed, creating a huge number of channels into which the fluid is divided. These channels intersect very often, without that chaotic turbulence (characteristic of random fluid flow) - e.g.: column with loose-fill.

4.2. Realization of heat exchange in reactors

In the chemical industry, the temperature at which processes take place is almost always an essential parameter. ***Heating*** is necessary to change the state of aggregation (melting, sublimation, evaporation), to increase the speed of certain physical (dissolution) or chemical processes, to bring certain properties (solubilities, viscosities) to suitable values or to carry out important unit operations (distillation, drying). The opposite of heating is ***cooling***. It is used to carry out condensation, desublimation, etc., or to temper exothermic physical or chemical processes.

The heating or cooling of materials is generally carried out using a heat (or cold) transfer medium, which in the case of heating takes the heat energy from a source, which may be chemical (fuel) or hydraulic (hydroelectric or electric power station), and transports it to the machine in which the heating is carried out. In the case of cooling, the cold carrier takes the heat energy from the material to be processed and transfers it to a cooling system (cooling tower, cold station, etc.).

The equipment in which the heat is exchanged is called a heat exchanger. They are characterised by their design and heat transfer surface. They may be stand-alone machines or may be parts of complex machines (mantles, coils, pipe bundles, spaces of different shapes, etc.).

Heating

The choice of heating method and thermal agent depends on the parameters of the technological process (temperature, heating rate, flow rates, pressure, nature of the chemical medium, etc.) and the economics of the chemical transfer process:

a) ***Heating with gases*** (usually flue gases) is uneconomical due to low partial transfer coefficients, which require high flow rates. It is also difficult to regulate a uniform and constant temperature, with the danger of local overheating.

They are mainly used for the production of steam (up to 100oC) and for catalytic processes in the heavy organic industry; and hot air in the drying processes of various solid products.

b) ***Steam heating*** has important advantages: high heat transfer coefficients, large amount of heat given up to condensation, uniform heating (condensation takes place at constant temperature) and easy regulation (by steam flow). Saturated or slightly superheated water vapour (steam) is used, or more rarely vapour of non-toxic and non-flammable liquids (e.g.: eutectic mixture: diphenyl-diphenyl-ether = diphenyl up to 380^{o}C without overpressure).

Indirect vapour heating is carried out by means of internal or external coils, heating mantles or in special multi-tubular machines (Fig. 4.26).

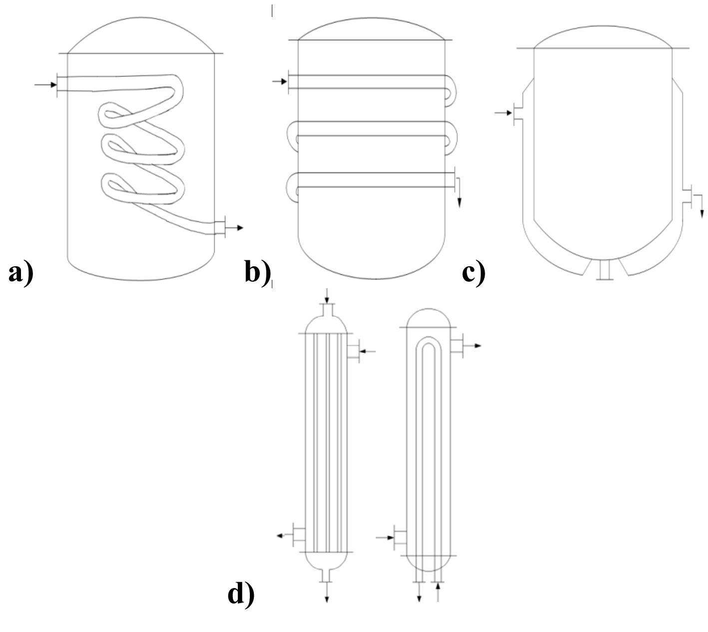


Fig.4.26. Heating appliances: a) indoor coil;
b) outdoor coil; c) mantle; d) pipe bundle

c) ***Heating with liquid carriers*** is relatively little used, offering no particular advantages:
water - up to 80°C (or above under pressure)
oils - max. 300°C (with decomposition)
diethyl - max. 400°C (under pressure)
molten salts (nitrites, nitrates)
molten metals (Na, K, Li)

d) ***Electric heating*** - takes place without a heat carrier. It is advantageous, allowing precise regulation of the heat transfer process, heating at higher temperatures without impurification of the reaction mass, but due to the high cost of electricity and sophisticated apparatus, it has limited applications.

It can be achieved using electrical resistors or by induction (by introducing a secondary current - usually the metal body of the reactor - through a primary coil placed on and insulated from the reactor).

In general, chemical reactors work in non-isothermal (start-up, shutdown and transient stages) and isothermal (steady-state operation) modes.

In technological processes, the aim is to keep the temperature at the required value throughout the reaction volume. In order to achieve this aim, thermal, heating or cooling agents are used which must meet the following conditions:

1. They must be thermodynamically advantageous. Thermal agents with a high specific gravity and specific heat, as well as low viscosity and high heat of vaporisation, are the most advantageous. It is desirable for thermal agents to have high temperatures and, at the same time, low pressures, which makes it easier to construct the apparatus.
2. They must be thermally stable and have no adverse influence on the materials of construction of the apparatus.
3. Be inexpensive and fairly widespread in national resources.

The following types of heat exchangers can be distinguished according to the heating and cooling method: heating with steam, gas or hot liquids, cooling with gas or liquid.

Of the various designs of reaction apparatus, the most common are blanket and serpentine heat exchangers.

The outer mantle occupies 80-90% of the height of the cylindrical part of the reactor, the entire bottom cover (without fittings) and even, in some cases, part of the top cover. The construction of the lower jacket can be done in several ways, as in the diagrams in the Fig. 4.27.

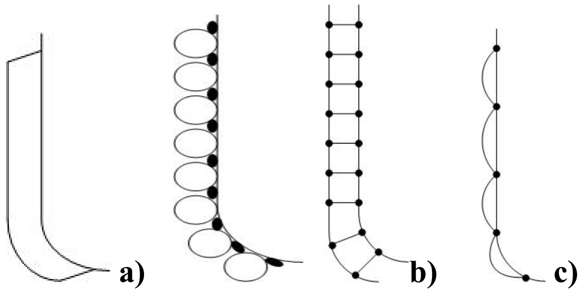


Fig. 4.27. Schemes for the construction of a reactor bottom shell
a-shell; b-welded serpentine tubes of various shapes;
c-welded serpentine half-pieces; d-various serpentine welded profiles

The use of the outer casing has the advantage of reducing the useful volume of the appliance, but has the disadvantage of more cumbersome cleaning and requires external insulation.

Inner coils or other heat transfer elements, such as pipe bundles or radiators, can only be used in a low viscosity reaction environment or when there is no possibility of adherent crusting. These heating elements can also be used as diffusers for propeller stirrers (Fig. 4.28 and 4.29.), but they have the disadvantage that they take up space in the reactor volume, are difficult to install and maintain, require clean thermal agents, and in the event of breakage may contaminate the reaction medium.

Heat exchange in chemical reactors can also be achieved by *external heat transfer*, where a component leaves the reactor, usually vapour, passes through an external heat exchanger and returns back to the reactor. This method of heat exchange has the following advantages:

- a constant temperature is maintained in the reactor
- does not take up any of the reactor's useful volume
- the condenser does not require cleaning, the vapours are clean
- depending on the steam flow rate, the amount of heat taken up can be easily adjusted

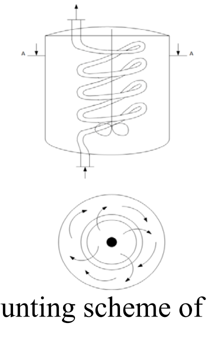


Fig. 4.28. Mounting scheme of an indoor coil

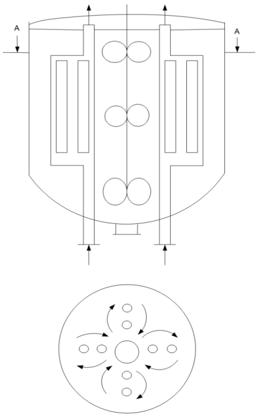


Fig. 4.29. Mounting scheme of an interior radiator

In some cases, recirculation of the entire reaction mass may also be used, when stirring is achieved at the same time.

The heat exchange models described above can also be combined with each other, always taking into account the advantages and disadvantages.

The introduction and discharge of thermal agents must be carried out in such a way as to obtain the simplest and most convenient connection of the apparatus with the pipes. The only exceptions are devices for the discharge of non-condensed gases and condensate from the vapour traps of the appliance. Condensate must always be discharged at the bottom of the vapour collector; and non-condensate gases must be discharged from the furthest area from the place where the heated vapour is introduced.

The direction of movement of the thermal bags should be chosen so that the direction of the forced flow of the liquid or gas coincides as far as possible with that of the free movement: heating from bottom to top, cooling from top to bottom. If the state of aggregation of the thermal medium does not change, the counter-current principle is preferred.

The space in which the heat transfer medium moves (in pipes or in the inter-tubular space) must be able to clean the deposits, and take into account the pressure and temperature of the heat transfer medium. Thus, at high pressures, small-diameter pipes are used so as not to stress the apparatus, using insulation to prevent heat loss. If the transfer agent is corrosive, it will flow through the pipes, so that the anti-corrosive materials needed to make the apparatus are placed inside, where they can be cleaned more easily, and the rest of the apparatus can be made of ordinary materials, or of those needed for the raw materials to be processed.

It is preferable to choose the construction solution that corresponds best from a technical and economic point of view.

Cooling

Like heating, cooling can be done with gaseous carriers (air - cheap, but requires high flow rates and does not allow cooling below ambient temperature) or liquids

Of the liquids, treated water (to avoid deposits) is the most common, with the major disadvantage of being dependent on the temperature of the water source (5°C in winter; 25°C in summer). Cooling water is recirculated through cooling towers (Fig. 4.30.).

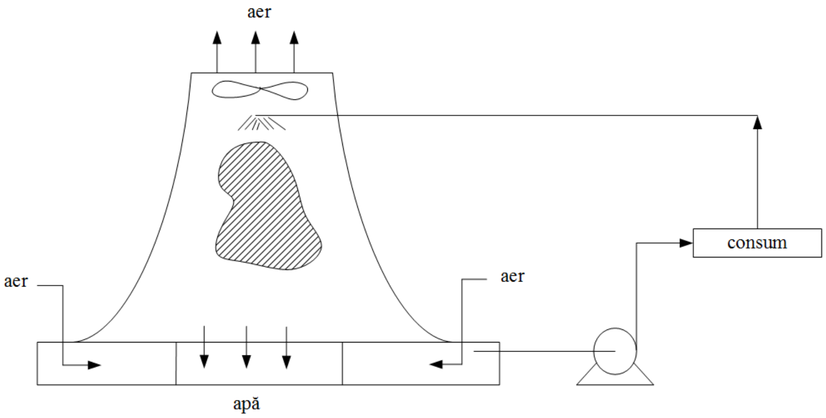


Fig. 4.30. Cooling tower

4.3. Reactor feed and discharge

The reactor feed must ensure the correct dosage of reactants, the optimum addition rate so as not to disturb the thermal equilibrium and the reaction rate can be controlled. At the same time, the raw materials must not be contaminated and must be handled with maximum safety. Losses of reactants or any other substances and materials through poor handling must be avoided.

The autoclave reactor lid is fitted with a series of connections (sockets) terminating in standardised flanges of various sizes. The supply of liquid materials is by piping, from day vessels, with or without level glass; or from measuring vessels, placed higher than the reactor, thus by free fall. These are fed from tanks by centrifugal pumps. In some cases, some of the reactants can be fed manually, from bottles, buckets or flasks. The liquids may sometimes be supplied by distribution devices (nozzles, injectors, etc.) which ensure rapid homogenisation of the reaction mass and the finest possible dispersion.

The feeding of solid materials is done through special fittings, with a larger diameter than those for liquids, connected to special installations. Thus, for larger quantities, it is done from hoppers, screw conveyors, pneumatic conveyors, etc.; and if smaller quantities are required, they are handled manually, by bag, barrel, box, etc. Measurement of quantities is done by dosing or direct weighing, or by difference.

The gas is supplied through distributor pipes at the bottom of the reactor, connected to fittings on the reactor cover. Measurement of the quantity of gas introduced is made by means of calibrated flow meters, in the case of high flow rates; or by calculation, from the indicated pressure and the known free volume of the reactor; or by differential weighing, in the case of liquefied gases from cylinders.

The exhaust of the reaction mass is usually carried out on the opposite side of the feed, i.e. on the lower side, through a larger diameter exhaust vent, which is fitted with a control lantern upstream. This discharge system makes it possible to observe the interface between two immiscible liquids and to separate the two layers. Due to the large diameter, it also allows for the emptying of suspensions.

Syphons can also be used to empty the phases separately or to empty the reactor when there is a slight overpressure.

On the top cover of the reactor are also mounted:

- temperature measuring connection - with immersion thermometer, mounted in a metal sheath, or thermocouple, etc., which is small in diameter
- pressure measuring connection - vacuum or overpressure gauges
- shielded connection with illuminated glass window - for observing the inside of the reactor with monitoring of stirring efficiency, foaming, reaction mass appearance
- unused fittings - shielded with materials resistant to the atmosphere inside - for reactor flexibility

4.4. Construction classification of reactors

Due to the wide variety of reactor designs, it is difficult to find scientific criteria for classification. Of all the design features, however, two can be determined, namely the mode of circulation in the reactor and the type of heat transfer surface.

The first characteristic makes it possible to classify reactors according to the known ideal types, thus linking the bases of reactor kinetic and constructive design. In each of the ideal types, the construction is influenced by the presence or absence of a heat transfer surface.

The main reactor types can be grouped according to the *design of the reactor body* as follows: reaction chamber reactors (with or without mechanical stirring); column reactors; heat exchanger reactors; furnace reactors.

1. *Reaction chamber reactors*

The reaction space of these types of reactors has approximately equal dimensions (length, width and height). Some types of reaction chamber reactors are shown in the Fig. 4.31.

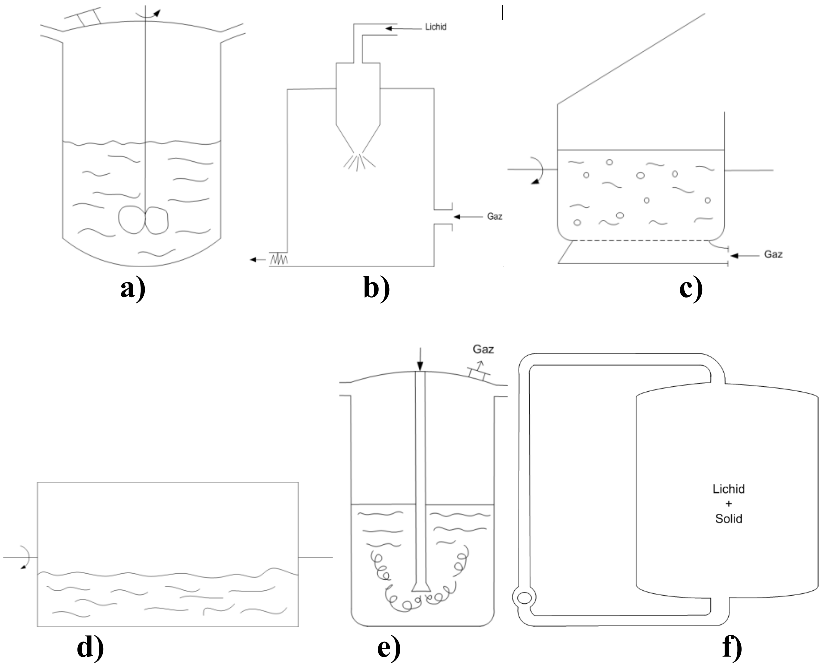


Fig. 4.31. Reaction chamber reactors
a-type autoclave; b-type reaction chamber; c-type converter;
d-type rotary drum; e-type bubbler; f-type recirculating autoclave

Autoclave type reactor (a)

This reactor is typical for homogeneous reactions in liquid phase or in heterogeneous systems (liquid-liquid, gas-liquid; liquid-solid; gas-liquid-solid) for organic synthesis processes. The autoclave reactor is in the form of a metal vessel and is covered with a lid to which are attached the charging, stirrer, sight glass, etc. It is one of the most widely used reactors and is easy to construct and operate. It can be built in a wide range of volumes, from a few litres up to 200m^3. It can be built from corrosion-resistant materials.

Reactions in autoclave reactors can be continuous, batch or semi-continuous; isothermal, adiabatic or non-adiabatic. It is designed for a wide temperature range (30-350ºC) and moderate pressures, and can be located alone or in cascade (Fig. 4.32).

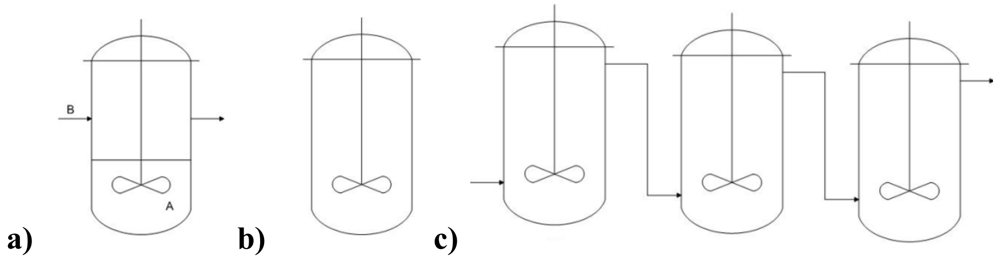


Fig. 4.32. Continuous reactor (a); Batch reactor (b); Reactor cascade (c)

Reaction chamber reactor (b)

This reactor is in the form of a parallelepipedic, cubic or cylindrical chamber, approximately equal in width to the diameter, constructed of a material resistant to the reaction medium.

Converter reactor (c)

A reactor in the form of a cylinder with a diameter greater than its height, used for processes occurring in a heterogeneous gas-liquid system.

Horizontal cylinder reactor (d)

This type of reactor is used in processes that do not require high stirring and the reaction mass may be pasty, and is used mainly in heterogeneous liquid-solid processes.

Bubbling reactors (e)

These reactors take the form of an autoclave in which the bubbler is mounted. Bubbling reactors with a low liquid layer height are used for high-speed reactions in the gas-liquid system.

Autoclave reactor with recirculating pump (f)

This type of reactor is used in processes where mechanical stirring is not possible. It usually works at high pressure and temperature, for heterogeneous liquid-solid systems.

2. *Column reactors*

Reactors in this category take the form of cylindrical vessels usually placed upright. Their construction is simple and cheap. Some types of reactors are shown in the figure 4.33.

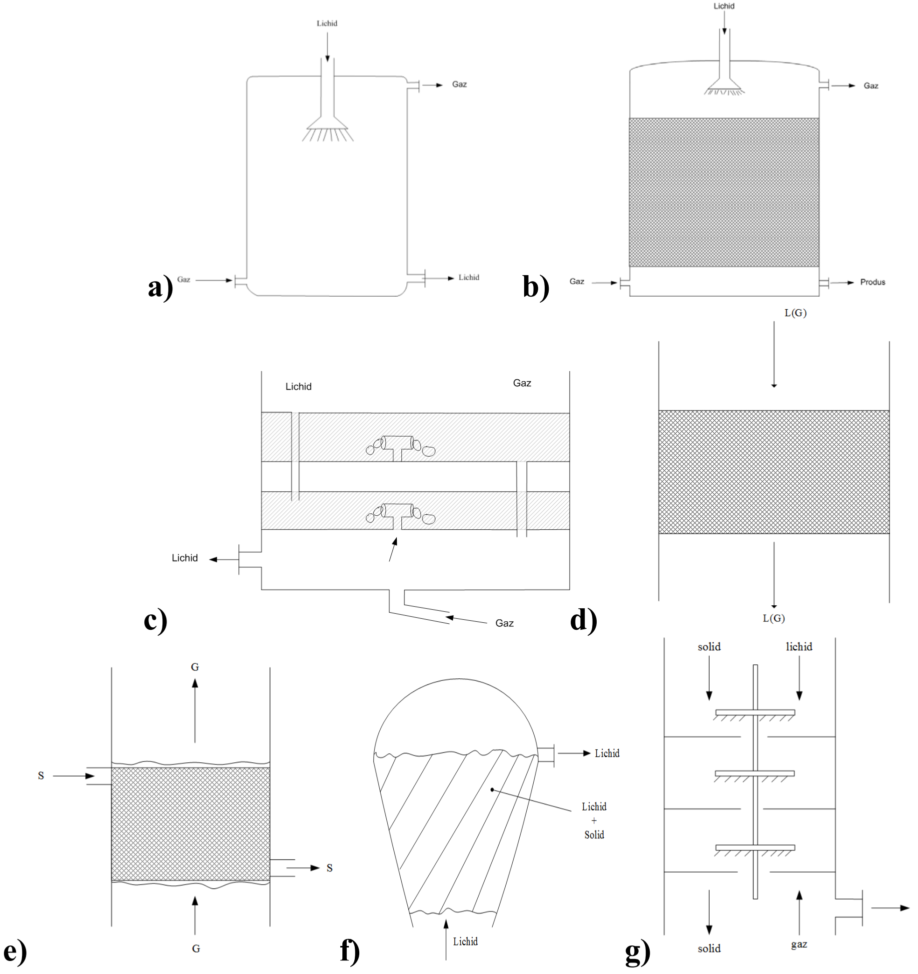


Fig. 4.33. Column reactors
a-type reaction tower; b-type packed column; c-type packed column;
d-fixed layer; e, f-fluidized layer; g-stage

Reaction tower reactor (a)

This is a vertical cylindrical vessel used in homogeneous liquid-phase or heterogeneous gas-liquid reactions. It may have fillers, sieves, trays, cooling coils, etc., as required.

Column reactor with packing (b)

This is used almost exclusively in heterogeneous gas-liquid system reactions and is often used in industry because of its simplicity of construction and safety in operation. The reactor is constructed in the form of a column with gratings to support the packing.

Column reactor with trays (c)

This reactor is used for the same purposes as the packed reactor. The advantage is that cooling can be carried out on the thimble, and in slow reactions or where the dilution of the reaction gas is too high, recirculation of the liquid is not required.

Fixed layer reactor (d)

Characteristic of reactions occurring in heterogeneous gas-solid and liquid-solid systems, and used in gas cleaning processes or water softening with ion exchangers.

Fluidised state reactor (e,f)

This type of reactor is a cylinder based on a support sieve, which also acts as a distributor, on which the material layer is placed and is used in heterogeneous gas-solid reactions. It can also have a conical shape (f) when used for heterogeneous liquid-solid reactions.

Staged reactor (g)

This reactor has several layers and is used in heterogeneous gas-liquid-solid reactions.

3. ***Furnace-type reactors (reaction stove)***

They are similar to the reactors described above, but can work at temperatures above 600°C. They can be built in two modes, namely: reactors with one of the above-described forms placed in the furnace or reaction furnaces of their own.

Some of these types of reactors are shown in the figure 4.34.

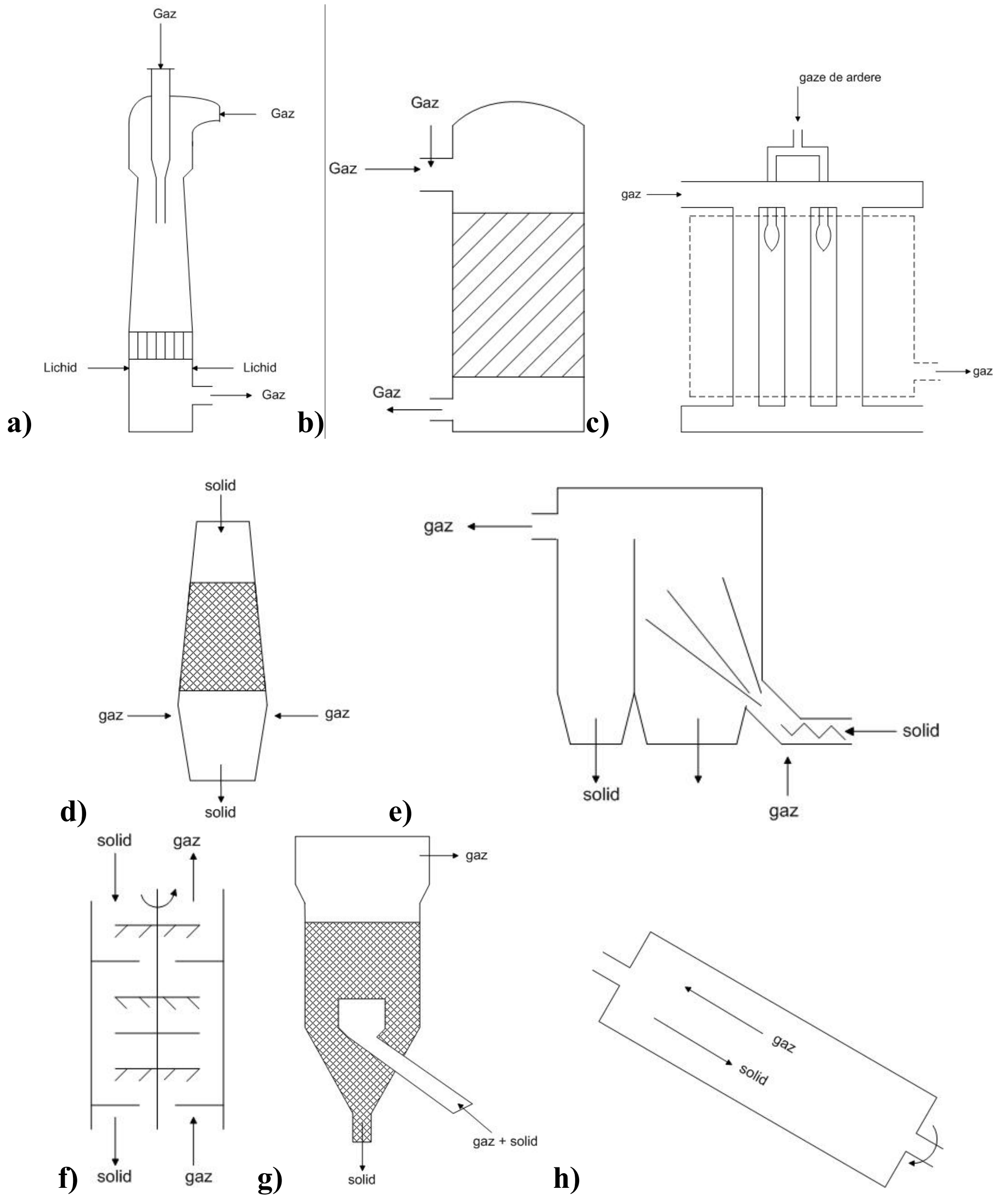


Fig. 4.34. Furnace reactors
a-gas premixed; b-cylindrical furnace type; c-heat exchanger type; d-type furnace; e-type chamber; f-type hearth; g-type fluidised bed; h-type rotary kiln

Gas Premix Reactor (a)

This reactor is constructed of refractory ceramic material or heat-resistant steels. It consists of a mixer-diffuser and a combustion chamber. The volume of the combustion (reaction) chamber depends on the gas burning rate, temperature, etc. In most reactors, the combustion chambers are made of refractory materials.

Cylindrical furnace reactor (b)

This furnace is constructed in the form of a tower lined with refractory material, with the reaction space free or filled with filler material or catalyst. Sometimes it is coupled with a reactor that produces combustion gases.

Heat exchanger reactor (c)

This type of reactor is constructed as a large chamber into which the reaction tubes or beam through which the gas flows are inserted. Inside the reaction tubes is sometimes the catalyst.

Blast furnace reactor (d)

It is constructed in the form of a truncated cone with a large downward base. The outer shell is made of steel lined with refractory brick.

Chamber reactor (e)

This reactor is in the form of a large chamber lined with refractory material on the inside, where reactions between solid particles, atomised by reaction gas, take place.

Hearth reactor (f)

It takes the form of vertical cylindrical chambers with several horizontal stacked glass panes, on which the material is moved (vertically) by means of arms.

Fluidised bed reactor (g)

This reactor consists of a vertically arranged cylindrical metal chamber lined with refractory material, in which a fluidised layer is maintained by introducing gases at the bottom.

Rotary furnace reactor (h)

This reactor is constructed as a horizontal cylindrical drum lined with refractory material. The reactor rotates by moving the solid material from one end to the other. The gases circulate in countercurrent.

5. APPARATUS USED FOR TRANSPORTING FLUIDS

Fluid transport is most often carried out by pumps. Some types of pumps are shown in the Fig. 5.1.

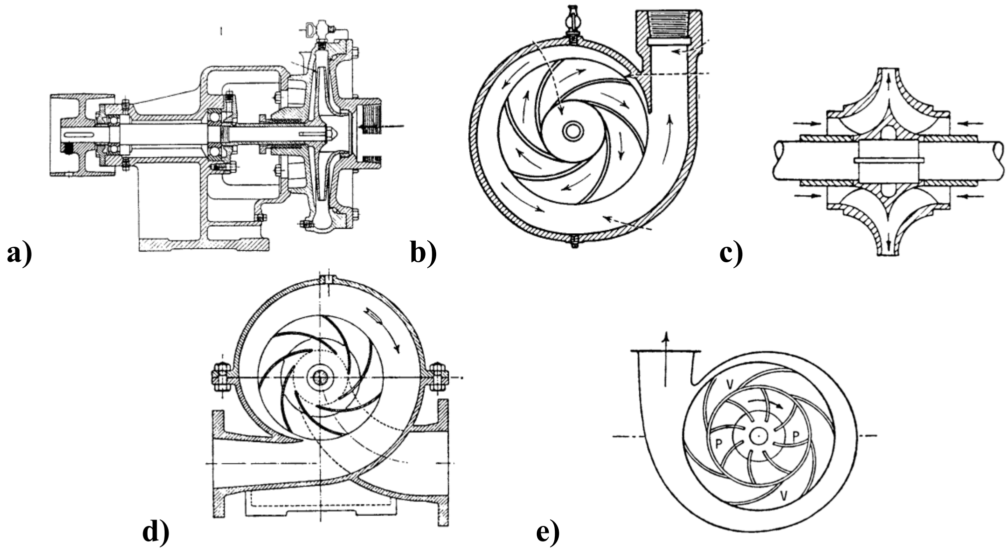


Fig. 5.1. Pumps: a-Piston pump; b-Pump impeller; c-Dual suction and axial discharge; d-Horizontal suction and discharge; e-Diffusion pump

Impellers inside centrifugal pumps can have different shapes depending on axial or radial flow (Fig. 5.2.).

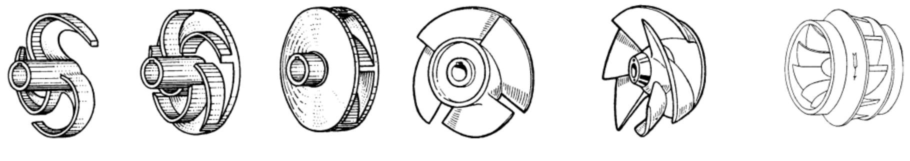


Fig. 5.2. Types of impellers inside centrifugal pumps

6. OPERATIONS AND MACHINERY FOR SEPARATION OF USEFUL PRODUCT

Sedimentation is the process of separating suspensions (heterogeneous liquid-solid systems) into component phases by the differential action of gravity on the phases in different densities.

Filtration is the operation of separating a suspension into its component phases by using filter surfaces (or certain filter layers) permeable only to the continuous (liquid) phase.

The sedimentation velocity can be calculated with the relation below:

$$w_B = \sqrt{\frac{4}{3} \cdot \frac{g}{\zeta} \cdot d_p \cdot \frac{\rho_1 - \rho_2}{\rho_2}} \quad (1)$$

where: ρ_1 – density of suspended particles, kg/m^3;
ρ_2 – liquid density, kg/m^3;
d_p – particle diameter, m;
g – gravitational acceleration, m/s^2;
ξ - drag coefficient ($\xi<1$; increases with increasing of Re).

The filtration speed can be calculated with the following relation:

$$w_f = \frac{sp}{r \cdot c \cdot q + R_s} \quad (2)$$

where: sp – pressure drop between the two sides of the filter (N/m^2);
r – unit volume resistance of the precipitate (kg/m^3.s);
c – volume of precipitate corresponding to 1 m^3 filtered, m^3/m^3;
q = V/A = volume of filtrate per unit area of filtrate (m^3/m^2);
Rs – resistance of the filter layer (kg/m^2.s).

Comparing relations (1) and (2) it can be seen that in sedimentation the process variables do not allow to increase too much the speed (ξ being the only operative factor), while in filtration it is possible to intervene both on Rs (choosing a suitable filtering material) and on sp (vacuum or pressure filtration).

Filtration is a non-stationary process, with the rate of filtration decreasing over time. For this reason filtering large volumes of suspensions is disadvantageous, preferring sedimentation (e.g. in water treatment). On the other hand, filtration is a much faster separation process than sedimentation and is preferred in the fine synthesis industry.

Filtration efficiency and speed are influenced by a number of factors:

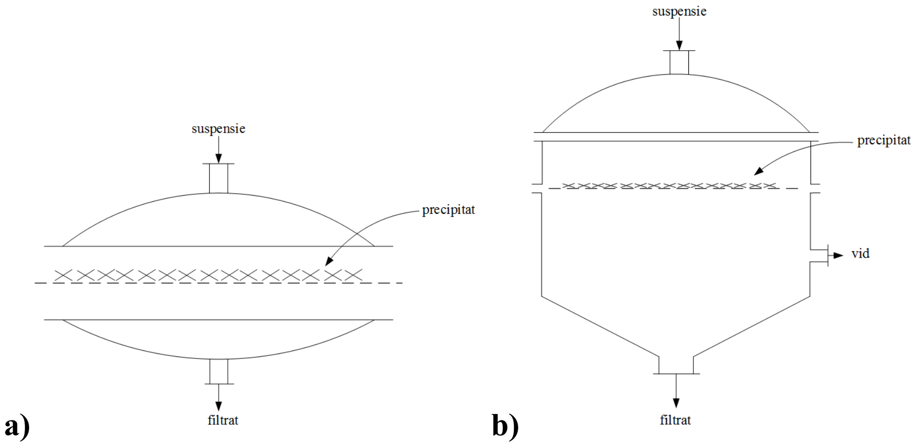
a) the nature of the filter suspension - filtration proceeds more easily when the solid particle sizes are larger and closer to spherical;

b) the viscosity of the filtrate - it should be as low as possible (possibly heating the suspension);

c) characteristics of the filter material - this is chosen according to the nature of the suspension to be filtered. The following are commonly used: textile fabrics (cotton, wool, synthetic silk); perforated sheets, sieves, metal mesh; porous plates; granular layers: sand, activated carbon, ceramic; layers of fibrous materials: asbestos, glass wool.

d) thickness of the precipitated layer at the end of the operation - depends on the concentration of the solid in the suspension, the amount of suspension and the filtering surface.

The filtration tools used in fine organic synthesis are usually lens filters (used at low slurry concentrations) and Nutsche filters, usually used under vacuum (0.75 at) or more rarely under pressure (4 at) (Fig. 6.1.).



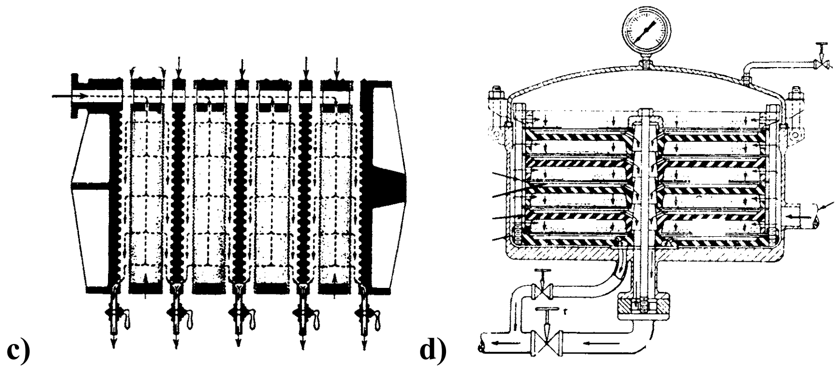


Fig. 6.1. Filter types: a-lens filter; b-Nutsche filter; c-plate and frame filter; d-horizontal plate filter

These types of filters are discontinuous in operation, with filter surfaces of 1 - 6 m^2, suitable for the amount of slurry resulting from one barge. The filter materials used are usually textile fabrics (cotton for alkaline and neutral media, wool in acidic media).

For high continuous filtration capacities, the rotating cell filter is used, which is less characteristic of organic synthesis.

By combining sedimentation with filtration and their intensification, the centrifugation operation is the result. The schematic diagram of a filter centrifuge is shown in Fig. 6.2.

The slurry is introduced at the top and by rotating at very high rotational speeds the filtrate passes through the filter layer and is discharged at the bottom, while the precipitate remains on the filter cloth from which it is recovered.

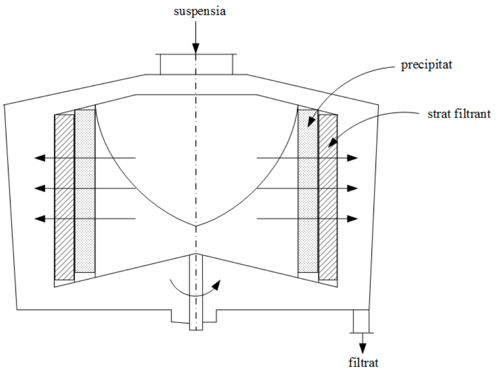


Fig. 6.2. Principle scheme of a filter centrifuge

Filter centrifuges are highly efficient devices, able to create fields 30 - 1000000 times stronger than the gravitational field.

Other devices are prezented in Figure 6.3.

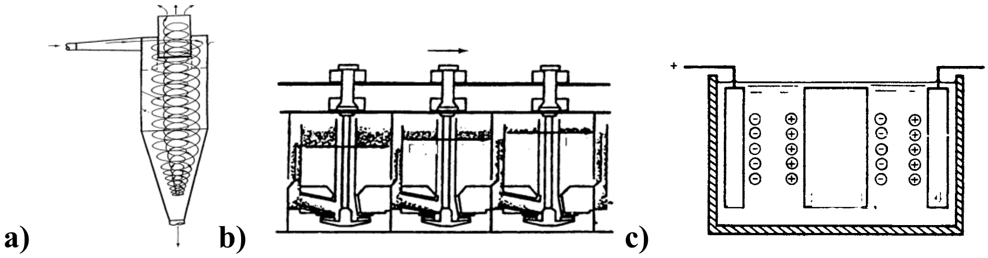


Fig. 6.3. Gas-solid separation apparatus: a-cyclones; b-flotation; c-electrolytic cells

They are used to separate solids from mixtures, most common being: cyclones, flotation separators or electrolytic cells.

7. EXTRACTION

Extraction is the process of total or partial separation of a mixture of substances having different solubilities in the same solvent.

When the mixture to be extracted is solid, the operation is called *solid-liquid* extraction (e.g. extraction of active ingredients from plant materials in pharmaceuticals and cosmetics). When the mixture to be separated is a solution of two or more liquids, the operation is called *liquid-liquid* extraction or selective solvent refining.

For the separation by extraction of a component from a homogeneous liquid mixture (either a liquid miscible with the other components, or a dissolved solid), this mixture is placed in intense contact with a selective solvent, insoluble or hardly soluble in the initial mixture, thus creating a system of 2 immiscible liquid phases. This system tends towards *equilibrium*, with the extract component migrating from the initial mixture to the selective solvent. The distribution of the extract component between the two phases is according to its *solubility ratio* in the two phases and is called the *distribution constant.*

The extraction products are called *extract* (the component dissolved in the selective solvent) and *refined* (the remainder of the original mixture left after extraction). These two phases are always mechanically separable.

The extraction takes place in *3 stages*:

(a) bringing the initial mixture into contact with the solvent as intensively as possible by vigorous mixing;

(b) separation of the newly formed phases (extract and raffinate) by sedimentation and/or settling;

(c) recovery of the solvent from the raffinate and extract.

The principle scheme of the extraction is given in Fig. 7.1.

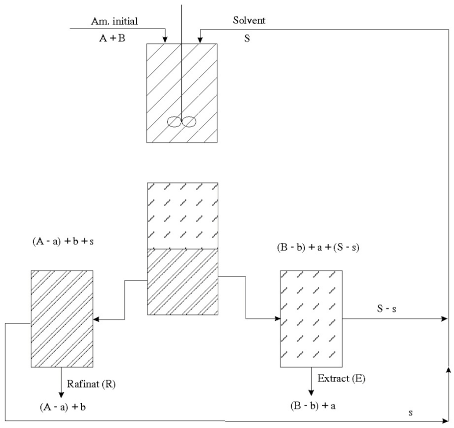


Fig. 7.1. Principle scheme of simple single contact extraction

Industrial extraction can be achieved by three processes:

a) simple single contact extraction (Fig. 7.1.);

b) simple extraction with multiple contact (Fig. 7.2.)

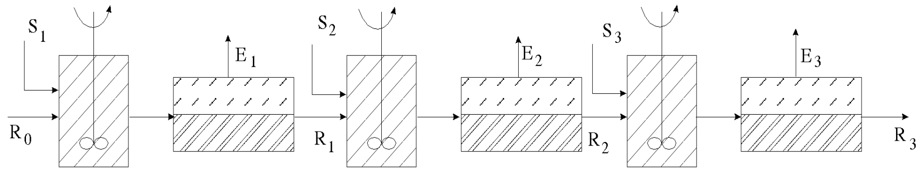


Fig. 7.2. Simple extraction with multiple contact

It can be seen that the circulation of the components is in equicurrent.

c) countercurrent multiple contact extraction (figure 7.3.)

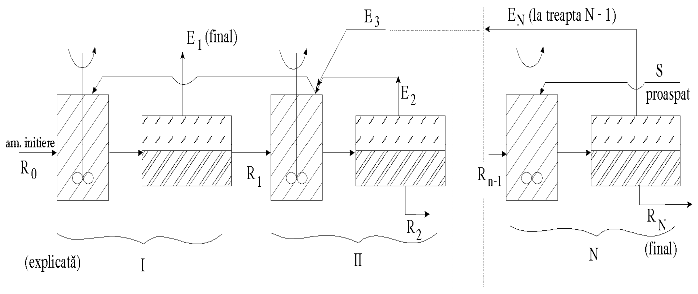


Fig. 7.3. Countercurrent multiple contact extraction

The initial mixture is introduced into the first mixing column together with the extract coming from the second phase. From the first step the final extract will result. In the last step the raffinate from the penultimate step and the fresh solvent are introduced. The extract from this step goes to the penultimate step and the raffinate is the final one.

The most efficient method of extraction is the multiple in-stream method, which is carried out in vertical columns, using shears, cutters, fillers, rotating discs, injectors, spray nozzles, etc. as contact devices between the two stages (Fig. 7.4. and Fig. 7.5.). In these columns the heavier phase runs from top to bottom and the lighter phase from bottom to top.

Fig. 7.4. Types of extraction columns: a-with chicanes;
b-with rotating discs and perforated cutters

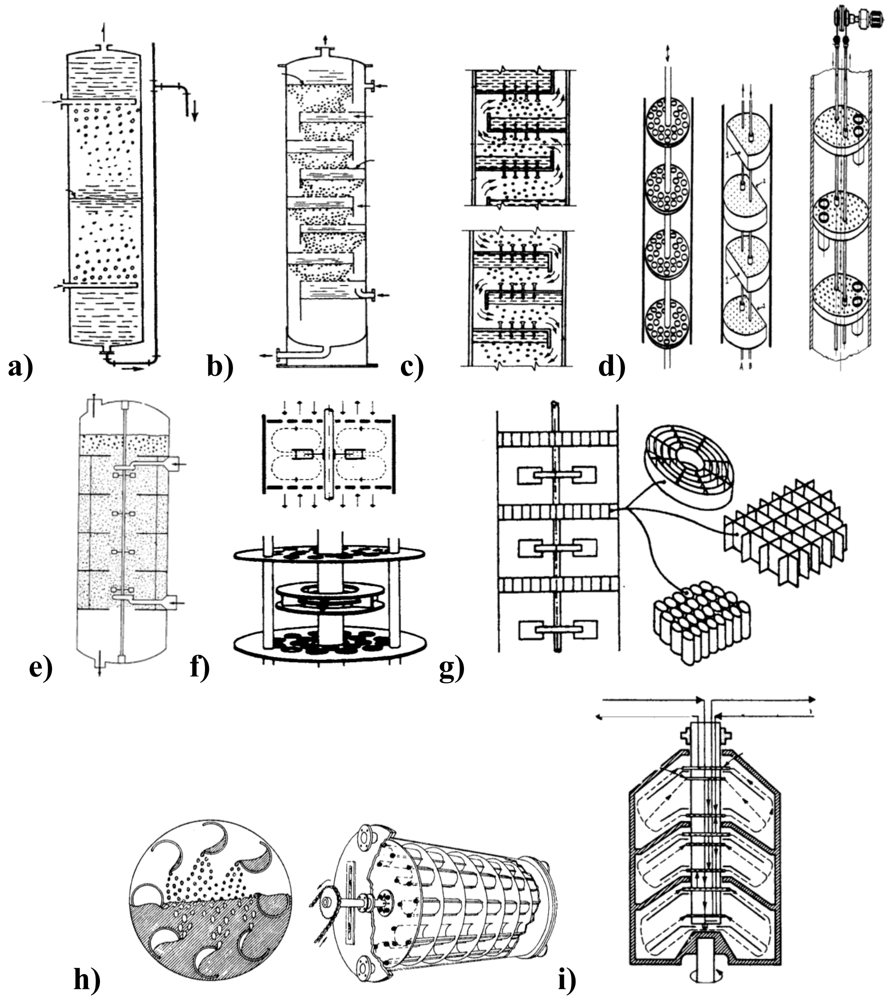


Fig. 7.5. Extraction towers
a-scattering tower with both phases dispersed; b-scattering tower with dispersed light phase; c-section of a tower with dispersed light phase (left) and dispersed heavy phase (right); d-types of cutters; e-extractor with turbine agitator; f-extractor with turbine agitator and perforated distribution plates; g-coalescence extractor; h-horizontal rotary extractor; i-centrifugal extractor

8. EVAPORATION AND CONCENTRATION

Evaporation and concentration are operations used to concentrate solutions formed from a non-volatile solid or liquid substance (the solute) dissolved in a volatile liquid substance (the solvent).

The heat required for evaporation is provided by a carrier agent (most commonly steam). This causes the solution to boil, removing the solvent in the form of vapours (called *secondary* vapours to distinguish them from the *primary* vapours of the thermal agent).

Solids decrease the vapour pressure of the solvent in which they are dissolved, as a result, solutions of solids boil at higher temperatures than pure solvent at the same pressure (Table 8.1).

Table 8.1. Aqueous NaCl solutions boiling at atmospheric pressure

	101	102	103	104	105	107
NaCl	6,19	11,03	14,67	17,69	20,32	25,09

To avoid thermal degradation of the dissolved product, evaporation is done under vacuum, when the boiling point of the solution is lower and the evaporation rate is higher. For example the boiling temperature of water at different pressures (Table 8.2).

Table 8.2. Boiling temperature of water at different pressures

Pressure [atm.]	0,5	0,7	0,9	1,0	1,2	1,4	2,0
t_f[°C]	80,9	89,3	96,2	99,1	104,2	108,7	119,6

The apparatus in which this operation takes place are called evaporators (Fig. 8.1.) and are usually of vertical construction, with a built-in heat exchanger at the bottom and a droplet separator at the top, which the secondary vapours entrain.

Mixing of the solution for thermal homogenisation is done by free convection or forced circulation with external pumps. In the central part of this type of evaporator there is a larger diameter tube, which circulates the solution in the evaporator. In the thinner boiling tubes, heating and vapour formation reduces the average density of the liquid, so the liquid circulates upwards through the tubes and returns through the central tube, where heating is weaker. Heating steam circulates through the pipes.

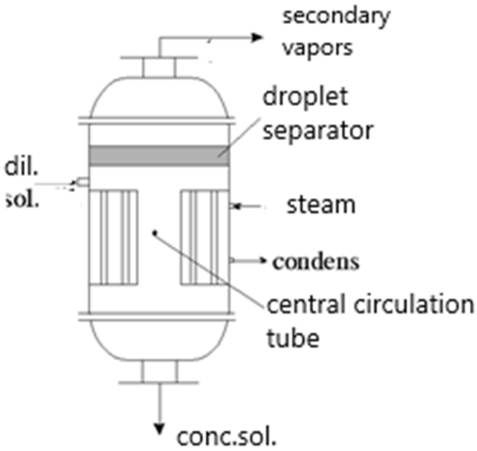


Fig. 8.1. Evaporator

These vaporizers can also be used for concentrating down to crystals if one or two chambers are added for crystal deposition and evacuation. The disadvantage is the weight of cleaning the crust deposited inside the tubes, the long time the liquid remains in the evaporator, etc. There are of course other constructions of such apparatus: with horizontal tubes, pellicular evaporators, etc. Some of these types of evaporators are shown in Fig. 8.2.

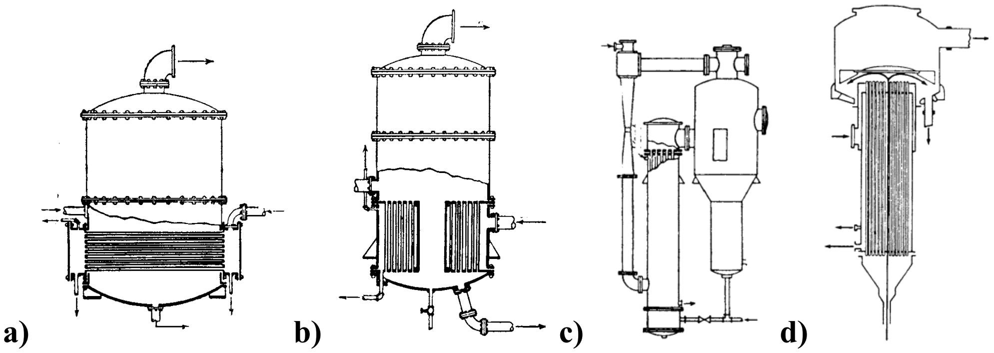


Fig.8.2. Types of evaporators
a-with horizontal heating tube; b-classic with heating chamber; c-with high vertical tube; d-film evaporator

9. DISTILLATION AND RECTIFICATION

Distillation is the operation of separating a liquid mixture by partial vaporisation of the liquid and separate recovery of both the vapour and the residue.

Separation by distillation is based on the fact that at the same temperature, the components of the mixture have different volatilities (vapour pressures). The vapour resulting from boiling the mixture will be richer in more volatile (lighter) components and the residue will be richer in less volatile (heavier) components. Distillation can be done batchwise or continuously.

Single or differential distillation is a batch operation, which is carried out by boiling a quantity of the mixture initially and removing the vapours from the kettle as they form. The resulting vapours are condensed in a condenser. The condensate is the distillate. At first the vapour is richer in the light component and the liquid in the heavy component. As the operation progresses, the vapour becomes richer and richer in the heavy component, making separation less efficient. The principle scheme of simple distillation is shown in the Fig. 9.1.

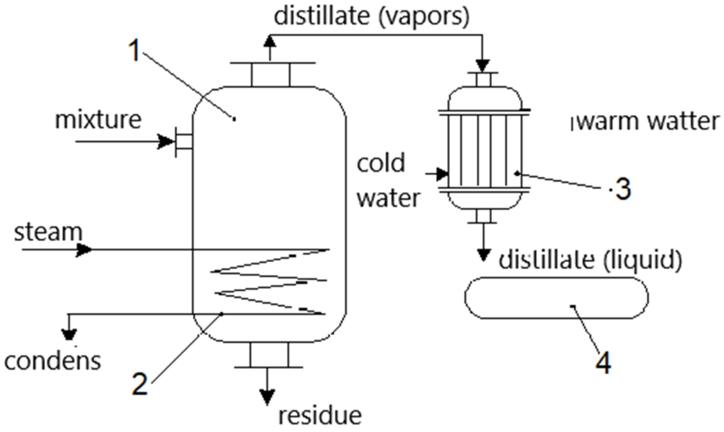


Fig. 9.1. Principle scheme of simple distillation

Simple distillation also applies to the separation (removal) of a volatile product from the non-volatile product in the mixture (devolatilisation, stirring).

A variant of simple distillation is ***fractional distillation***, in which portions of the distillate are collected separately, the first portions - the distillation heads - are richer in more volatile components than the last portions - the distillation tails.

If the vapours resulting from the boiling of the mixture are not discharged as they are formed, as in differential distillation, but are kept in contact with the liquid from which they came, the liquid-vapour system is always in equilibrium. This operation, which is applied more as a continuous, steady-state operation, for example, in the distillation of crude oil, is called ***equilibrium distillation*** or ***integral distillation***. The crude oil is passed through the tubes of a tube furnace and heated to a suitable temperature so that the product has the desired proportion of vapour when it leaves the furnace tubes. The vapour is separated from the liquid at the outlet of the furnace.

Another way of achieving distillation is by ***entrainment with water vapour***. This method is used when the mixture is practically immiscible with water. Since in the case of totally immiscible systems the boiling temperature is lower than the boiling temperatures of the components, the process is applicable to the separation of organic mixtures with high boiling and thermolabile temperatures, which cannot be easily separated by ordinary distillation (in the purification of fatty acids, in the recovery of certain solvents - trepentine, aniline, etc.) by entrainment with water vapour.

The operation is carried out by bubbling water vapour into a kettle, the resulting vapour of constant composition is condensed in a condenser and the liquid heterogeneous mixture resulting from condensation is separated on the basis of different densities in a liquid separator.

The schematic diagram of a vapour drive is shown in Fig. 9.2.

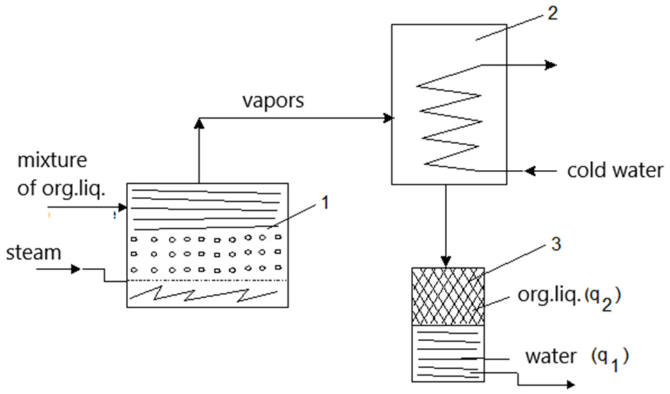


Fig. 9.2. Principle scheme of a steam drive
1-drive vessel; 2-condenser; 3-separator ($\rho_1 > \rho_2$)

Rectification is the process of separating a liquid mixture by successive partial vaporisations and condensations as a result of direct contact between the liquid phase and vapour with countercurrent circulation in column-type apparatus. Part of the condensed vapour that has left the column is reintroduced at the top of the column and mixed with the vapour at the top of the column. The reintroduced condensate is called ***reflux***. The vapour flowing from the bottom to the top causes the light component to volatilise from the reflux, and as it moves up the column it becomes enriched in this component, while the liquid flowing down will become enriched in the heavy component.

The separation efficiency is far superior to that achieved by simple distillation. The principle scheme of a rectification is shown in the Fig. 9.3.

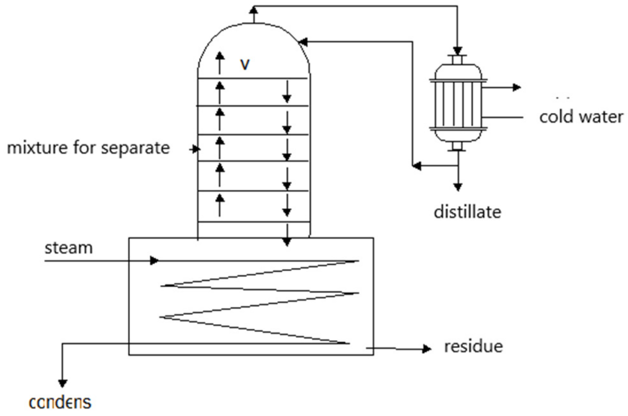


Fig. 9.3. Principle scheme of a rectification

The machines in which grinding is carried out are columns of several types: with perforated plate or screen cutters; with bell cutters; with filling (on the whole column or arranged on the cutters); of special construction (Fig. 9.4).

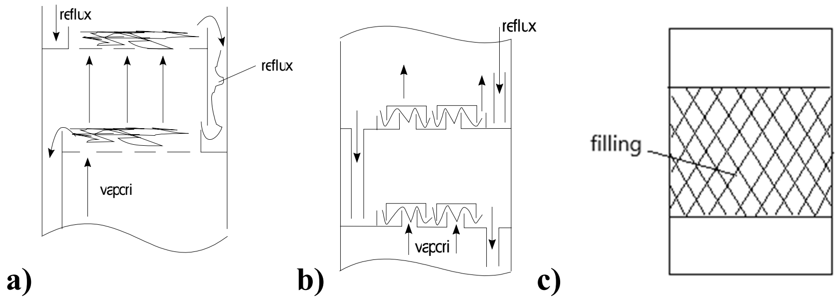


Fig. 9.4. Types of cutters for grinding columns
a-with screen; b-with bell cutters; c-with filler

In these columns the vapour has an ascending path, bubbling through the liquid phase which has a descending path.

10. PRODUCT PURIFICATION OPERATIONS

The separate useful product usually does not meet the purity qualities required for a fine synthetic product (e.g. drug, food additive, odorant, etc.) and requires additional purification operations.

If the useful product is in liquid form, distillation and rectification are the operations that can ensure purity, however advanced. If the useful product is solid, crystalline, its purification involves recrystallisation from suitable solvents, followed by drying. In some rare cases, purification of solids can be achieved by sublimation.

10.1. Drying

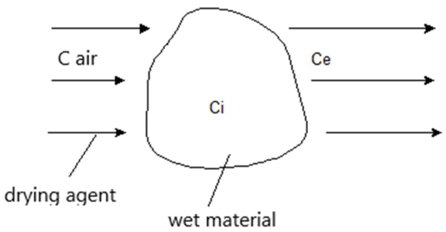
Drying is the process of removing moisture (water or other liquids) from solid, liquid or gaseous materials by thermal vapour.

This process is carried out after purification by recrystallisation of the solids, with the aim of: increasing the stability and purity of the product (generally degradable under the action of moisture), recovery of the recrystallisation solvent, economy of transport, etc.

The drying of some thermodegradable materials is carried out by lowering the drying temperature and the combined use of vacuum.

Drying is a complex process, involving distinct phenomena that occur simultaneously: evaporation of moisture from the surface of the material; diffusion and capillary movement of moisture from the inner layers of the material to the surface (Fig. 10.1).

Both phenomena occur as a result of differences in moisture concentration at the surface of the material and in the surrounding environment, i.e. the surface and the interior of the material.



Ci > Ce > Cair

Fig. 10.1. Drying a wet material with a drying agent

Drying can take place spontaneously, in the air, at low speed. This is why it is preferable to use a drying agent (usually air) which is forced over the wet material, from which it takes up moisture.

The heat required to evaporate the moisture can be given either to the drying agent or to the wet material 10.2.

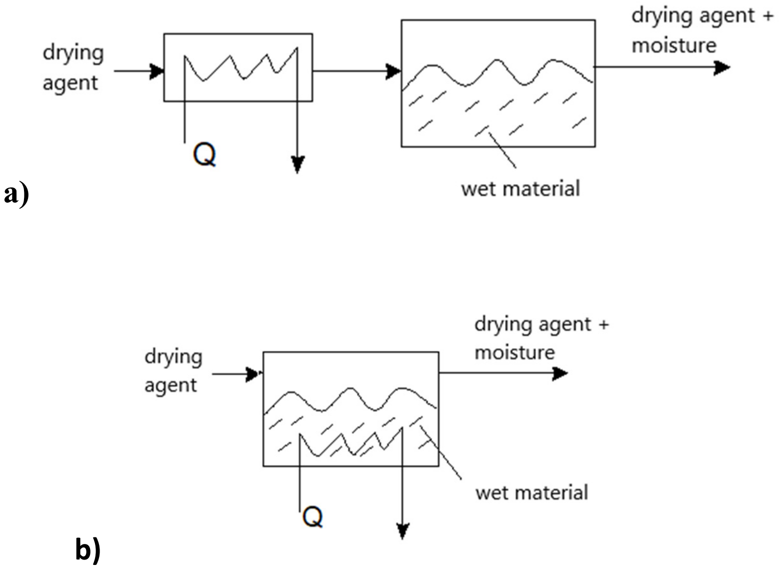


Fig. 10.2. How heat is lost in the drying process:
(a) the drying agent; (b) the wetted material

The construction and operation of dryers must meet the requirements of the drying process: achieving a certain drying speed; ensuring the desired degree of drying (residual moisture) under conditions of uniform drying and thermal maintenance of the material; ensuring the best possible contact between the material and the drying agent.

Due to the small quantity of products subject to drying in the fine organic synthesis industry, this operation is usually carried out discontinuously.

The most commonly used machine is the cabinet dryer (or drying chamber) (Fig. 10.3.).

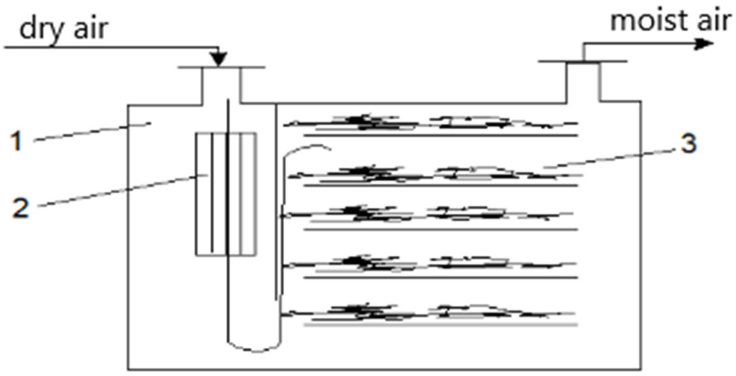


Fig.10.3. The cupboard dryer
1-drying chamber; 2-heater; 3-drawers for wet material

The dry air is heated in the radiator and then passes over the wet material taking up the moisture, after which it is exhausted outside.

A number of types of dryers are described in the literature, with and without agitation, vacuum, fluidised bed, etc.

A fast, efficient and thermally gentle drying method is atomisation (Fig 10.4.), used for the rapid drying of liquids - solutions, suspensions or perhaps thin films. This increases the contact area of the drying agent by finely atomising the liquid through nozzles or discs at high speeds against a stream of hot air, thus protecting the product from prolonged contact with the heating source.

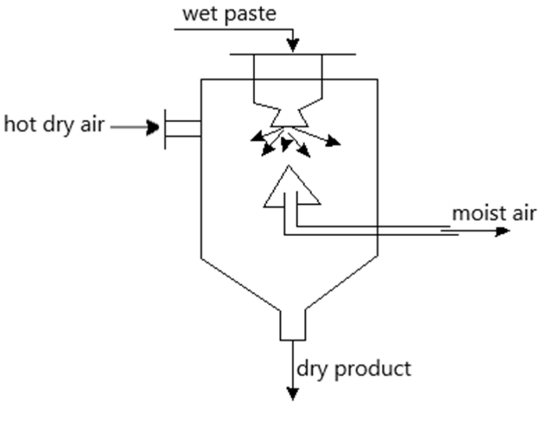


Fig. 10.4. Principle scheme of an atomizer

10.2. Recristalization

Crystallisation is the process of obtaining a solid phase from its supersaturated solutions (or melts). Crystallisation is the opposite of dissolution.

Recrystallisation of a solid product for the purpose of purification involves dissolving the crude solid product in a suitable solvent, called the recrystallisation solvent, bringing the solution to saturation and crystallising the dissolved solid again.

Separation by crystallisation is based on the property of solids to dissolve to a certain extent in different liquid solvents. The degree of solubility is determined by the chemical nature of the solvent and the solvent and the temperature. Generally solubility increases with temperature.

The solution which at a given temperature contains the maximum possible amount of dissolved substance is called a ***saturated solution***. Decreasing the temperature of a saturated solution causes some of the dissolved substance to separate; the amount of dissolved substance remaining in the solution will correspond to its saturated state at the temperature to which it has been cooled. This is determined from the solubility diagram shown in Fig. 10.5.

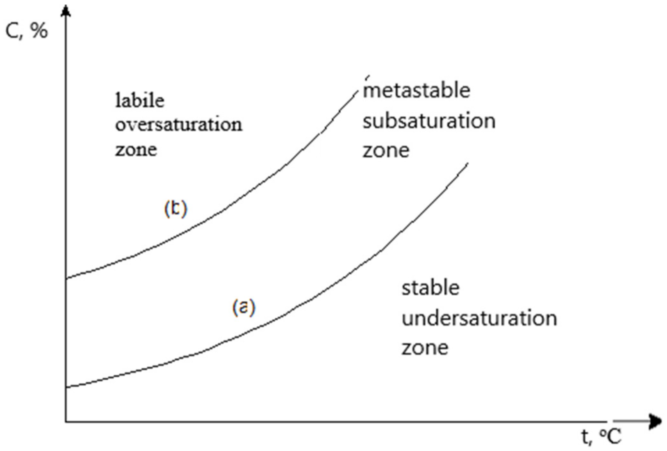


Fig.10.5. Diagrama de solubilitate:
a) curba de solubilitate; b) curba de suprasolubilitate

In the metastable zone the solution does not crystallize spontaneously, but crystallizes upon introduction of crystallization centers, upon mechanical shocks.

In the labile zone the solution spontaneously crystallises, usually at a very high rate, resulting in impure crystals.

The crystallisation process is based on the relationship between the solubility of a substance and its temperature: lowering the temperature by cooling or removing some of the solvent from the solution - by evaporation or boiling - causes the solution to become supersaturated. Some of the solvent passes into the solid phase as crystals. The solution remaining after separation of the crystals by filtration or centrifugation is saturated and is called a mother solution.

The crystallisation process involves two distinct states: the formation of crystals (due to the solubility threshold being exceeded) and the growth of the crystals formed.

The formation of crystals involves the appearance in solution of specific (solvent crystals or other isomorphic crystals) or non-specific (impurities, glass splinters, dust, etc.) crystallisation centres. The number of crystallisation centres influences the shape and size of the crystals: a low number of centres favours the formation of large crystals, which grow slowly, filter easily and are purer. A large number of centres leads to the formation of small, poorly filterable and poorly developed crystals (in the form of needles or plates).

For convenient industrial crystallisation, the solution is seeded with pure substance crystals (which act as crystallisation centres of controlled concentration), and for convenient crystal growth, convection currents are intensified by forced stirring (which favours the supply of dissolved substance to the growing crystal faces).

On an industrial scale, several crystallisation methods can be applied (depending on how the supersaturation state is reached):

a) Crystallisation by cooling the solution - this is used to obtain substances whose solubility varies greatly with temperature (or from melts);

(b) crystallisation by partial removal of the solvent, which may be achieved by: vaporisation (conversion to vapour at temperatures and vapour pressures below saturation temperature); - evaporation (boiling at temperatures corresponding to the total pressure of the system), which may be achieved at atmospheric pressure or under vacuum;

(c) Crystallisation by cooling and partial removal of the solvent (lyophilisation).

Crystallisation processes can also be classified into:

a) ***simple recrystallization***: in a crystallizer, bring the mixture of substances (A + B) - to which B = impurity, add the solvent (S), bring the solution to supersaturation, separate the crystals (C) and the mother solution (M).

The scheme of the simple recrystallisation is shown in Figure 10.6.

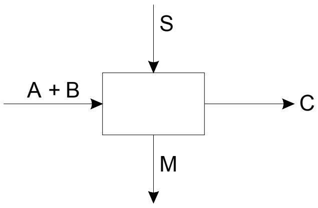


Fig. 10.6. Scheme of the simple recrystallisation

b) ***repeated recrystallisation***: if the crystals obtained from simple recrystallisation are not sufficiently pure, they are dissolved in a new quantity of fresh solvent, repeating the operation until the required purity is obtained.

The scheme of repeated recrystallisation is shown in Fig. 10.7.

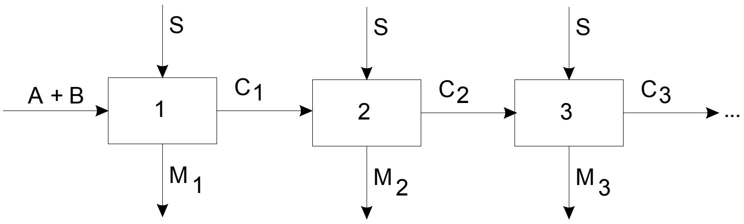


Fig.10.7. Scheme of repeated recrystallisation

c) **multi-contact countercurrent recrystallisation** is used to recover losses of useful substance (A) from discharged foam solutions in which some substance is dissolved.

d) ***directional processes (zonal melting):*** these are those in which the impure system is processed in bar form, being purified by recrystallisation directed along the system (Fig. 10.8.).

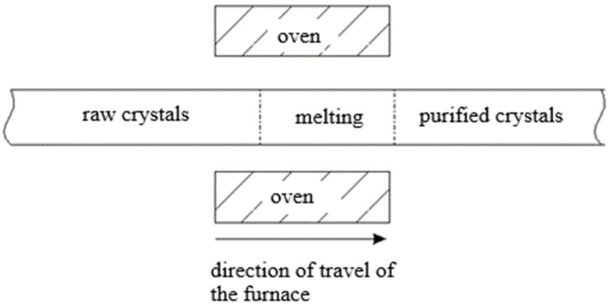


Fig. 10.8. Topirea zonală

The system is initially solid, bar-shaped. A small furnace slowly runs along the bar, forming a molten zone that moves forward. Impurities accumulate in the molten zone and are reduced at one end of the bar. The process is used to purify naphthalene, benzoic acid, etc. It also produces the high purity silicon and germanium needed to make conductors.

As mentioned above, solvents are chosen for the recrystallisation process to ensure ease and safety as well as optimum recrystallisation yield.

Decolourisation of the solution is carried out with activated carbon, talc, alumina, adsorbent silicon dioxide or by chemical processes (treatment with Pb or Ag salts).

After the decolourisation step, the decolourising product is removed by hot filtration (to avoid loss of dissolved solids through premature crystallisation) and the purified solution is subjected to crystallisation by one of the methods described above.

The apparatus in which crystallisation is carried out is very different in design, depending on the crystallisation method chosen (Fig. 10.9).

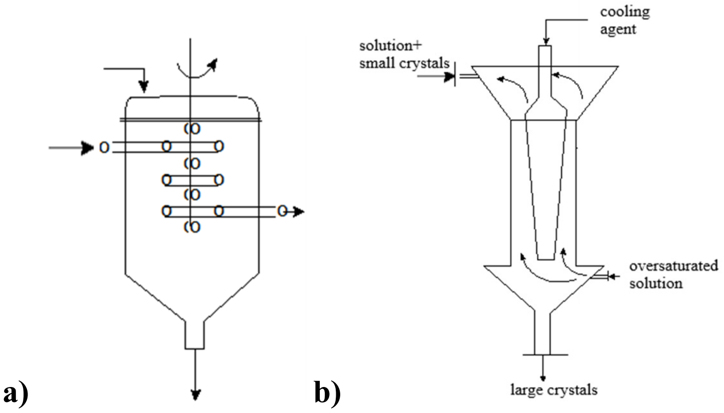


Fig. 10.9. Types of crystallizers
a-with mixing and cooling; b-conical with crystal separation

In the mixing and cooling crystallizer, the solution is introduced at the top and passed under stirring over a scale-cooled coil. The crystals are discharged at the conical bottom.

The conical crystalliser makes it possible to carry out both crystallisation and ***hydraulic sorting*** in the same apparatus in order to obtain uniform crystals of the desired size. The solution enters at the bottom and flows upwards. In the conical zone, crystals are obtained under the influence of the cooling agent. Large crystals fall and settle at the base of the cone, where they drain away, and small crystals are carried upwards by the liquid stream. On their way, the crystals grow to the size where they can no longer be carried by the liquid.

There are also vacuum, or fluidised bed, crystallisation processes.

10.3. Sublimation

Sublimation is the process of separating and purifying certain solid substances by changing them from a solid state directly into a gaseous state under certain pressure and temperature conditions. The reverse process of sublimation is called desublimation.

Therefore, substances such as naphthalene, benzoic acid, salicylic acid, camphor, iodine, sulphur, zinc, etc. can be purified (ice can also be sublimed).

This property of ice is used to remove moisture from thermolabile substances (freeze drying).

Purification of these substances is done by sublimation-desublimation cycles. A cycle is carried out by heating the raw product to sublimation temperature (slightly lower than melting temperature) followed by cooling the vapour (desublimation).

The phase diagram for a pure substance is shown in Figure 10.10.

The plotted lines separate the domains of existence of the phases of a pure substance. The three lines are concurrent at point **T**, the triple point.

The triple point of water is: $t_T = 0.01^oC$; $p_T = 609$ Pa (4.57 torr; 1torr=1mmHg)

- the TA curve represents the liquid-vapour equilibrium, the curve continues dotted TA' and below the triple point, representing the labile equilibrium between the subcooled liquid and its vapour.
- line TB represents liquid-solid equilibrium; it slopes slightly towards lower temperatures with increasing pressure;
- the TC curve represents the solid-vapour equilibrium.

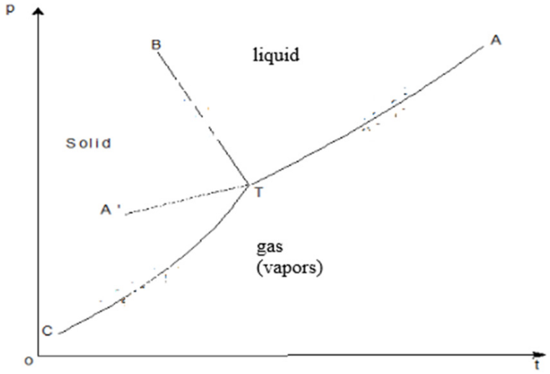


Fig. 10.10. Phase diagram

The dots outside the lines on the diagram represent the substance in one phase, and those on the equilibrium lines correspond to the coexistence, in equilibrium, of two neighbouring phases. The triple point corresponds to the coexistence of the three states.

Sublimation can be achieved in the following ways:

a) ***Simple sublimation*** - when the gas phase of the system contains no other gases or vapours in the mixture. The operation is carried out at a pressure below the triple point pressure of the substance, the sublimation temperature corresponding to this pressure, according to the phase diagram.
b) ***Entraining sublimation*** - when the gaseous phase of the system is a mixture of the sublimating component and an entraining gas, which lowers the partial pressure of the gaseous component, reducing the sublimation temperature.
c) ***Fractional sublimation*** may be achieved by gradually varying the temperature in the vaporizer and decreasing the temperature in the condenser so that the product is condensed (desublimated) into fractions of different purity or, if a mixture, into its components. This operation corresponds to fractional distillation.

10.4. Ion exchanger separation

It is the operation of retaining by ionic bonding a substance from an aqueous solution and recovering it by elution with solutions of appropriate composition.

It is applied to the concentration of components in complex aqueous solutions, such as acids (citric, malic, etc.), amino acids (glutamic, lysine), antibiotics (cycloserine, streptomycin, neomycin), enzymes, hormones, etc.

Ion exchangers (ions) are solid (or liquid) resins or polymers which carry ionisable groups of acidic or basic character. Anions contain basic groups: $-NH_2$, $-NHR$, $-NR_3$ and retain compounds of anionic character carrying negative charges. Cations contain acid groups: $-COOH$; $-SO_3H$; $-OH$; $-SH$ and retain positively charged substances.

The process involves several steps: retention of a specific chemical species on the ionites; removal of the remaining compounds from the mixture by simple washing; recovery of the sorbed components by treatment with aqueous solutions of appropriate chemical activity; regeneration of the sorption capacity of the ionite.

Fractionation of a complex mixture is also possible. This is done by selective sorption (with two ions of different strength) or selective elution (with eluents of different ionic strength from the same ionite).

The working apparatus is very simple: vertical columns into which the ions are introduced on a sieve at its base. The columns are provided with fittings for washing with distilled water, acidic and basic solutions for elution and regeneration, NaCl solutions for activation and formaldehyde for sterilisation. Usually the liquid streams pass in a gravitational direction and the column packing is tared. For loosening and easing the flow a compressed air stream can be passed through the base of the column.

10.5. Chromatography

Chromatography is a process for separating the components of a mixture based on the different distribution between a solid support, a stationary and a mobile phase.

A mobile phase carries the components along a column containing the support and/or stationary phase. Because of their interaction (steric, van der Waals, polar or ionic), the components move at different speeds.

In analytical chromatography they are identified on the column (paper, thin layer, electrophoresis), at the exit of the column (gas-liquid, liquid-liquid chromatography, etc.) or by immobilisation (electrophoretic focusing).

In preparative chromatography larger quantities are worked with, the separated components (fractions) can be collected, concentrated and used.

The size of the columns and their three components and the working conditions are chosen so as to achieve separation of the components of the mixture, which usually consists of structurally similar substances with similar physico-chemical properties. Even under these conditions it is not always possible to separate chemically pure species, but fractions with a major component may be obtained.

11. LOCATION OF A CHEMICAL PLATFORM

When siting a chemical platform, several aspects must be taken into account, namely:

1. The necessary infrastructure

- The location of the platform - this should take into account the quality of the soil on which it will be built, the height it will be above ground, the weather conditions in the area (whether there are high wind conditions or not), etc.
- Access road - as many industrial units require various forms of accessibility, it is necessary to create a road and/or rail transport network, both for the supply of raw materials and shipment of products, and for the transport of personnel.
- Water sources and sewerage - because every industrial process needs running water, both for production and for other needs such as water for fire-fighting, water for steam generation, and the possibility of discharging used water into the sewer after it has been passed through a treatment plant to remove polluting materials. It should also be noted that the possibility of draining the soil on which the platform is located must be taken into account in the event of heavy rainfall, in order to avoid flooding. It is therefore vital to have a water pumping station from the water source, reservoirs and distribution network, as well as a water recirculation system.

  - In every chemical plant there must be a central heating plant providing the necessary steam, which has several uses, namely:
  - low parameter steam - used for heating, air conditioning, hot water;
  - high parameter (superheated) steam - used to drive turbine-type machinery;
  - steam used to generate electricity.

  The most common steam is 5-8 atm and high pressure steam 16-25 atm. The parameters are chosen so that the steam does not condense along the route.
- Electrical networks - both for machine operation and for lighting, computer networks, etc.
- Telephone network - for internal and external communication.

2. Availability of raw materials needed for the process - by creating the above-mentioned transport networks.

3. Availability of personnel - by locating the platform close to a locality, and possibly creating transport networks for people.

4. Ensuring safe conditions around the platform - safe working conditions for platform personnel, safe handling of materials and operation of facilities, avoidance of material losses and avoidance of soil and environmental contamination in general.

11.1. Organisational structure of a chemical platform

In a chemical platform, similarly as in other economic units, there are various specialised departments that ensure the smooth running of the business in that unit.

If one considers the aspects concerning the materials processed, there are the following important departments:

1. The supply or logistics department, which supplies the chemical platform with raw materials and materials needed for production.
2. Production department - where the unit-specific production is actually carried out.
3. Quality control department, comprising the laboratories and the CTC (Technical Quality Control) department - which controls the quality of both raw materials and finished products. It also carries out checks during production to prevent any errors or, if they occur, to correct them as quickly as possible.
4. Distribution department - which ensures the delivery of finished products to the beneficiaries.
5. Marketing department - which deals with advertising and publicity for the finished product.
6. Research department - whose main goal is to find new and efficient alternatives for production at lower costs and the possibility to obtain new and better quality products.
7. Machine maintenance department - with maintenance specialists, electricians, mechanics, etc.
8. Mould department - with the possibility of making moulds if the technological process requires it.

If the employees of the unit are considered, there are the following main departments:

1. Personnel department - which is in charge of hiring qualified personnel, possibly organising on-the-job qualification courses.
2. Financial accounting department - which is responsible for ensuring staff salaries, but also for assessing production costs, prices, etc.
3. Health department - it is vital that in a chemical platform there is a medical practice with medical staff and occupational health doctor.
4. Canteen in the economic unit - it is useful that workers also benefit from this facility.
5. Work protection department - which provides training for staff on work protection, rules of conduct in a chemical plant, hazards that may arise and how to avoid them, etc.
6. Technical department - with qualified staff, engineers, dealing with production, control, research, etc.
7. IT department - with responsibility for the computer side of both machinery and offices.
8. Legal department - dealing with legal issues arising.
9. Transport department - possibly there can be such a department, which deals with internal (within the unit) and external transport machines, their maintenance, etc.
10. Administrative and management department - with qualified staff, responsible for the smooth running of all the unit's activities.

11.2. The role and responsibilities of the technological engineer

The technological engineer is responsible for the design and modification of the production system and auxiliary equipment, for the selection and specification of the production system, for the organisation of the operation and maintenance of the system, for the safety of the plant, for the control of energy consumption and environmental pollution, for the overhaul and intervention in case of failures, and for the optimisation of the process.

12. DESIGN CONCEPTS

12.1. The technological process

The description of the technological process is made by technological phases, with the logical sequence of the technological stages of preparation and processing of raw materials, chemical or physical, processing of the resulting mixtures with the obtaining of the intended products, purification or conditioning of the finished product and recovery of reusable materials. The description is based on a technological scheme

The technological scheme is a schematic representation of the sequence of processes and operations involved in obtaining an intermediate or finished product (in a manufacturing phase or for the entire technological process). The diagram shows the machinery in which chemical transformations take place (reactors), as well as the other apparatus necessary for unit operations (filters, distillation columns, storage vessels, etc.), and the materials involved in the process and their flow.

Some of the most commonly applied rules in establishing process technology schemes in the organic technologies industry are: - the plant is laid out on 2-3 levels to make maximum use of the free fall in the circulation of materials; - heavy machinery (tanks, massive reactors) and those generating vibrations (pumps, compressors) will be placed at zero level (the ground); - measuring vessels are placed at the same level as the reactors they serve, fixed on scaffolding or supports; - the reactors are suspended between levels with the cover at operational level, only the small ones will be provided with legs and will be placed on a landing (level); - the centrifugal pumps will be placed below the minimum level of the tanks for complete emptying and self-priming; - the large capacity reactors will be supported by bottom supports at zero level; - distillation columns shall have the bottom at zero level, except for those attached to a reactor acting as a bottom which may be suspended at a certain level; - steam heating of reactors requires feeding at the top of the jacket or coil and water or brine cooling, or forced flow fluid heating requires feeding at the lowest level of the heating element; - the condensation of vapours in heat exchangers takes place in the intertubular space and the circulation of water in the intratubular space (for the possibility of cleaning deposits); - volatile liquids are worked with in closed apparatus, toxic or toxic-volatile solutions are worked with in installations under slight vacuum with absorption in washing-neutralisation vessels.

In the technological scheme each machine is given a number (position) under which it will be recognised in the description of the technological process and in the specification of the machines. In the case of schemes with many similar machines various abbreviations can be used: P - pump, R - reactor, F - filter, C - column, S - heat exchanger. Thus, a description of the technology can refer to centrifugal pump 2 and reactor 3 or to P 2 and R 3 respectively.

The description of the technology should give all the information concerning the quantity and quality of the materials entering the process, the name and position of the machines, the working conditions, the time and method of controlling the technology, the method of carrying out an operation, etc., from the transfer of raw materials from the day tanks and the section's hand store to the packaging of the product.

For example, Figure 12.1. shows a schematic of the process for the manufacture of p-nitrobenzoic acid by oxidation with sodium dichromate followed by a description of the oxidation step in the process.

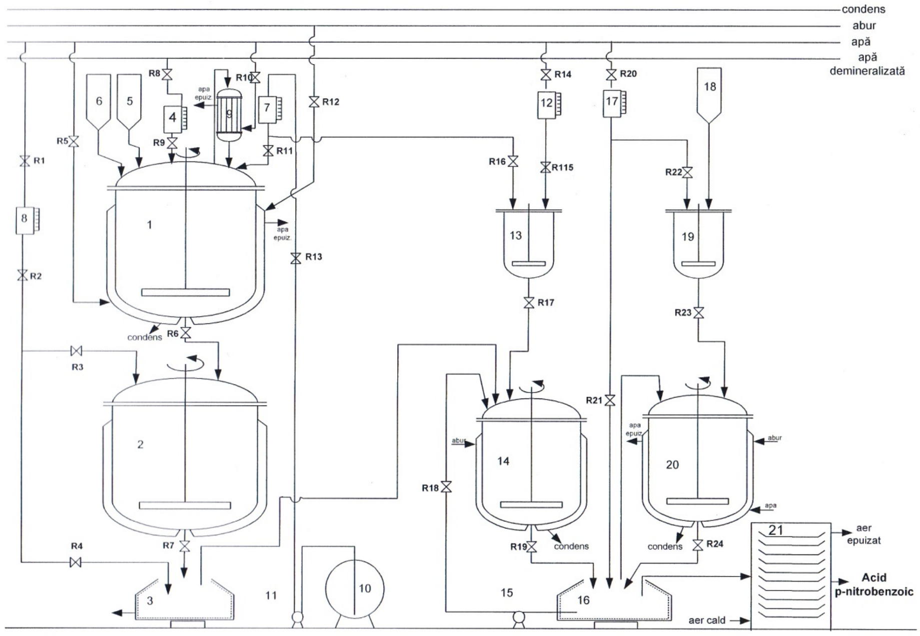


Fig.12.1. Scheme of the manufacturing process of p-nitrobenzoic acid by oxidation with sodium dichromate

Caption

1 - oxidation reactor	12 - water measuring vessel
2 - dilution reactor	13 - mixing vessel for sulphuric acid 5%
3 - filter centrifuge	14 - acidification reactor
4 - demineralised water measuring vessel	15 - centrifugal pump
5 - p-nitrotoluene feed hopper	16 - filter centrifuge
6 - sodium dichromate feed hopper	17 - water measuring vessel
7 - 98% sulphuric acid measuring vessel	18 - sodium hydroxide feed hopper
8 - water measuring vessel	19 - mixing vessel
9 - heat exchanger	20 - alkalinization reactor
10 - 98% sulphuric acid day tank	21 - cabinet dryer
11 - centrifugal pump	R1 - R24 - taps

Description of the oxidation step in the technological process for the manufacture of p-nitrobenzoic acid by oxidation with sodium dichromate

1. Oxidation

183,7 kg p-nitrotoluene is fed into the stirred reactor (1) from the feed hopper (5), then 541,8 kg sodium dichromate is fed from the feed hopper (6). A volume of 900 L of demineralised water is added by opening the tap (R9). From the day tank (10) a volume of 375 L concentrated sulphuric acid (half as much as necessary so that the heat released melts the p-nitrotoluene) is transferred to the measuring vessel (7) by means of the centrifugal pump (11). After homogenization, add from the measuring vessel (7) a further volume of 375 L concentrated sulphuric acid in portions to prevent packing of the reaction. The reaction mixture is kept under stirring and boiling for 1,5 hours.

12.2. Material balaance

The material balance is the basis for technological calculations to evaluate the number and size of the main machines needed to carry out a process, given a production capacity, in a manufacturing line. The material balance is based on the law of conservation of matter.

$$\Sigma\ m_{incoming} = \Sigma\ m_{outgoing}$$

For continuous processes, the masses are calculated in mass flow rates (kg/h), and for batch processes, the masses are calculated per barge (kg/barge). For individual substances or mixtures of known composition, masses may be expressed in moles (kmol).

The material balance is usually drawn up on the basis of a stoichiometric equation. Technical calculations are, however, based on a manufacturing regulation or recipe. The material balance is drawn up for each technological stage or unit operation in which the input materials undergo a quantitative or qualitative change (in composition). Consequently, heating-cooling, compression, de-icing, transport operations are exempted from the calculation of the material balance, the equivalence of input/output masses being obvious.

The material balance is prepared for all compounds and all stages, in which case the total material balance is obtained, or for one compound and all stages or all compounds for one stage, in which case partial material balances are obtained.

The balances are presented analytically in tabular form (as in Table 12.1.) or graphically in the form of scale diagrams (Sankey diagrams) (Fig. 12.2.).

Table 12.1. Analytical material balance

No. Crt	**Material name**	**Quantity**			**Vol. [l]**	**Obs.**
		Tech. [kg]	**Pure [kg]**	**kmol**		
1	**2**	**3**	**4**	**5**	**6**	**7**
1.	***Input material*** *Write the name of the substance, not the chemical formula*					*ou can write molar masses, densities, composition, etc.*
TOTAL		Σm_i				
1.	***Outgoing materials*** *Write the name of the substance, not the chemical formula*					
TOTAL		Σm_e				$\Sigma m_i = \Sigma m_e$

In this diagram, the quantities of the substances present are represented proportionally by the width of the arrows for each substance. The quantity of material out must equal the sum of the quantities of material in.

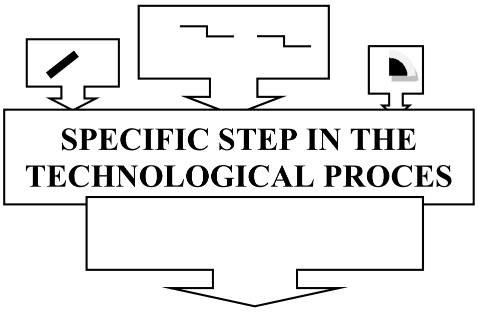


Fig. 12.2. Sankey chart example

12.3. Heat balance

The heat balance (BT) of a chemical plant aims to track heat flows, thermal agent consumption, determine thermal efficiencies and sizing of equipment.

The heat balance of chemical reactors provides the necessary information to determine the heat transfer surface of the apparatus, to choose the appropriate construction and insulation materials, to select a thermal agent suitable for the existing working conditions and advantageous in terms of price, in a quantity appropriate to the technological process.

The heat balance of the chemical reactor - an expression of the law of energy conservation - can be written as follows:

- in its general form:

$$\Sigma Q_i = \Sigma Q_e$$

Explaining the terms of the heat balance equation for reactors in which the fundamental processes of the synthetic organic industry take place gives the following general form:

$$Q_1 + Q_2 + Q_3 = Q_4 + Q_5 + Q_6 + Q_7$$

where:

- Q1 - the amount of heat entering the apparatus with the raw materials
- Q2 - the quantity of heat carried by the heat transfer medium
- Q3 - the thermal effect of the process

- Q4 - the amount of heat contained in the reaction products
- Q5 - amount of heat consumed in heating the apparatus
- Q6 - amount of heat lost to the environment
- Q7 - amount of heat of reflux

Observations:

1) Q_3 - the thermal effect of the process includes both the thermal effect of chemical reactions and the thermal effect of the accompanying physical processes (evaporation, concentration variations, dilutions of acids, dissolutions, etc.), so that its estimation for each process has certain particularities.

2) In calculating the heat balance, the amount of heat to be introduced or removed in a given phase ($\boldsymbol{Q_2}$) is taken as ***unknown***.

3) Units of measurement for Q: kJ or kcal; and if we have substance flows, it is expressed in kW.

Time-temperature diagram

In the time-temperature diagram, the abscissa represents the time when the process takes place and the ordinate the corresponding temperature range. This process is represented in the diagram in figure 12.3.3.

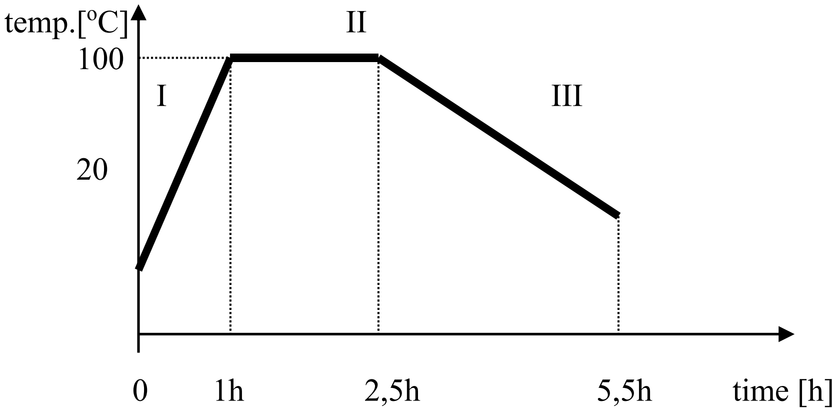


Fig.12.3.3. Time-temperature diagram

12.4. Machine sizing

When determining the machinery requirements in a technological plant, the following aspects must be taken into account: type of machinery, optimum capacity, productivity, technological and mechanical dimensions, etc.

The design theme requires the size of the machine gauge or the hourly capacity of the plant. The time to develop a slab is given by the phase that takes the most time.

Calculation of reactor volume. In the case of batch processes, based on the material balance for the operation (phase) in question, the volume of material, V (m^3) to be used in 24 hours is determined. The following terms are also used: total reactor volume, Vt (m^3); useful volume of the apparatus, Vu (m^3).

The degree of filling of the apparatus, φ is calculated with the relation:

$$\varphi = \frac{Vu}{Vt}$$

The degree of filling for processes that do not produce foam or massive outgassing has values between: 0.7 ÷ 0.85; and for processes accompanied by foaming or boiling level rise has values between: 0.4 ÷ 0.6.

The number of shots, n, which are carried out in an apparatus in 24 hours is calculated with the equation:

$$n = \frac{V}{Vu}$$

If τ is the duration of the process (hours), the number of shifts that are performed with a single machine in 24 hours, *m*, will be:

$$m = \frac{24}{\tau}$$

Knowing the number of machines working:

$$N = \frac{n}{m}$$

the number of devices to be fitted for the operation will be:

$$Nm = N(1 + \frac{d}{100})$$

where: d - capacity reserve, 10 ÷ 15 %

In *continuous processes*, the size of the rector is determined by the flow rate of the substances passing through it, which is required by the material balance to ensure a certain production capacity. If the volumetric flow rate of the substances in the apparatus is q (m^3/h) and the time required to carry out the process is τ (h) - determined for kinetic and thermodynamic or experimental reasons - the volume of the apparatus (m^3) is given by the relation:

$$V = q \cdot \tau$$

If several appliances are used in parallel, N, the volume of an appliance (m^3) becomes:

$$V = \frac{q \cdot \tau}{N}$$

The cross-section of the apparatus (m^2) is calculated with the relation:

$$S = \frac{q \cdot 3600}{N \cdot w}$$

where: w - speed through the machine (m/s)

The following dimensionless criteria are used to determine the stirring power in liquid media: K_P şi Re_{ag}:

$$Re_{ag} = \frac{\rho n d^2}{\eta} \quad ; \quad K_P = \frac{P}{\rho n^3 d^5} = \frac{c}{Re_{ag}^m}$$

where: P - power required by the agitator in operating mode, W

ρ - liquid density, kg/m3

η - liquid viscosity, Pa-s

n - stirrer speed, rot/s

d - agitator diameter

c, m - constants dependent on the type of agitator construction and for the mixing mode

The starting power is 2÷3 times the power of the engine: Pp = 2 - P

The installed power of the electric motor is calculated knowing that its efficiency is 0,95 and taking a power addition of 20%.

Thermal sizing. Heat sizing ensures that the amount of heat exchanged in the equipment of a process stream is accurately determined. The heat transfer surface area (A) is calculated in terms of the amount of heat exchanged by an apparatus, knowing the general heat transfer equation:

$$Q_{ced} = Q_{tr} = Q_{nec}$$

where: Qced - heat released by the thermal agent, W :

$$Q_{ced} = \mathbf{m_{ab}} \cdot r_{ab}^{p} \quad \text{sau} \quad Q_{ced} = \mathbf{m_{apa\ răcire}} \cdot c_{p,\,apă} \cdot \Delta t_{apă}$$

Q_{tr} - heat transmitted through the heat transfer surface, W :

$$Q_{tr} = K \cdot \mathbf{A_{tr}} \cdot \Delta t_{med}$$

Q_{nec} - heat required for the process (calculated from the heat balance = Q_2), W

K - total heat transfer coefficient, W/m^{2}K

A_{tr} - heat transfer surface, m^2

Δt_{med} - average temperature difference between hot and cold agent, ^{o}C

m_{ab} - steam flow (thermal agent), kg/s

r_{ab}^{p} - latent heat of steam at pressure *p*, kJ/kg

For a flat surface, the total heat transfer coefficient is determined with the relation:

$$K = \frac{1}{\frac{1}{\alpha_1} + \Sigma r + \frac{1}{\alpha_2}}$$

where: α1 and α2 - partial convective heat transfer coefficients for the two fluids, W/m^{2}K

Σr - sum of all thermal resistances, m^{2}K/W

$$\Delta t_{med} = \frac{\Delta t_M - \Delta t_m}{2{,}3 \cdot lg \frac{\Delta t_M}{\Delta t_m}}$$

where: ΔtM , Δtm - the differences between the maximum and minimum temperatures at the ends of the heat exchanger respectively, ^{o}C.

The partial convective heat transfer coefficients α1 and α2 are calculated for the particular cases under consideration from the similarity criteria: *Re, Nu, Pr, Ga, Gr.*

Calculation of a centrifugal pump. The centrifugal pump motor power (P, kW) is calculated with the relation:

$$P = \frac{V \cdot \rho \cdot g \cdot H_m}{1000 \cdot \eta} = \frac{V \cdot \Delta p}{1000 \cdot \eta}$$

where: V - pump volume flow rate (flow rate of liquid conveyed), m^3/s;

ρ - density of pumped liquid, kg/m^3;

g - gravitational acceleration, m/s^2;

Hm - total lift height of the pump, m

Δp - total hydraulic resistance of the network, Pa

η - total efficiency of the pumping installation, which is the product of pump efficiency, transmission efficiency and motor efficiency

The installed engine has a slightly higher installation power (Pinst) than the one calculated with the previous relation, in order to have a reserve for a possible overload:

$$P_{inst} = \beta \cdot P$$

where: β - the safety factor of power, which is chosen, depending on the value calculated for P, from the Table 12.2.

Table 12.2. Pump power safety factor values
as a function of its calculated motor power

P, kW	β
< 1	2 - 1,5
1 - 5	1,5 - 1,2
5 - 50	1,2 - 1,15
> 50	1,1

The total hydraulic resistance of the network can be calculated from the following relationships:

$$\Delta p = \frac{\rho w^2}{2} \cdot \left(1 + \lambda \cdot \frac{L}{d} + \Sigma\zeta\right) + \rho \cdot g \cdot H + (p_2 - p_1)$$

or

$$\Delta p = \frac{\rho w^2}{2} \cdot \left(1 + \lambda \cdot \frac{L + L_{ech}}{d}\right) + \rho \cdot g \cdot H + (p_2 - p_1)$$

where: w - velocity of liquid flow through the pipe, m/s;

λ - coefficient of friction of the liquid flowing through the pipe;

L - length of pipe, m;

Σζ - sum of coefficients of given local resistances (found in tables);

Lech - equivalent length of a straight pipe with the same hydraulic resistance as the given local resistance, m

H - geometric head of the pump, m;

p1, p2 - pressures in the suction and discharge space respectively, Pa

The liquid flow velocity through the pipe is calculated from the flow rate of the liquid conveyed:

$$w = \frac{V}{A}$$

where: A - cross-section of the pipeline, m^2

The coefficient of friction as the liquid passes through the pipe depends on the flow regime (Re) and the d_{ech}/e ratio,
where: d_{ech} - equivalent pipe diameter, which is calculated with the relation below, m

$$d_{ech} = \frac{4 \cdot A_{ud}}{P_{ud}}$$

where: Aud - wetted area of fluid, m^2;

Pud - perimeter wetted by fluid, m

The head or total lift of the pump is calculated with one of the following relationships:

$$H_m = \frac{p_2 - p_1}{\rho \cdot g} + H + h_p$$

or

$$H_m = \frac{p_{ref} - p_{asp}}{\rho \cdot g} + H_0 + \frac{w_{ref}^2 - w_{asp}^2}{2 \cdot g}$$

where: pref, pasp - the pressures in the delivery and suction lines of the pump, Pa;

H_o - the vertical distance between the points where pref and pasp are measured, m;

w_{ref}, w_{asp} - liquid velocities in the delivery and suction lines respectively, m/s

The material balance equations are used for filtration calculations:

$$m_{susp} = m_l + m_s$$
$$m_{susp} = m_f + m_{pp\ um}$$
$$m_{pp\ um} = m_s + m_{lr}$$
$$m_l = m_f + m_{lr}$$
$$m_s = x \cdot m_{susp} = (1-u_m) \cdot m_{pp\ um}$$

where: msusp - suspension mass, kg;
m_l - total mass of liquid in suspension, kg;
m_s - mass of solid in suspension, kg;
m_f - mass of filtrate, kg;
$m_{pp\ um}$ - mass of wet precipitate obtained after filtration, kg;
m_{lr} - mass of liquid retained in the wet precipitate, kg;
x - concentration of the suspension relative to the solid phase, % mass;
u_m - moisture content of wet precipitate, % mass of liquid retained

The filtering equation:

$$V^2 + 2 \cdot C \cdot V = K \cdot \tau_f$$

where: C - filter cloth constant, m^3/m^2;
K - precipitation constant, m^2/s;
V - specific filtrate volume, m^3/m^2; $V = \frac{V_f}{A_f}$
V_f - filtrate volume, m^3; $V_f = \frac{m_f}{\rho_f}$
ρ_f - filtrate density, kg/m^3;
A_f - filtration area, m^2

In the case of a plate and frame filter having n frames of dimensions *l x l x δ*, The filtration area (A_f) and the volume of wet precipitate ($V_{pp\ um}$) are determined as follows:

$$A_f = n \cdot l \cdot l \cdot 2 \qquad V_{pp\ um} = n \cdot l \cdot l \cdot \delta$$

Filtration speed - $dV/d\tau$, $m^3/(m^2s)$ - is calculated with the relation:

$$\frac{dV}{d\tau} = \frac{K}{2(C + V)}$$

Washing speed - $(dV/d\tau)_{sp}$ - in backwashing is 4 times lower than the filtration speed.

The washing time (τ_{sp}) is determined with the relation:

$$\tau_{sp} = \frac{\frac{V_{apa\,sp}}{A_f}}{(\frac{dV}{d\tau})_{sp}}$$

where: $V_{apa\ sp}$ - volume of wash water, m^3

13. LABOUR PROTECTION

In order to continuously improve working conditions in industry in general and in the chemical industry in particular, and to prevent accidents at work and occupational illnesses, the authorities have issued rules for the protection of workers, which must be observed by all employees, each in their own sector of activity, within the limits of their duties.

The work protection measures must be effectively applied, extended and improved, the ultimate aim being to ensure that the work process is carried out in complete safety in production, research, pilot stations and laboratories.

Since 01.10.2006, infringements of the legislation are punishable by fines if the legal obligation to assess the health and safety risks to workers, including the choice of work equipment, the chemical substances or preparations used and the layout of workplaces, is not complied with. Failure to comply with legal obligations concerning the organisation of prevention and work protection activities also constitutes an infringement.

The following is some of the legislation in force on labour protection:

Legea 319/2006 – Occupational Safety and Health Act.

Norme metodologice de aplicare a Legii 319/2006.

Contractul colectiv de munca unique at national level 2007-2010.

HG nr. 1058 din 09.08.2006 - Minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres.

HG nr. 1091 din 16.08.2006 - Minimum safety and health requirements for the workplace.

HG nr. 1146 din 30.08.2006 - Minimum safety and health requirements for the use of work equipment by workers at work.

HG nr. 1875 din 22 decembrie 2005 - Protection of workers' health and safety from risks due to exposure to asbestos.

HG nr. 600 din 13.06.2007 - Protecting young people at work.

HG nr. 752 din 14.05.2004 - Establishing use in potentially explosive atmospheres.

HG nr. 809 din 14.07.2005 - Amendment of Government Decision No 115.2004 on the establishment of requirements for personal protective equipment.

HG nr. 971 26.07.2006 - Minimum requirements for safety and/or health signs at work.

Legea nr. 108 din 16 iunie 1999 - Establishment and organisation of the Labour Inspectorate, republished in the Official Monitor of Romania no. 740 of 10 October 2002.

Legea nr. 130 din 20 iulie 1999 - Some protective measures for people in employment.

Legea nr. 155 din 26 iulie 2000 - Approval of Government Emergency Ordinance No 16.2000 on the ratification of certain Conventions adopted by the International Labour Organization.

Legea nr. 177 din 18 octombrie 2000 - Amendment and completion of the Labour Protection Law no.90.1996.

Legea nr. 31 din 22 martie 1991 - Setting working hours below 8 hours a day for employees working in special, harmful, arduous or dangerous conditions.

Legea nr. 53 din 24 ianuarie 2003 - Labour Code.

Legea nr.245/2004 - General product safety.

Legea nr.436/2001 - Approval of Government Emergency Ordinance No 99.2000 on measures that may be applied during periods of extreme temperatures for the protection of persons at work.

Amenzi Protecţia Muncii - Fines imposed by ITM inspectors for various irregularities reported in the employer's occupational safety and health activity.

PSI legislation - Fire prevention and extinguishing

HG 1739 din 6.12.2006 - Approval of categories of buildings and installations subject to fire safety approval and/or authorisation.

Legea nr. 15 din 28.02.2005 - Approval of Government Emergency Ordinance No 21/2004 on the National Emergency Management System.

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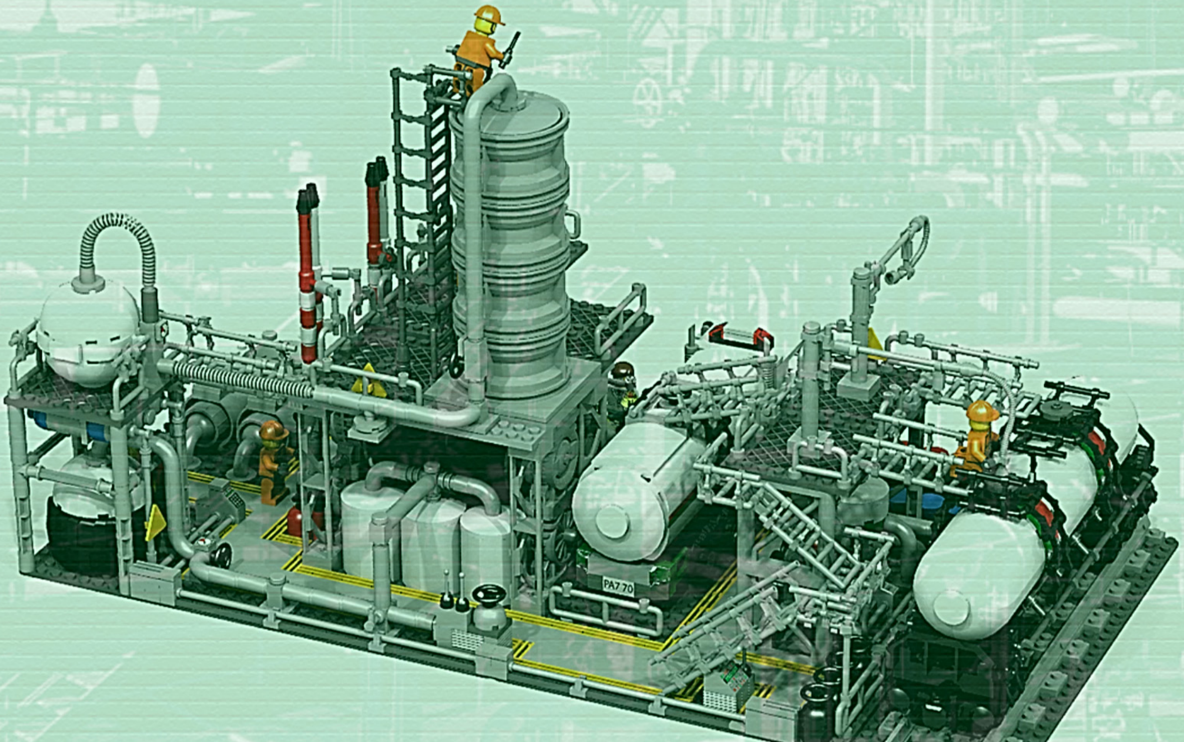

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