CATALYST SCIENCE & REACTOR TECHNOLOGY

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INTRODUCTION

- Reactor is the heart of Chemical Process.
- A vessel designed to contain chemical reactions is called a reactor.
- An industrial reactor is a complex chemical device in which heat transfer, mass transfer and diffusion may occur along with chemical with the provisions of safety and controls
- All chemical processes are centered in a chemical reactor. The design of a chemical reactor Is the most important factor in determining the overall process economics.

BASIC REACTOR ELEMENT

- Material Balances
- Heat Transfer and Mass Transfer

MATERIAL BALANCES

- Also called mass balance.
- The mass that enters a system must, by conservation of mass, either leave the system or accumulate within the system .
- Mathematically the mass balance for a system without a chemical reaction is as follows

  Input = Output + Accumulation

MASS TRANSFER

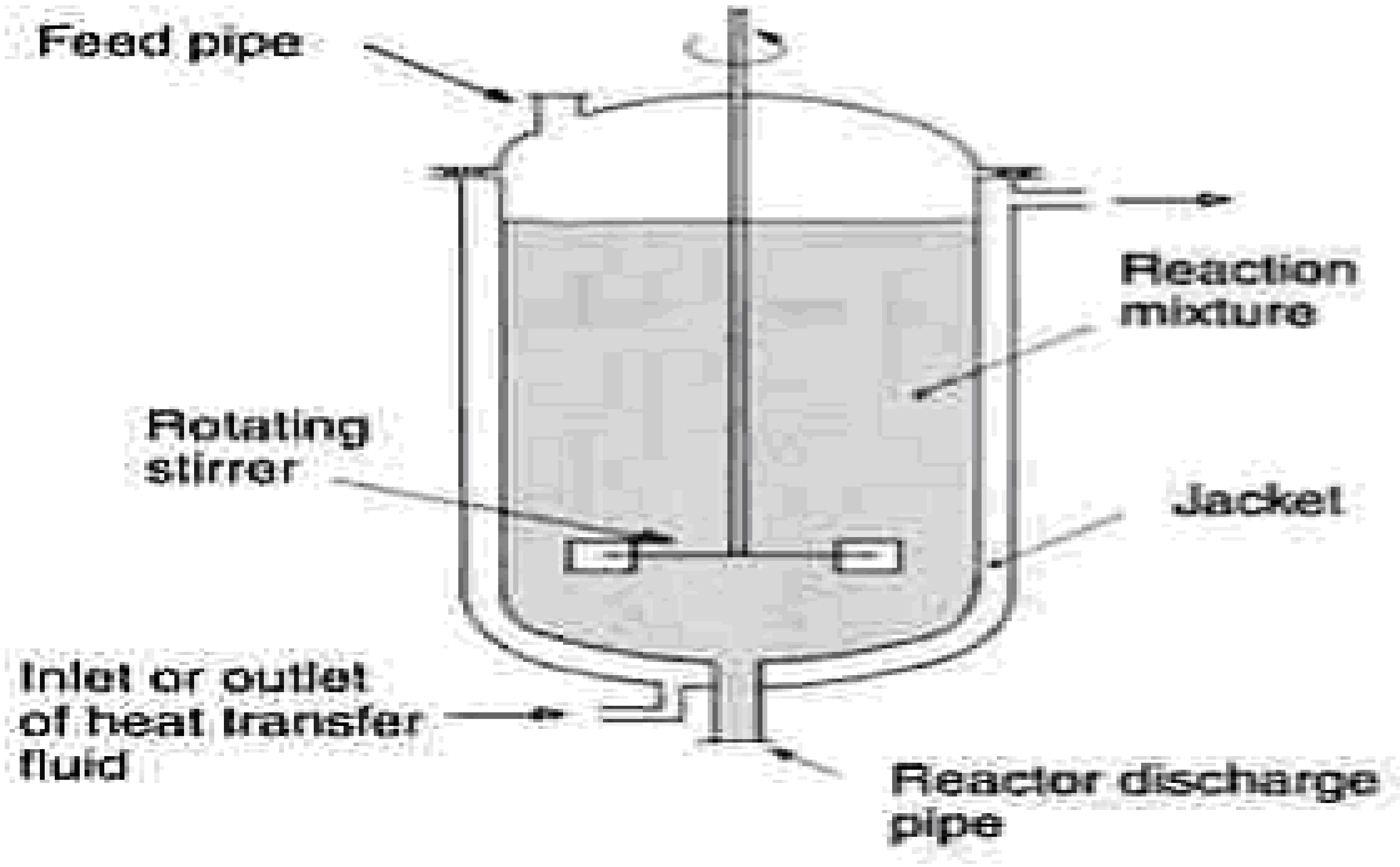
- Is the phrase commonly used in engineering for physical processes that involve molecular and convective transport of atoms and molecules within physical system.
- Transfer of mass from high concentration to low concentration.

HEAT TRANSFER

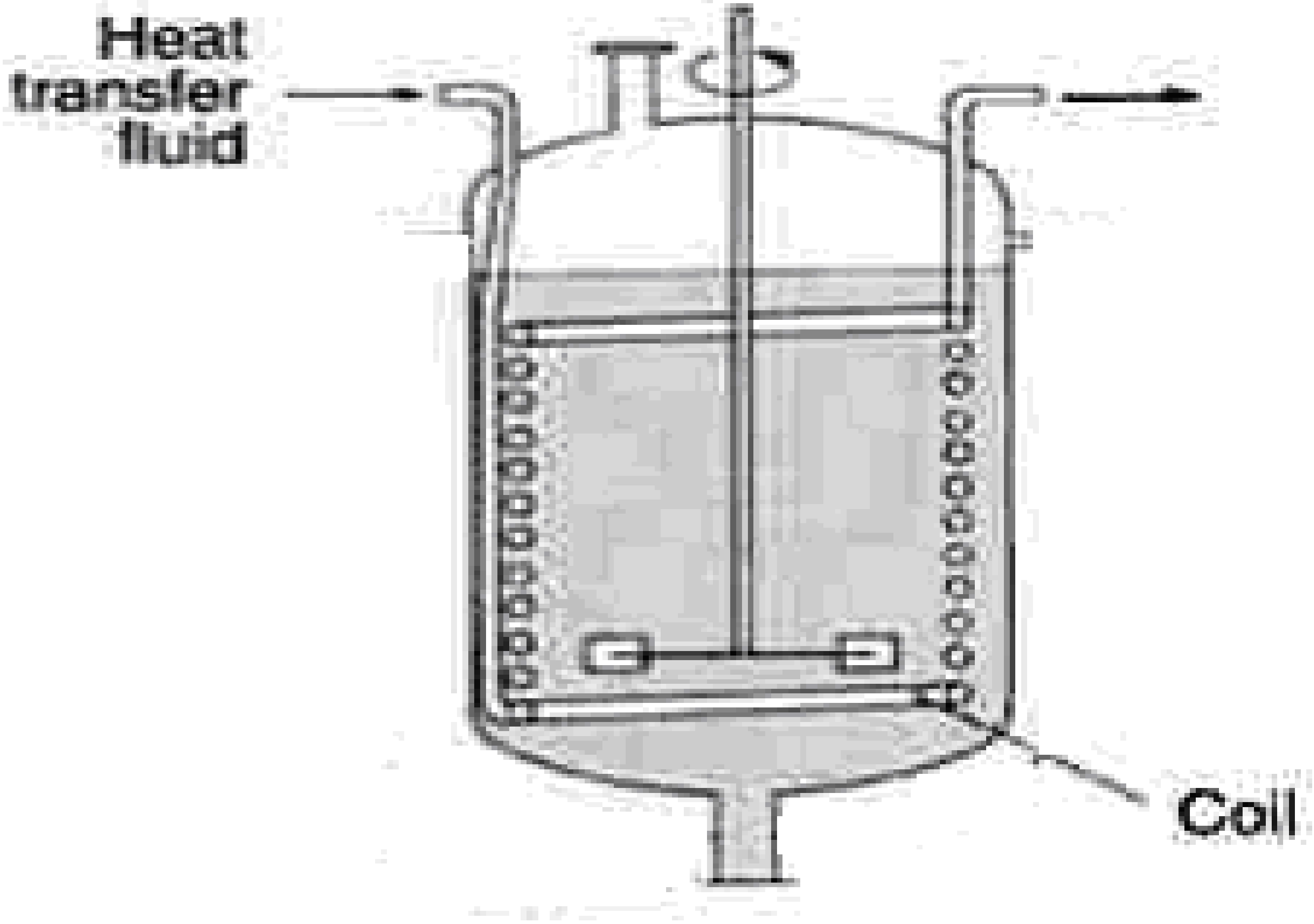
- Is the transition of thermal energy from a heated item to a cooler item.
- Transfer of Thermal Energy

MODES OF HEAT TRANSFER

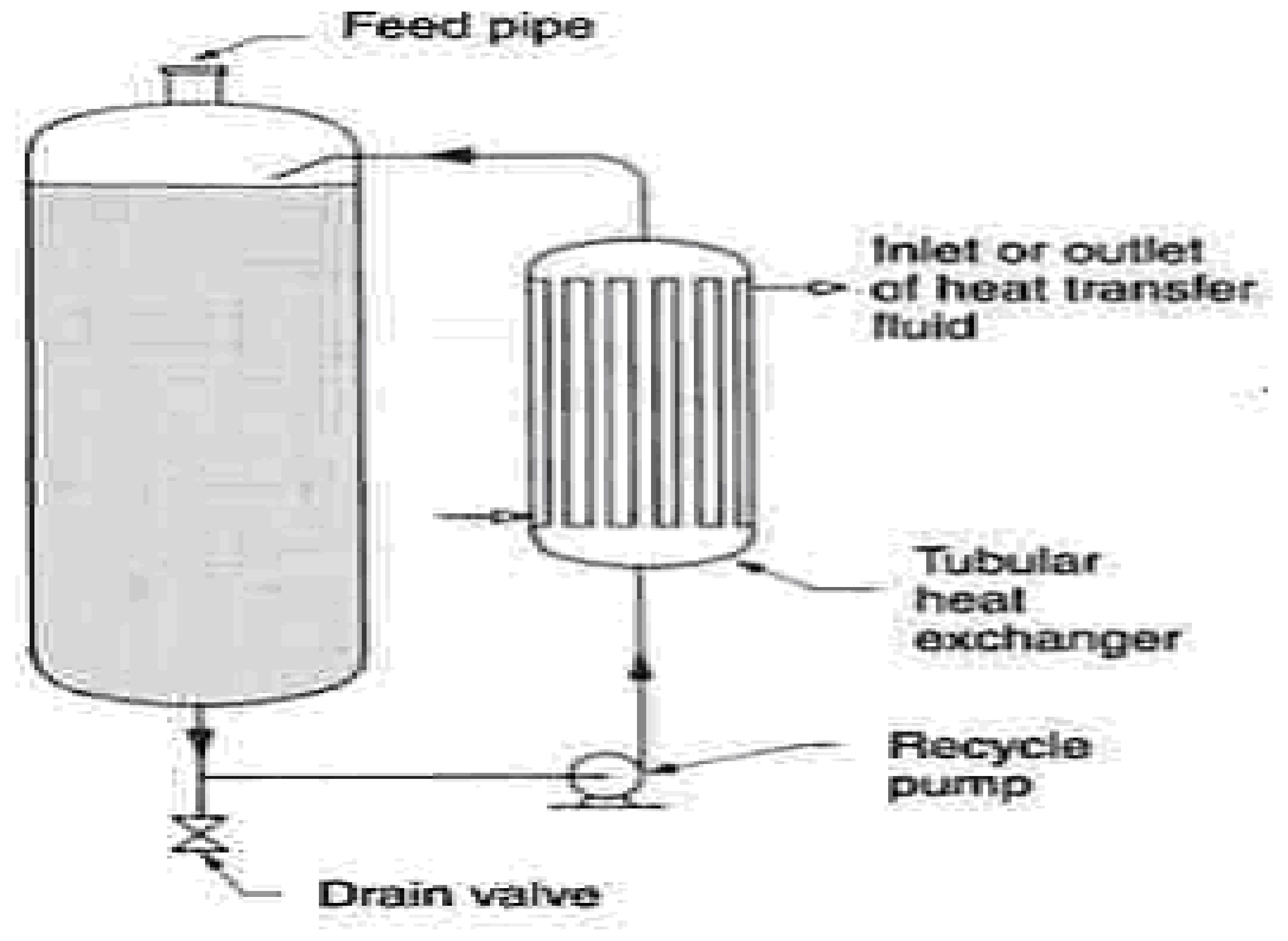
- Jacket,
- Internal coils,
- External heat exchanger,
- Cooling by Vapor Phase Condensation
- Fired heater.


Feed pipe
Reaction mixture
Rotating stirrer
Jacket
Inlet or outlet of heat transfer fluid
Reactor discharge pipe

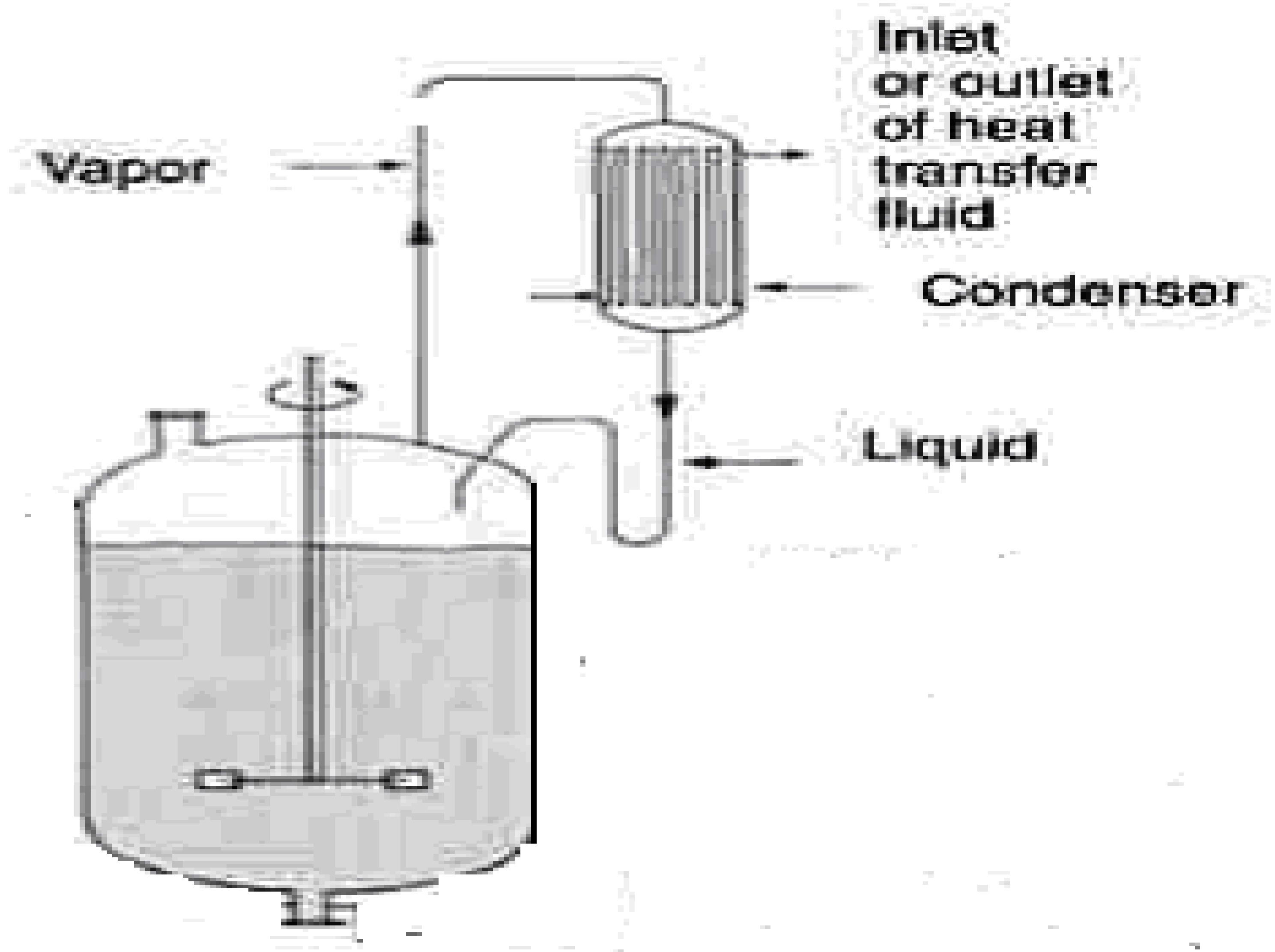
JACKET



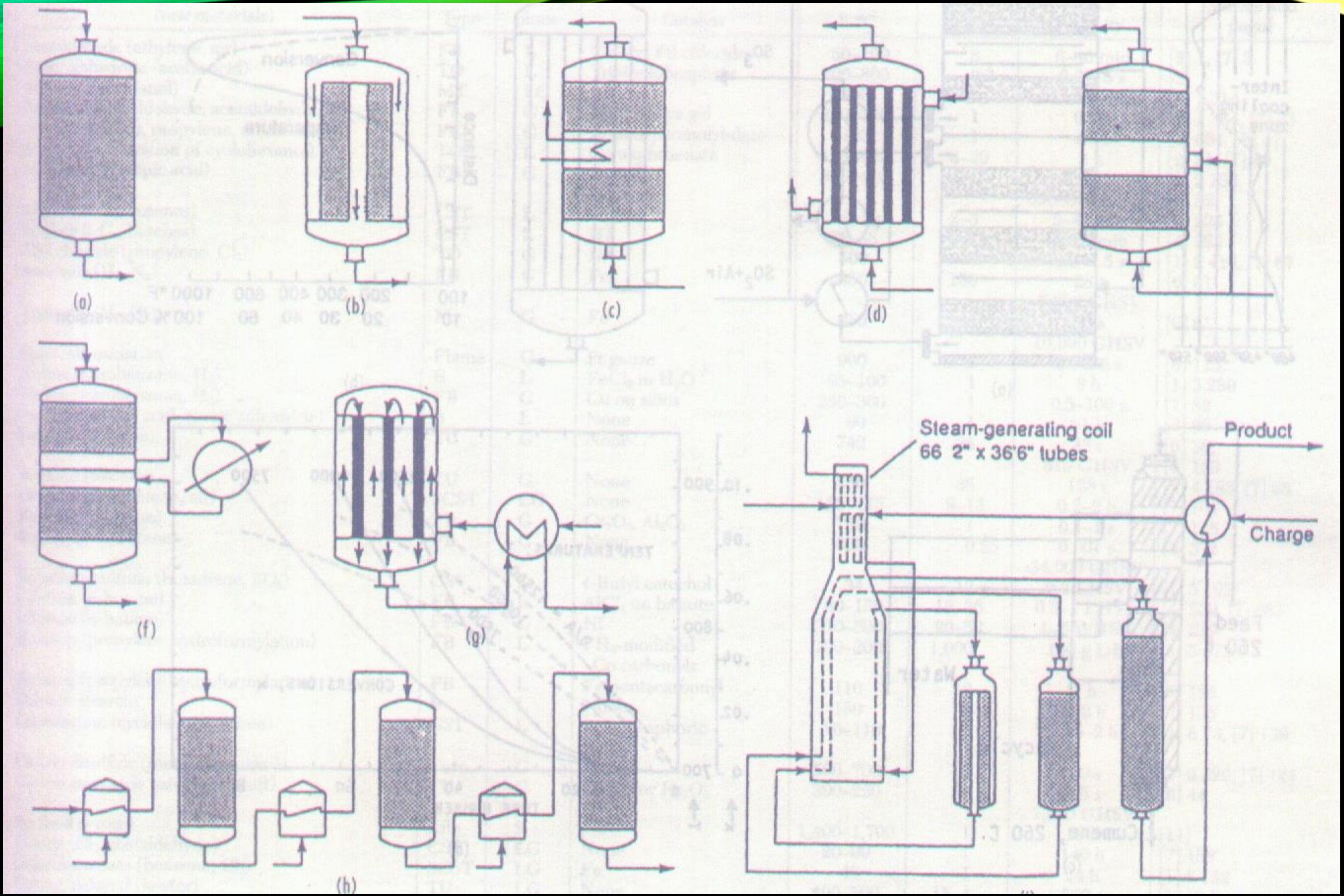
INTERNAL COIL



EXTERNAL HEAT EXCHANGER



COOLING BY VAPOR PHASE CONDENSATION



Heat Exchange in Packed Reactors

BASICS FOR REACTOR DESIGN

- Reaction Type
- Removal/addition of heat
- Need for catalyst
- Phases involve
- The mode of temperature and pressure control.
- Production capacity or flow

BASICS FOR REACTOR DESIGN

- Residence time
- Contact/mixing between the reactants
- Corrosion - erosion characteristics of any potential hazard associated with reaction system.
- Reaction Rate

REACTION RATE

- Speed at which a chemical reaction proceeds, in terms of amount of product formed or amount of reactant consumed per unit time.

FACTORS INFLUENCING REACTION RATE

- Concentration
- The nature of reaction
- Temperature
- Pressure
- Catalyst

REACTION TYPES

- Direct Combination or Synthesis Reaction

$A + B = AB$

- Chemical Decomposition or Analysis Reaction

$AB = A + B$

REACTION TYPES

- Single Displacement or Substitution Reaction

$$A + BC = AC + B$$

- Metathesis or Double Displacement Reaction

$$AB + CD = CB + AD$$

REACTOR TYPES

1. Mode of operation
2. End use application
3. No of Phases
4. A catalyst is used

Reactors

- **Mode of Operation**
  1. Bacth Type
  2. Continous type
  3. Semi batch
- **End Use base Classification**
  1. Polymerization reactors
  2. Biological reactors
  3. Electrochemical reactors
- **Phases based Classification**
  1. Single Phase
  2. Multiphase
- **Catalyst Base**
  1. Homogenous
  2. Heterogeneous

REACTOR TYPES

They can be classified according to the;

1. Mode of operation
2. End use application
3. No of Phases
4. A catalyst is used

CLASSIFICATION BY MODE OF OPERATION

CLASSIFICATION BY MODE OF OPERATION

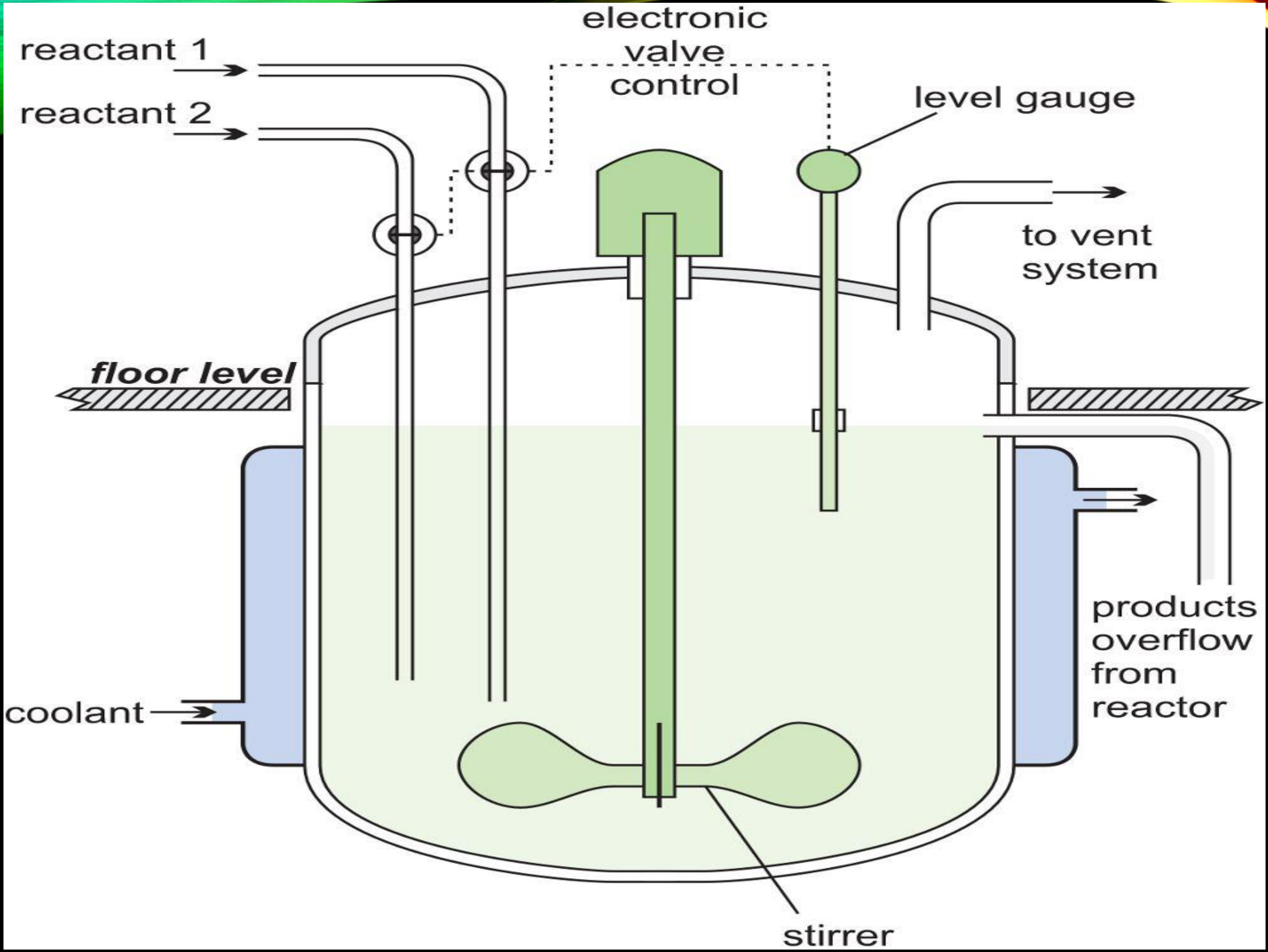
- Batch Reactors
- Continuous reactors
- Semi-batch reactors

BATCH REACTOR

- A “batch” of reactants is introduced into the reactor operated at the desired conditions until the target conversion is reached.
- Batch reactors are typically tanks in which stirring of the reactants is achieved using internal impellers, gas bubbles, or a pump-around loop where a fraction of the reactants is removed and externally recirculated back to the reactor.

BATCH REACTORS

- Temperature is regulated via internal cooling surfaces (such as coils or tubes), jackets, reflux condensers, or pump-around loop that passes through an exchanger.
- Batch processes are suited to small production rates, too long reaction times, to achieve desired selectivity, and for flexibility in campaigning different products


electronic valve control
reactant 1
reactant 2
level gauge
to vent system
floor level
products overflow from reactor
coolant
stirrer

APPLICATIONS OF BATCH REACTOR

- Fermentation
- Waste water treatment

CONTINUOUS REACTORS

- Reactants are added and products removed continuously at a constant mass flow rate. Large daily production rates are mostly conducted in continuous equipment.

CONTINUOUS REACTORS

- CSTR
- Plug Flow Reactor

CSTR

- A continuous stirred tank reactor (CSTR) is a vessel to which reactants are added and products removed while the contents within the vessel are vigorously stirred using internal agitation or by internally (or externally) recycling the contents.

CSTR

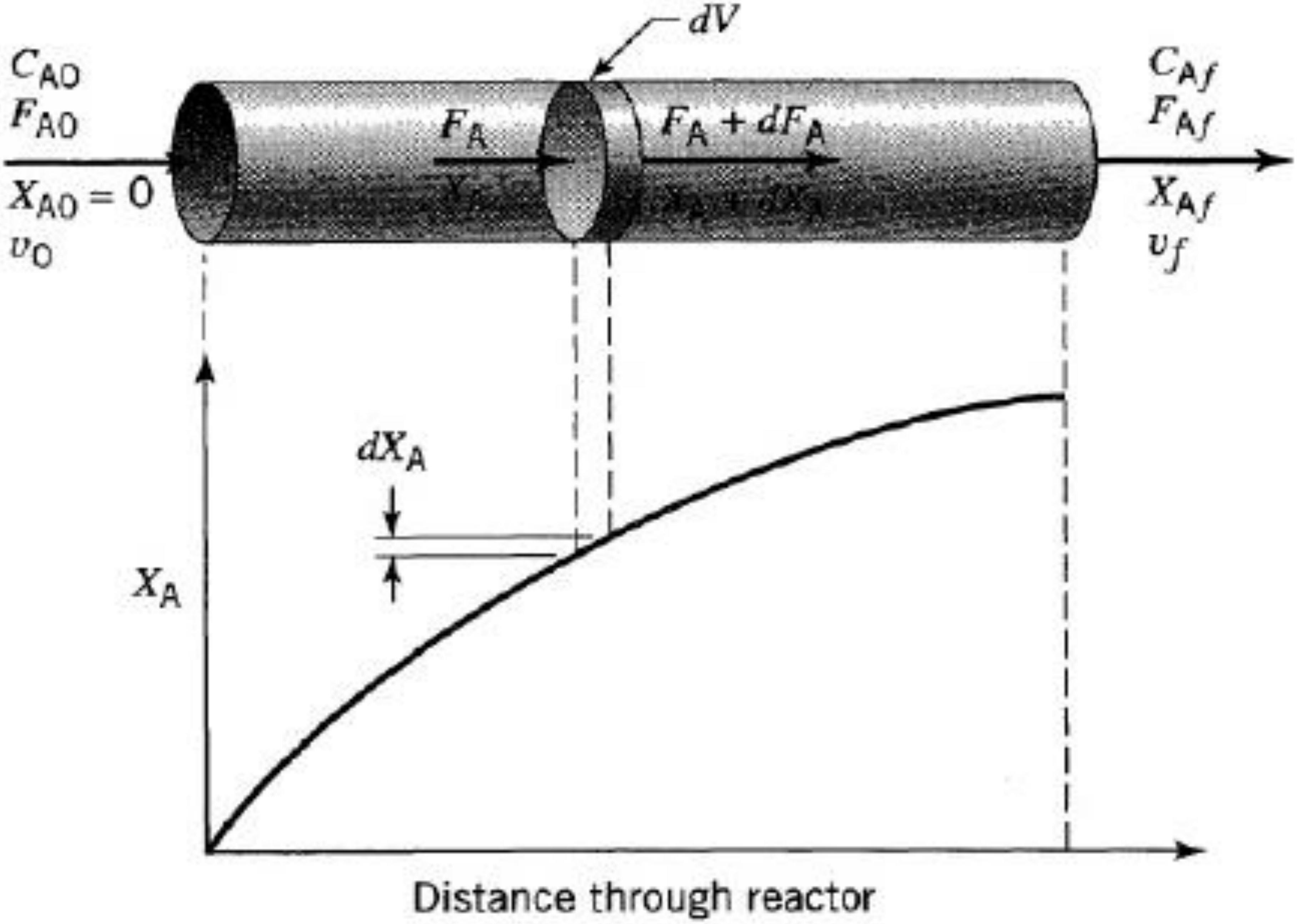
- Residence time – average amount of time a discrete quantity of reagents spend inside the tank
- Residence time = $\frac{\text{volumetric flow rate}}{\text{volume of the tank}}$

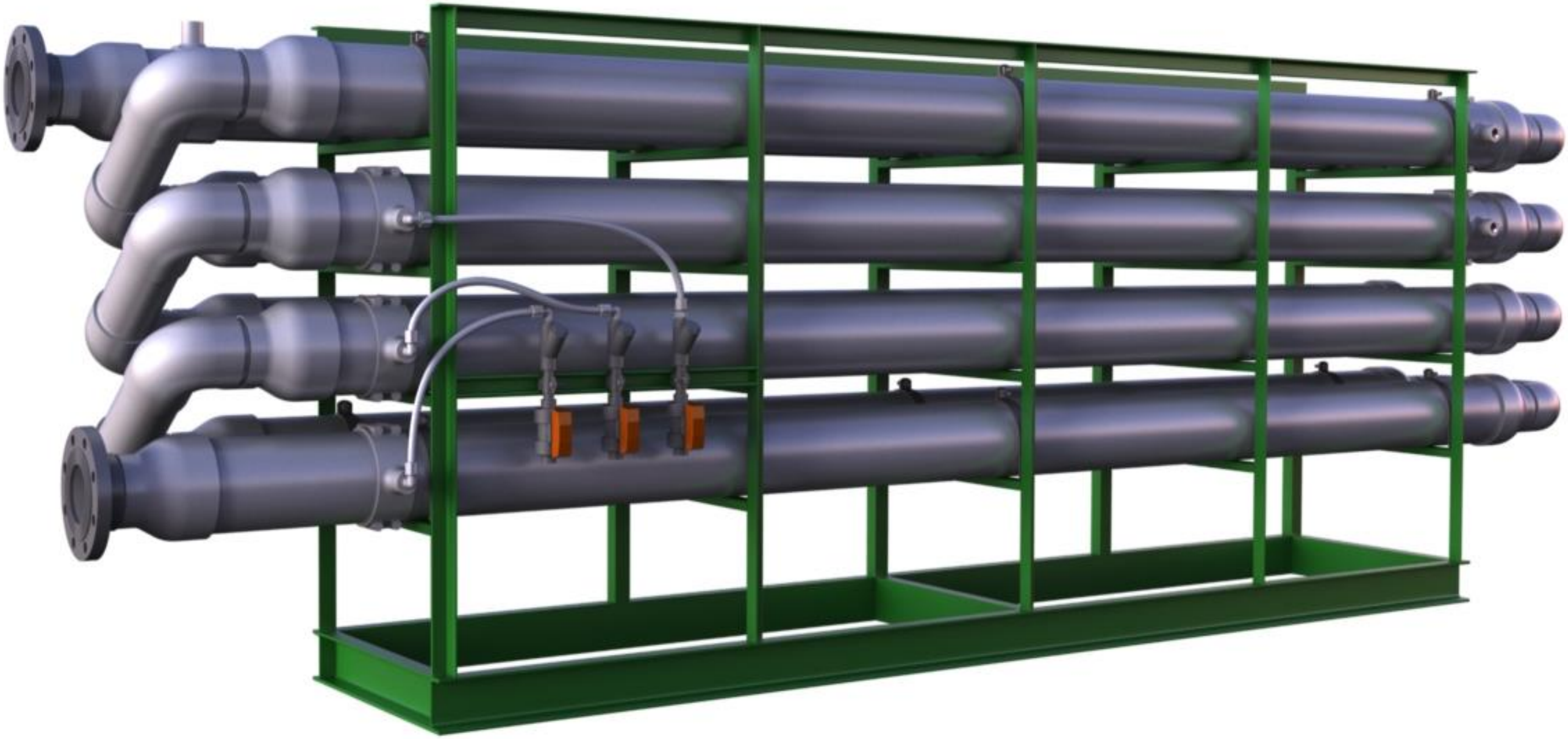
CSTR APPLICATIONS

- Continuous stirred-tank reactors are most commonly used in industrial processing, primarily in homogeneous liquid-phase flow reactions, where constant agitation is required.
- Fermentors are CSTRs used in biological processes in many industries, such as brewing, antibiotics, and waste treatment. In fermentors, large molecules are broken down into smaller molecules, with alcohol produced as a by-product.

PLUG FLOW REACTOR

- Plug flow, or tubular, reactors consist of a hollow pipe or tube through which reactants flow.
- Has a higher efficiency than a CSTR at the same value


dV
C_{A0}
F_{A0}
$X_{A0} = 0$
v_0
F_A
X_A
$F_A + dF_A$
$X_A + dX_A$
C_{Af}
F_{Af}
X_{Af}
v_f
dX_A
X_A
Distance through reactor



APPLICATIONS OF PLUG FLOW REACTOR

- Plug flow reactors have a wide variety of applications in either gas or liquid phase systems. Common industrial uses of tubular reactors are in gasoline production, oil cracking, synthesis of ammonia from its elements, and the oxidation of sulfur dioxide to sulfur trioxide.

SEMI BATCH REACTOR

- Semibatch (semiflow) reactors operate much like batch reactors in that they take place in a single stirred tank with similar equipment. However, they are modified to allow reactant addition and/or product removal in time.
- A normal batch reactor is filled with reactants in a single stirred tank at time t=0 and the reaction proceeds. A semibatch reactor, however, allows partial filling of reactants with the flexibility of adding more as time progresses. Stirring in both types is very efficient, which allows batch and semibatch reactors to assume a uniform composition and temperature throughout.

SEMI BATCH REACTOR

- Some of the reactants are loaded into the reactor, and the rest of the reactants are fed gradually. Alternatively, one reactant is loaded into the reactor, and the other reactant is fed continuously.
- Once the reactor is full, it may be operated in a batch mode to complete the reaction. Semi-batch reactors are especially favored when there are large heat effects and heat-transfer capability is limited. Exothermic reactions may be slowed down and endothermic reactions controlled by limiting reactant concentration.

SEMI BATCH REACTOR

The flexibility of adding more reactants over time through semibatch operation has several advantages over a batch reactor. These include:

- **Improved selectivity of a reaction**
- **Better control of exothermic reactions :** Exothermic reactions release heat, and ones that are highly exothermic can cause safety concerns. Semibatch reactors allow for slow addition of reactants in order to control the heat released and thus, temperature, in the reactor.

SEMI BATCH REACTOR

- **Product removal through a purge stream** : In order to minimize the reversibility of a reaction one must minimize the concentration of the product. This can be done in a semibatch reactor by using a purge stream to remove products and increase the net reaction rate by favoring the forward reaction.

CLASSIFICATION BY END USE

CLASSIFICATION BY END USE

Chemical reactors are typically used for the synthesis of chemical intermediates for a variety of specialty (e.g., agricultural, pharmaceutical) or commodity (e.g., raw materials for polymers) applications.

- Polymerization Reactors
- Bio-reactors
- Electrochemical Reactors

POLYMERIZATION REACTORS

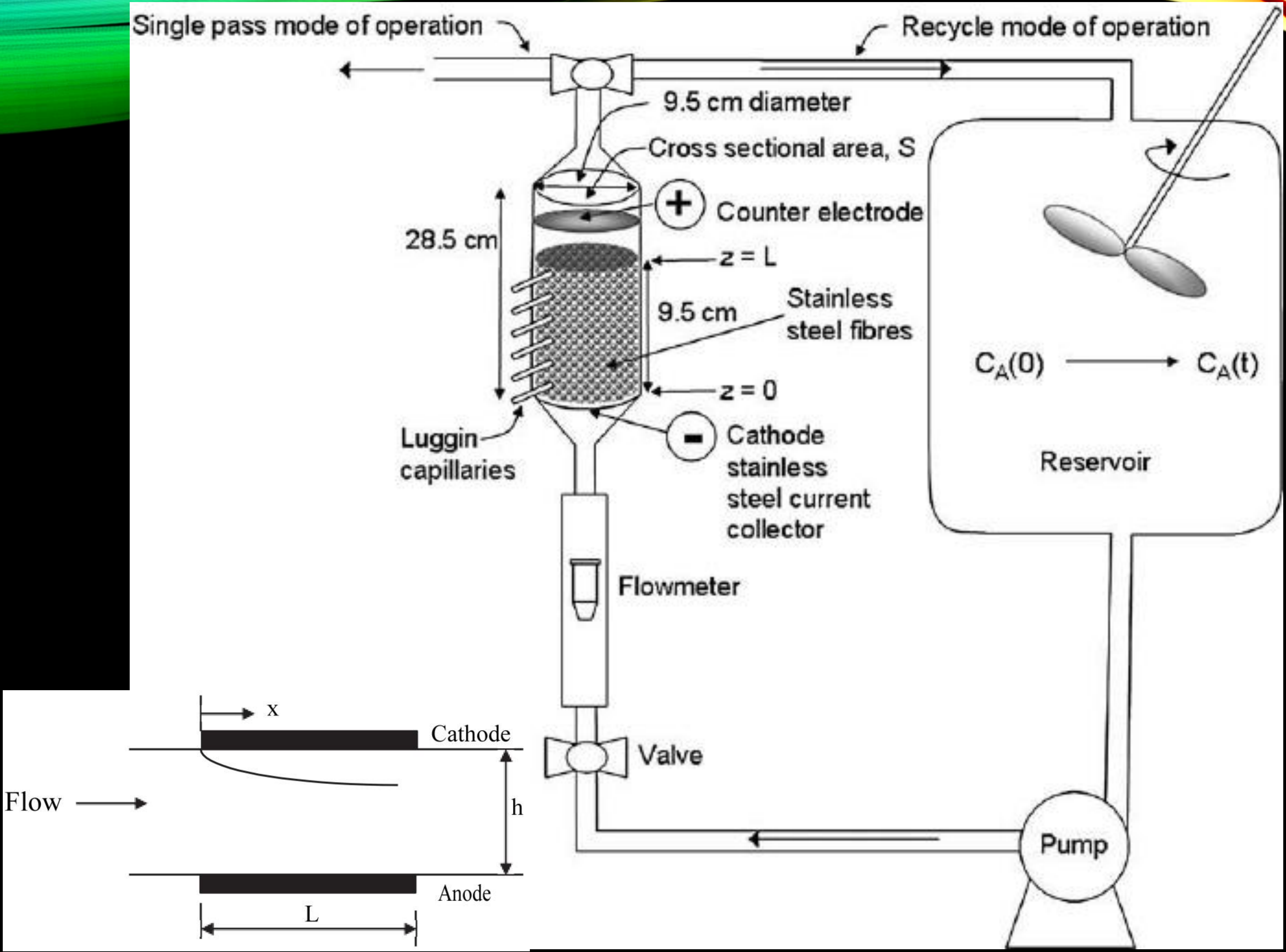
- Polymerization reactors convert raw materials to polymers having a specific molecular weight and functionality.
- The difference between polymerization and chemical reactors is artificially based on the size of the molecule produced.

BIO REACTORS

- Bioreactors utilize (often genetically manipulated) organisms to catalyze biotransformations either aerobically (in the presence of air) or an-aerobically (without air present).

ELECTROCHEMICAL REACTORS

- Electrochemical reactors use electricity to drive desired reactions.
- Examples include synthesis of Na metal from NaCl and Al from bauxite ore.


Single pass mode of operation
Recycle mode of operation
9.5 cm diameter
Cross sectional area, S
28.5 cm
+
Counter electrode
z = L
9.5 cm
Stainless steel fibres
z = 0
Luggin capillaries
-
Cathode stainless steel current collector
Flowmeter
Valve
$C_A(0)$ → $C_A(t)$
Reservoir
Pump
x
Cathode
Flow
h
Anode
L

CLASSIFICATION BY PHASE

CLASSIFICATION BY PHASE

- Despite the generic classification by operating mode, reactors are designed to accommodate the reactant phases and provide optimal conditions for reaction.
- Reactants may be fluid(s) or solid(s), and as such, several reactor types have been developed.
- Single phase reactors are typically gas (or plasma) or liquid-phase reactors.
- Two-phase reactors may be gas-liquid, liquid-liquid, gas-solid, or liquid-solid reactors.

CLASSIFICATION BY PHASE

- Multiphase reactors typically have more than two phases present. The most common type of multiphase reactor is a gas-liquid-solid reactor; however, liquid-liquid-solid reactors are also used.

CATALYST BASE

THE PHENOMENON CATALYSIS

- It is the acceleration of chemical reaction by means of substance called catalyst.
- In theory, an ideal catalyst would not be consumed, but this is not the case in practice. Owing to competing reactions, the catalyst undergoes chemical changes, and its activity becomes lower (catalyst deactivation). Thus catalysts must be regenerated or eventually replaced.

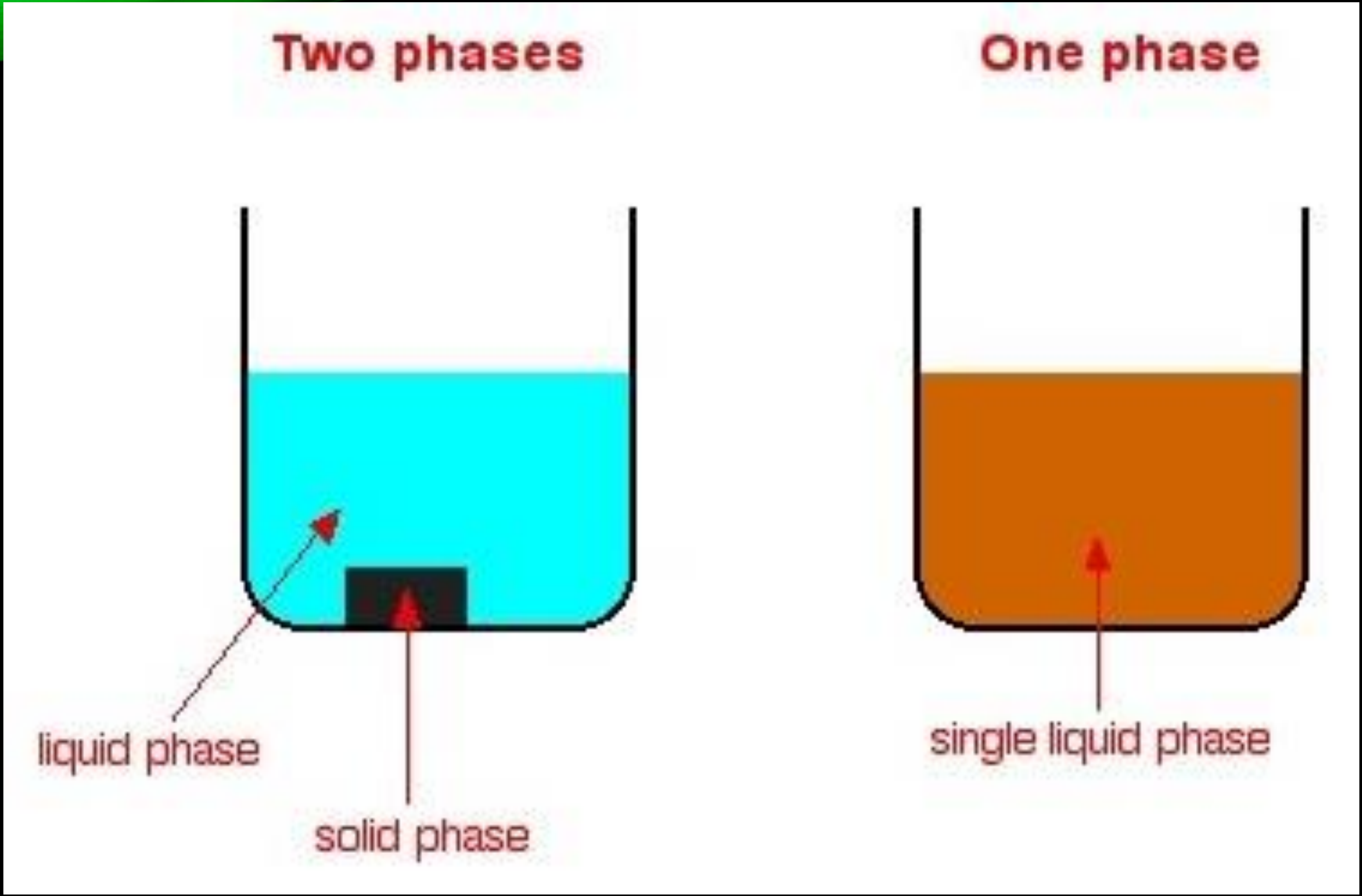
TWO TYPES OF CATALYST:

- Homogeneous (one phase)

the catalyst in the same phase as the reactants.

- Heterogeneous (two phases)

Involves the use of a catalyst in a different phase from the reactants.

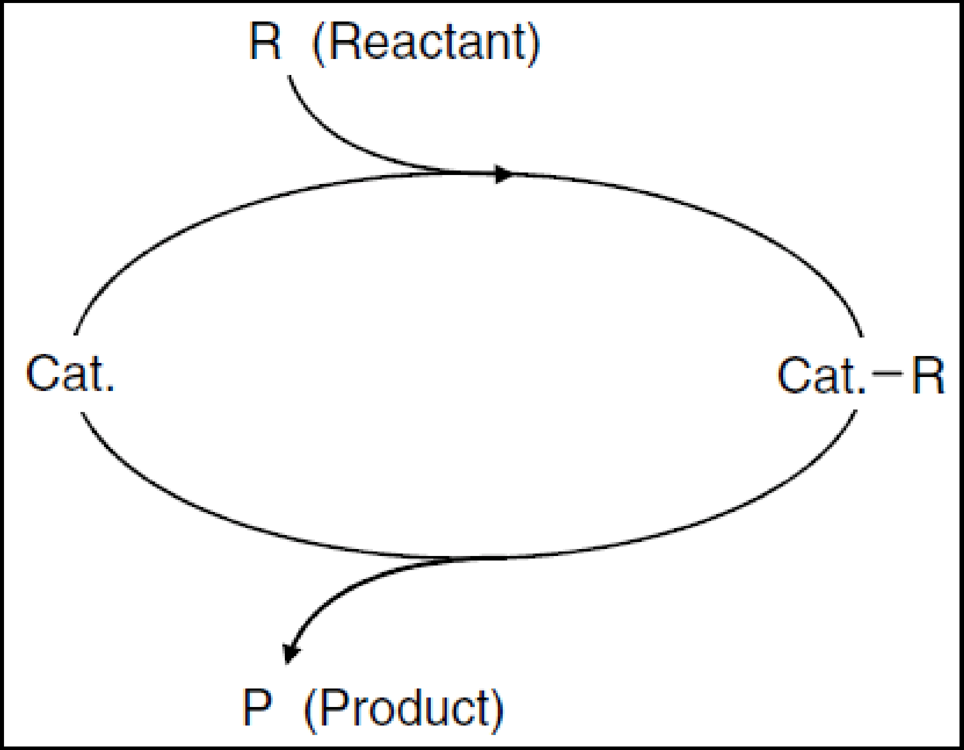


Two phases

One phase

HETEROGENEOUS CATALYTIC CYCLE

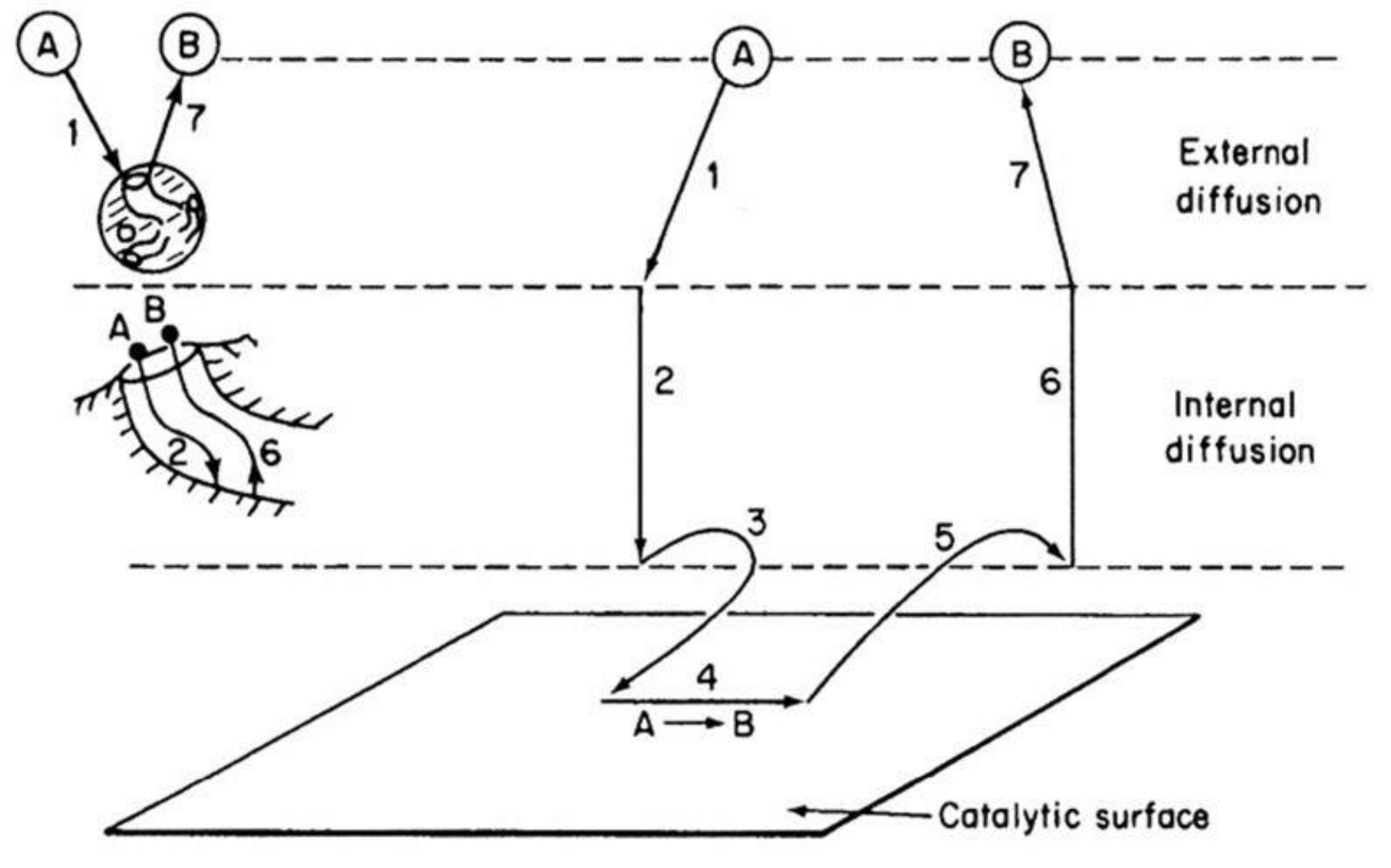
R (reactant) ⟶ P (product)



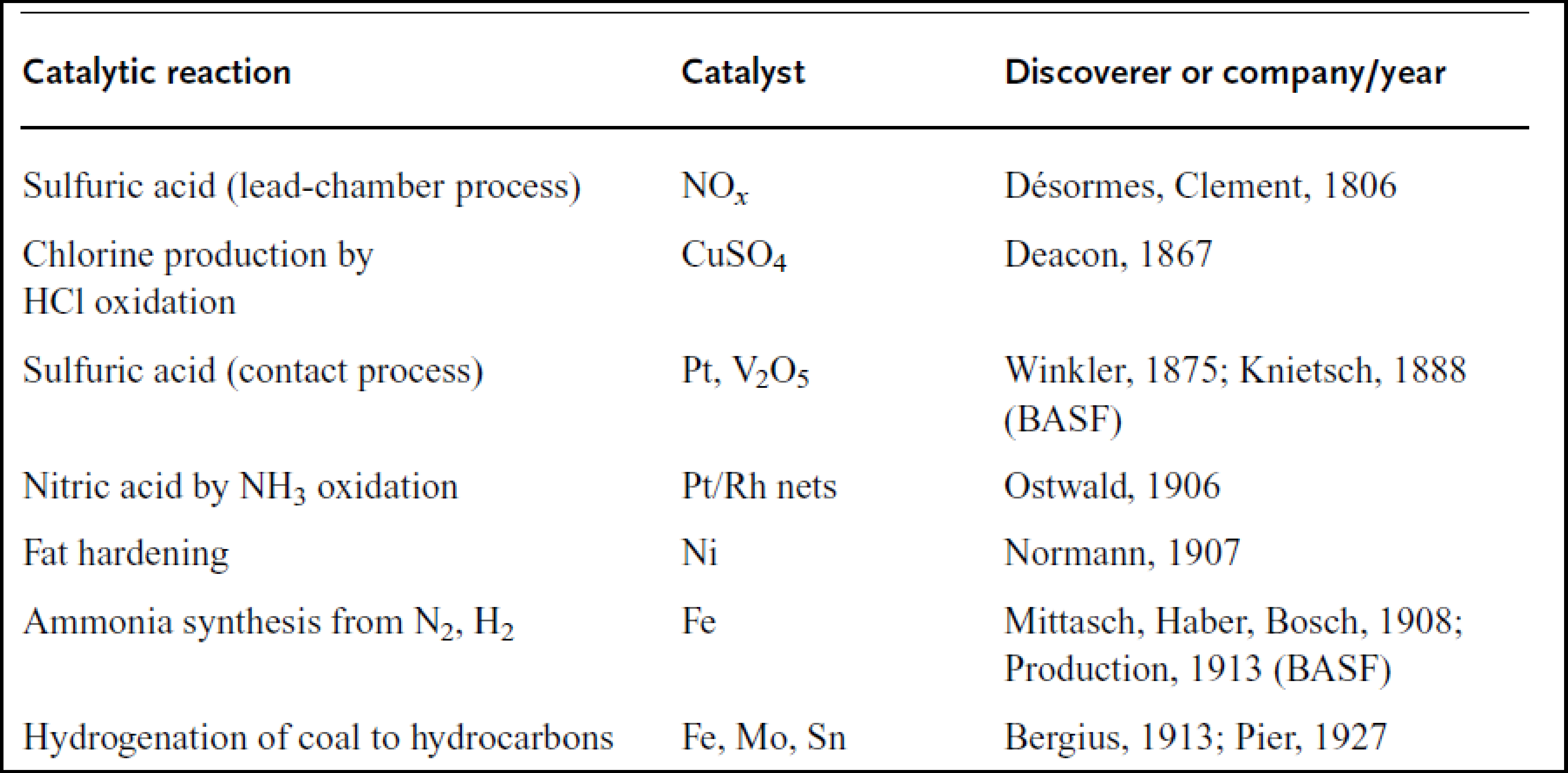
STEPS IN A CATALYTIC REACTION

- Adsorption : Is where something sticks to a surface.
- Active Sites : Is a part of the surface which is particularly good at adsorbing things and helping them to react.
- Desorption : means that the product molecules break away.

STEPS IN A CATALYTIC REACTION

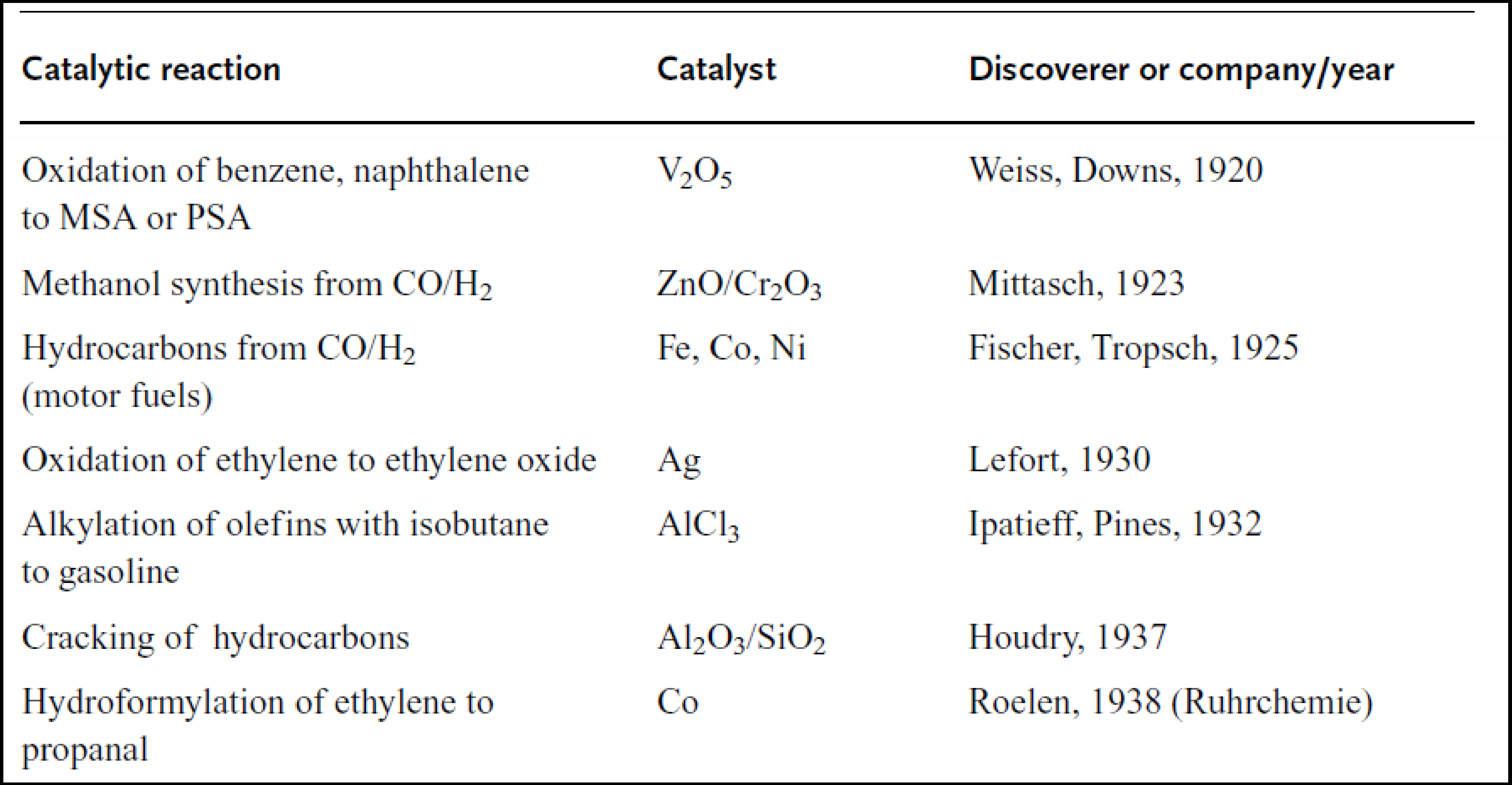


HISTORY OF THE CATALYSIS OF INDUSTRIAL PROCESSES



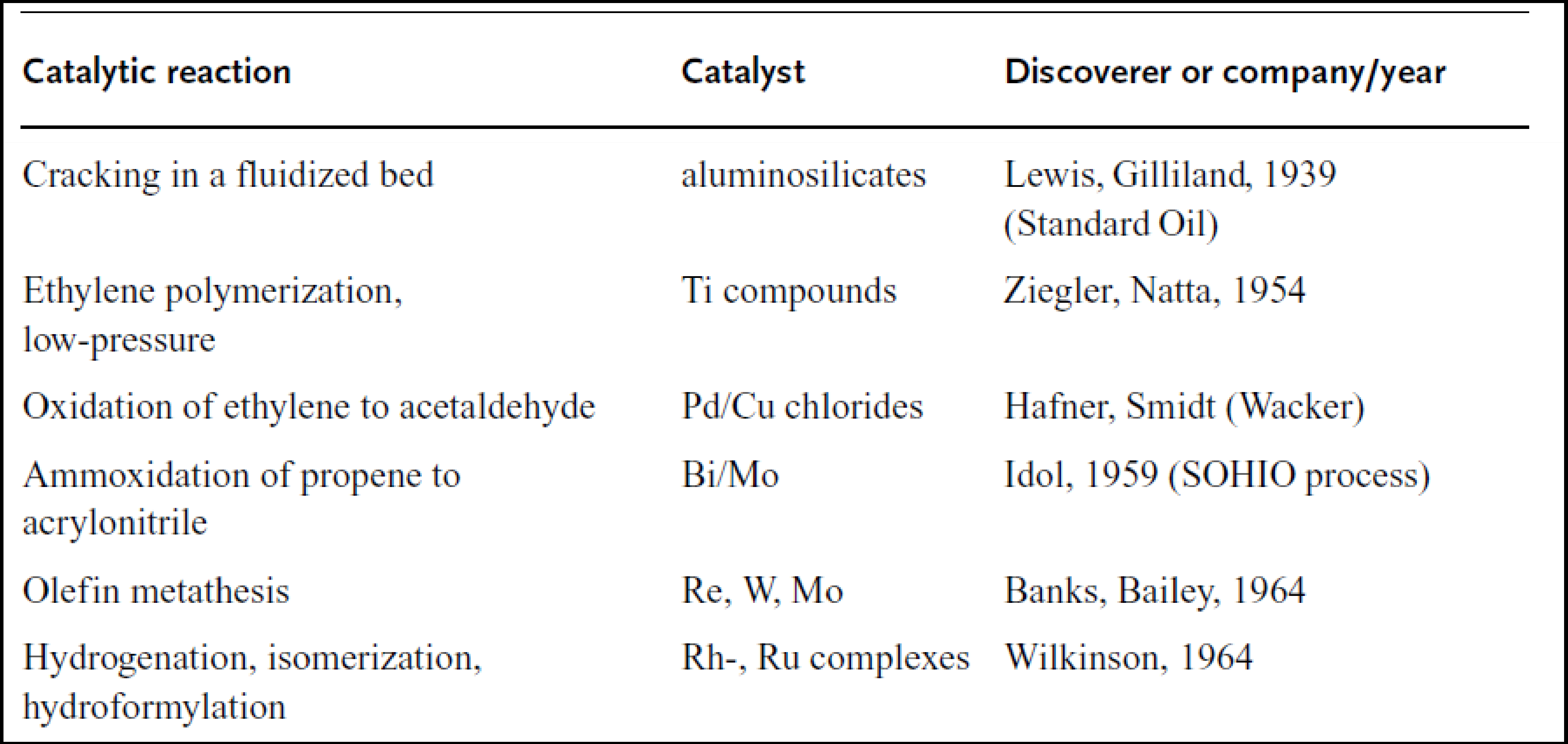
Catalytic reaction	**Catalyst**	**Discoverer or company/year**
Sulfuric acid (lead-chamber process)	NO_x	Désormes, Clement, 1806
Chlorine production by HCl oxidation	$CuSO_4$	Deacon, 1867
Sulfuric acid (contact process)	Pt, V_2O_5	Winkler, 1875; Knietsch, 1888 (BASF)
Nitric acid by NH_3 oxidation	Pt/Rh nets	Ostwald, 1906
Fat hardening	Ni	Normann, 1907
Ammonia synthesis from N_2, H_2	Fe	Mittasch, Haber, Bosch, 1908; Production, 1913 (BASF)
Hydrogenation of coal to hydrocarbons	Fe, Mo, Sn	Bergius, 1913; Pier, 1927

HISTORY OF THE CATALYSIS OF INDUSTRIAL PROCESSES



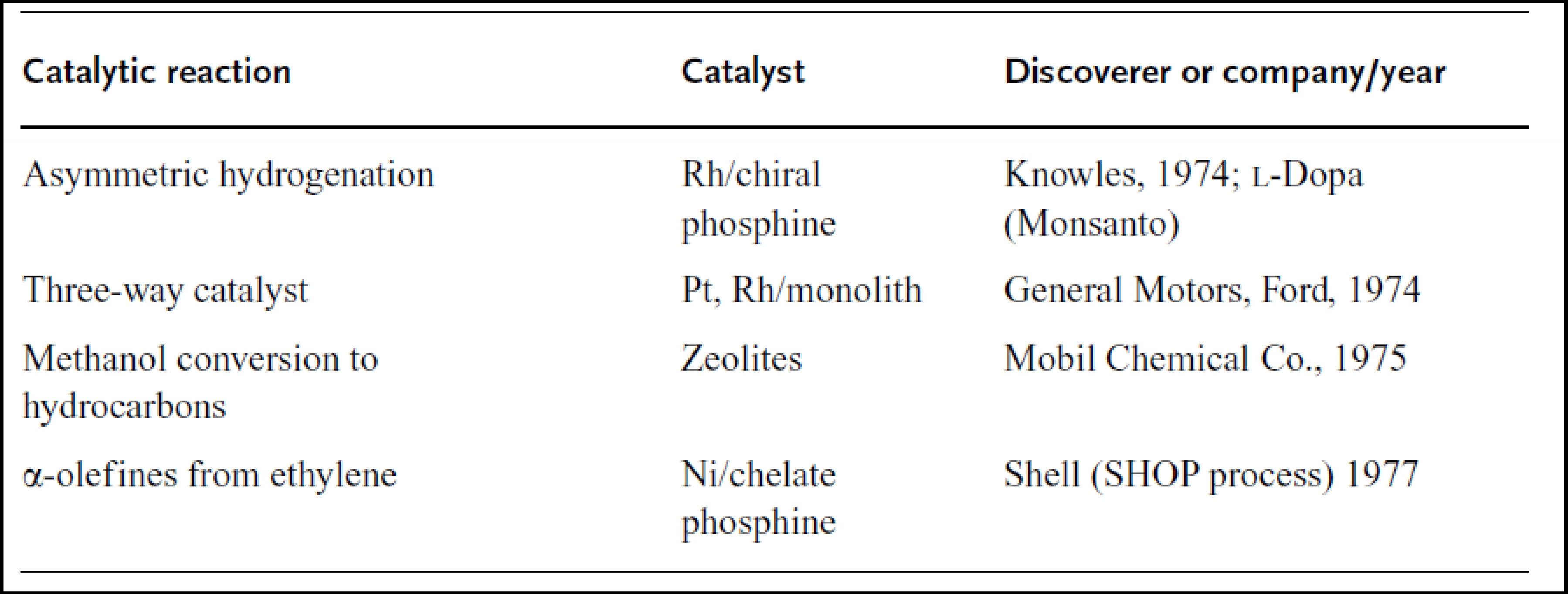
Catalytic reaction	Catalyst	Discoverer or company/year
Oxidation of benzene, naphthalene to MSA or PSA	V_2O_5	Weiss, Downs, 1920
Methanol synthesis from CO/H_2	ZnO/Cr_2O_3	Mittasch, 1923
Hydrocarbons from CO/H_2 (motor fuels)	Fe, Co, Ni	Fischer, Tropsch, 1925
Oxidation of ethylene to ethylene oxide	Ag	Lefort, 1930
Alkylation of olefins with isobutane to gasoline	$AlCl_3$	Ipatieff, Pines, 1932
Cracking of hydrocarbons	Al_2O_3/SiO_2	Houdry, 1937
Hydroformylation of ethylene to propanal	Co	Roelen, 1938 (Ruhrchemie)

HISTORY OF THE CATALYSIS OF INDUSTRIAL PROCESSES



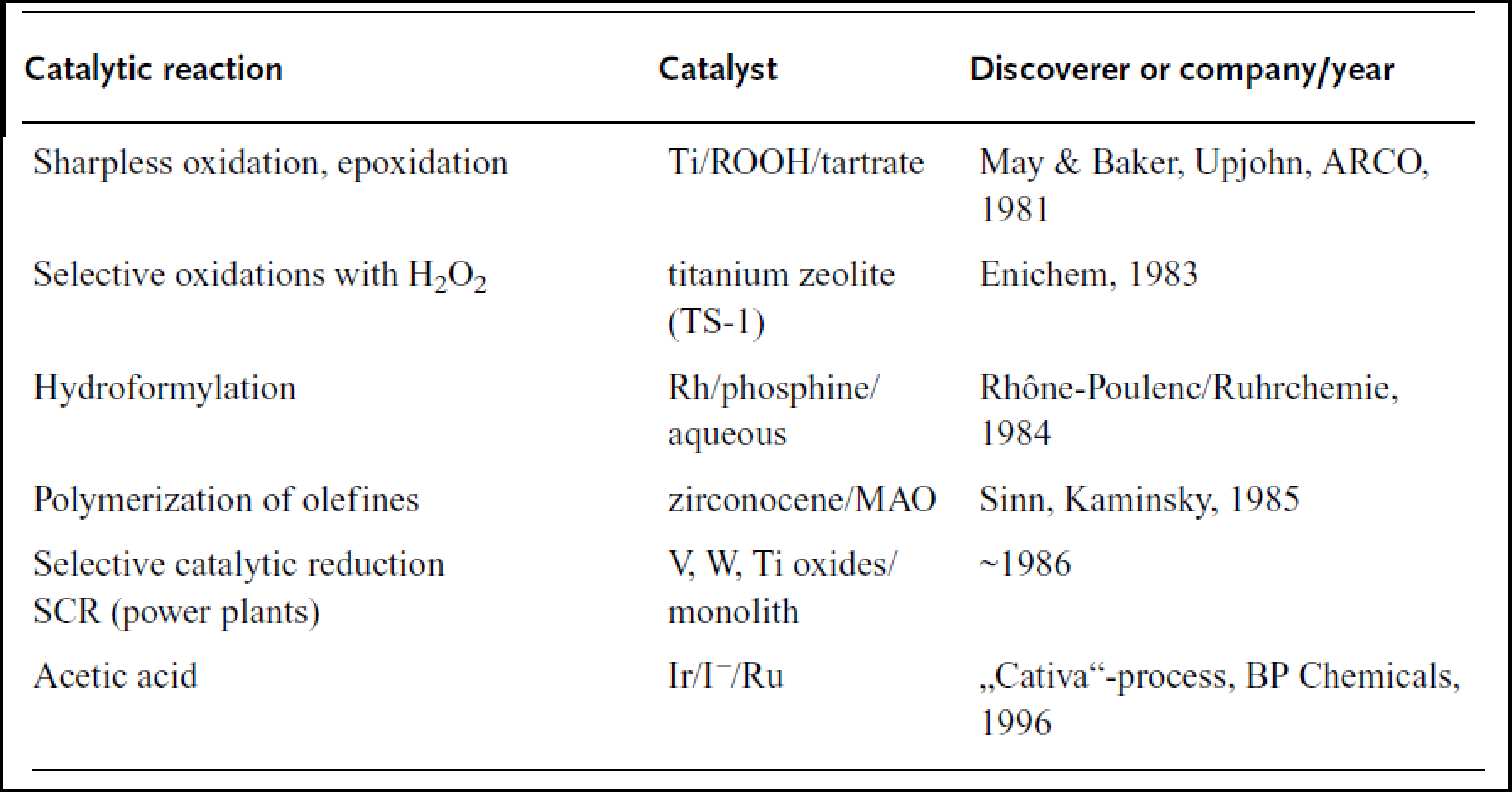
Catalytic reaction	Catalyst	Discoverer or company/year
Cracking in a fluidized bed	aluminosilicates	Lewis, Gilliland, 1939 (Standard Oil)
Ethylene polymerization, low-pressure	Ti compounds	Ziegler, Natta, 1954
Oxidation of ethylene to acetaldehyde	Pd/Cu chlorides	Hafner, Smidt (Wacker)
Ammoxidation of propene to acrylonitrile	Bi/Mo	Idol, 1959 (SOHIO process)
Olefin metathesis	Re, W, Mo	Banks, Bailey, 1964
Hydrogenation, isomerization, hydroformylation	Rh-, Ru complexes	Wilkinson, 1964

HISTORY OF THE CATALYSIS OF INDUSTRIAL PROCESSES



Catalytic reaction	Catalyst	Discoverer or company/year
Asymmetric hydrogenation	Rh/chiral phosphine	Knowles, 1974; L-Dopa (Monsanto)
Three-way catalyst	Pt, Rh/monolith	General Motors, Ford, 1974
Methanol conversion to hydrocarbons	Zeolites	Mobil Chemical Co., 1975
α-olefines from ethylene	Ni/chelate phosphine	Shell (SHOP process) 1977

HISTORY OF THE CATALYSIS OF INDUSTRIAL PROCESSES



Catalytic reaction	Catalyst	Discoverer or company/year
Sharpless oxidation, epoxidation	Ti/ROOH/tartrate	May & Baker, Upjohn, ARCO, 1981
Selective oxidations with H_2O_2	titanium zeolite (TS-1)	Enichem, 1983
Hydroformylation	Rh/phosphine/aqueous	Rhône-Poulenc/Ruhrchemie, 1984
Polymerization of olefines	zirconocene/MAO	Sinn, Kaminsky, 1985
Selective catalytic reduction SCR (power plants)	V, W, Ti oxides/monolith	~1986
Acetic acid	$Ir/I^-/Ru$	„Cativa"-process, BP Chemicals, 1996

MODE OF ACTION OF CATALYSTS

The suitability of a catalyst for an industrial process depends mainly on the following three properties:

- Activity
- Selectivity
- Stability (deactivation behavior)

ACTIVITY

- Activity is a measure of how fast one or more reactions proceed in the presence of the catalyst.
- Activity can be defined in terms of kinetics or from a more practically oriented viewpoint. In a formal kinetic treatment, it is appropriate to measure reaction rates in the temperature and concentration ranges that will be present in the reactor.

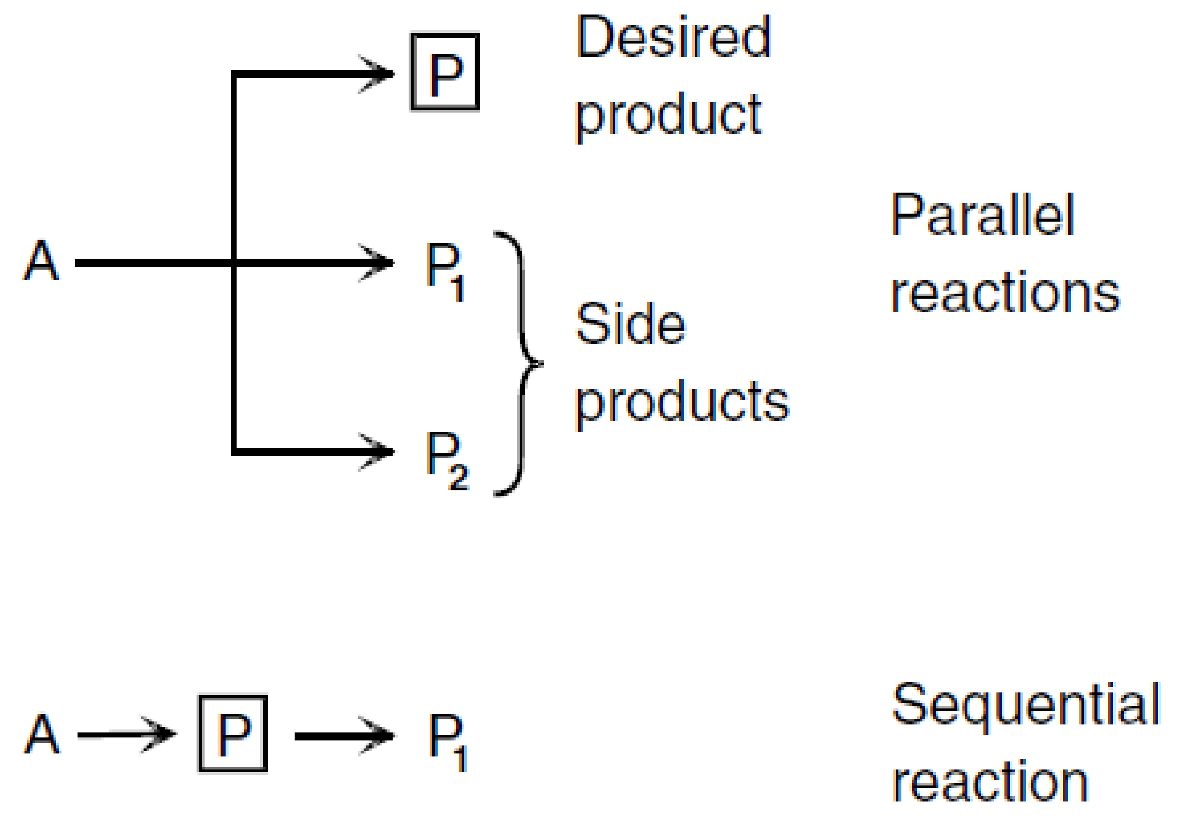
Small reactor, less catalyst == lower cost

SELECTIVITY

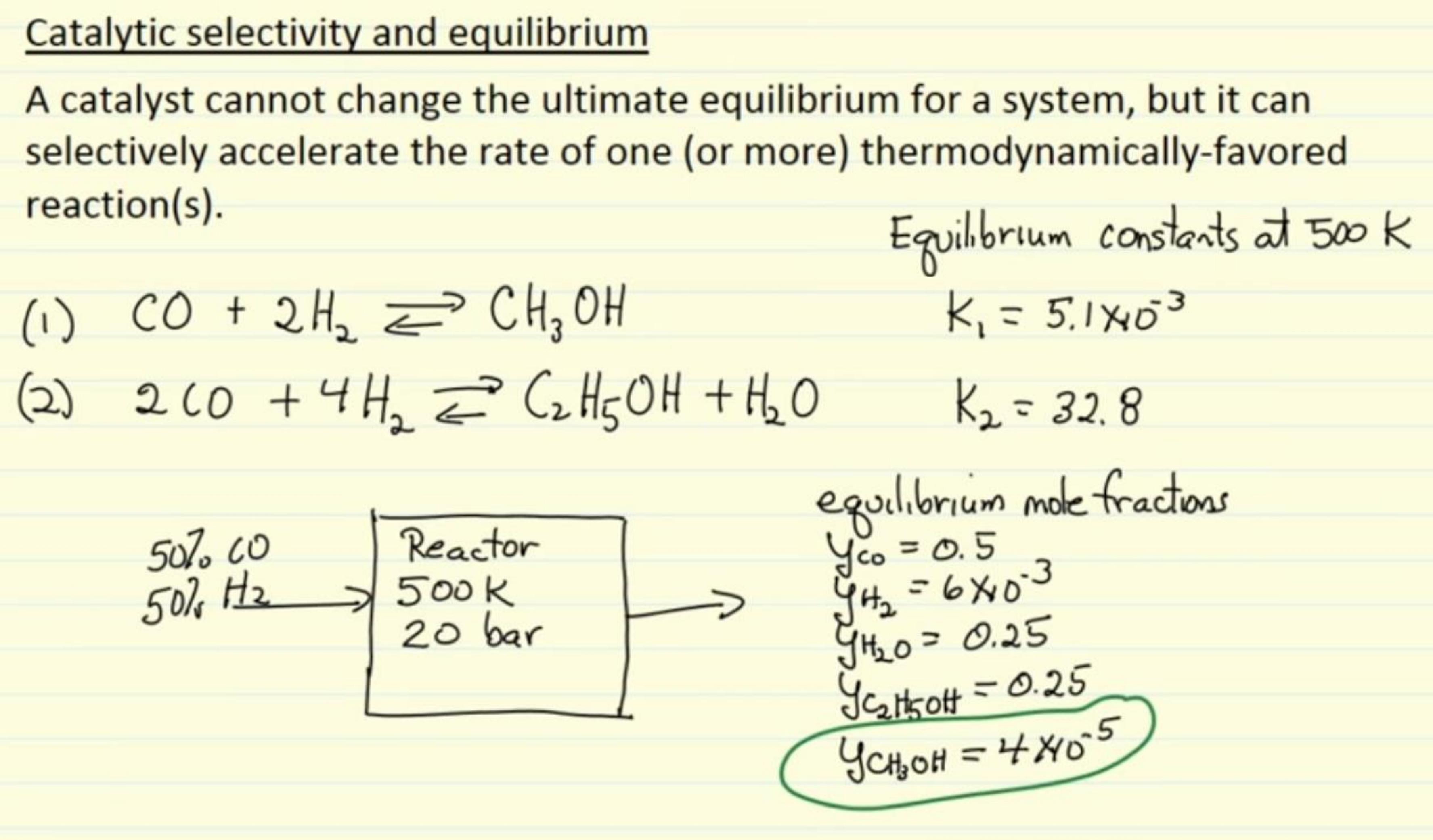
- The selectivity of a reaction is the fraction of the starting material that is converted to the desired product.
- It is expressed by the ratio of the amount of desired product to the reacted quantity of a reaction partner and therefore gives information about the course of the reaction.
- In addition to the desired reaction, parallel and sequential reactions can also occur

Less reactant, less energy, less waste (less byproduct) == lower cost

SELECTIVITY



SELECTIVITY



Catalytic selectivity and equilibrium

A catalyst cannot change the ultimate equilibrium for a system, but it can selectively accelerate the rate of one (or more) thermodynamically-favored reaction(s).

Equilibrium constants at 500 K

(1) $CO + 2H_2 \rightleftharpoons CH_3OH$ $\quad K_1 = 5.1\times10^{-3}$

(2) $2CO + 4H_2 \rightleftharpoons C_2H_5OH + H_2O$ $\quad K_2 = 32.8$

50% CO
50% H_2 →

Reactor
500 K
20 bar

→

equilibrium mole fractions

$y_{CO} = 0.5$

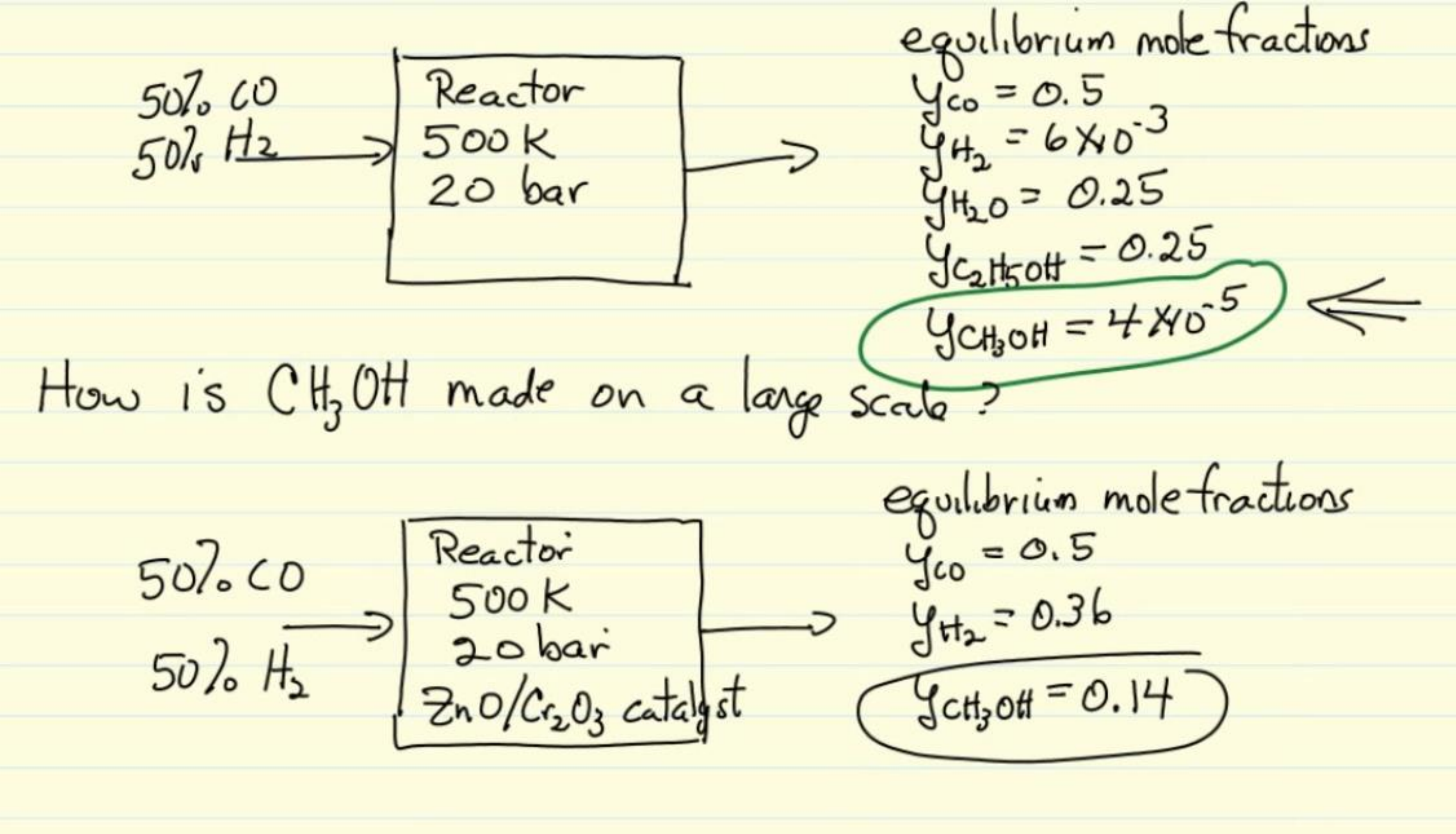
$y_{H_2} = 6\times10^{-3}$

$y_{H_2O} = 0.25$

$y_{C_2H_5OH} = 0.25$

$\boxed{y_{CH_3OH} = 4\times10^{-5}}$

SELECTIVITY



50% CO
50% H_2 → Reactor 500 K 20 bar →

equilibrium mole fractions
$y_{CO} = 0.5$
$y_{H_2} = 6 \times 10^{-3}$
$y_{H_2O} = 0.25$
$y_{C_2H_5OH} = 0.25$
$y_{CH_3OH} = 4 \times 10^{-5}$ ⇐

How is CH_3OH made on a large scale?

50% CO
50% H_2 → Reactor 500 K 20 bar ZnO/Cr_2O_3 catalyst →

equilibrium mole fractions
$y_{CO} = 0.5$
$y_{H_2} = 0.36$
$y_{CH_3OH} = 0.14$

STABILITY

- The chemical, thermal, and mechanical stability of a catalyst determines its lifetime in industrial reactors. Catalyst stability is influenced by numerous factors, including decomposition, coking, and poisoning.
- Catalyst deactivation can be followed by measuring activity or selectivity as a function of time.

Long time to all catalyst deactivation == lower cost

MODE OF ACTION OF CATALYSTS

- Today the efficient use of raw materials and energy is of major importance, and it is preferable to optimize existing processes than to develop new ones.
- For various reasons, the target quantities should be given the following order of priority:

Selectivity > Stability > Activity

KINDS OF CATALYST

1. Acid Catalysis
2. Base Catalysis
3. Metal oxides, Sulfides, and Hydrides

KINDS OF CATALYST

- Acid Catalysis
- Base Catalysis
- Metal oxides, Sulfides, and Hydrides

ACID CATALYSIS

- transfer of protons from an acidic catalyst to the reactant
- Acid catalysis is mainly used for organic chemical reactions.
- Acid used for acid catalysis include hydrofluoric acid (in the alkylation process), phosphoric acid, toluenesulfonic acid, polystyrene sulfonate, heteropoly acids, zeolites.

BASE CATALYSIS

- transfer of protons from the reactant to a basic catalyst.
- Often referred to as an alkali if OH− ions are involved.
- The reactions catalyzed by solid base catalysts can be classified into three types: double bond isomerization, addition of anion and proton to various double bonds, and alcohol decomposition. These are represented by 1-butene isomerization, hydrogenation of conjugated 1,3-butadiene and dehydration of 2-butanol.

METAL OXIDES, SULFIDES, AND HYDRIDES

- Form a transition between acid/base and metal catalysts.

FLUID AND SOLID CATALYSIS

Multitubular reactors

Fluidized beds

Fixed Bed

Spray Tower

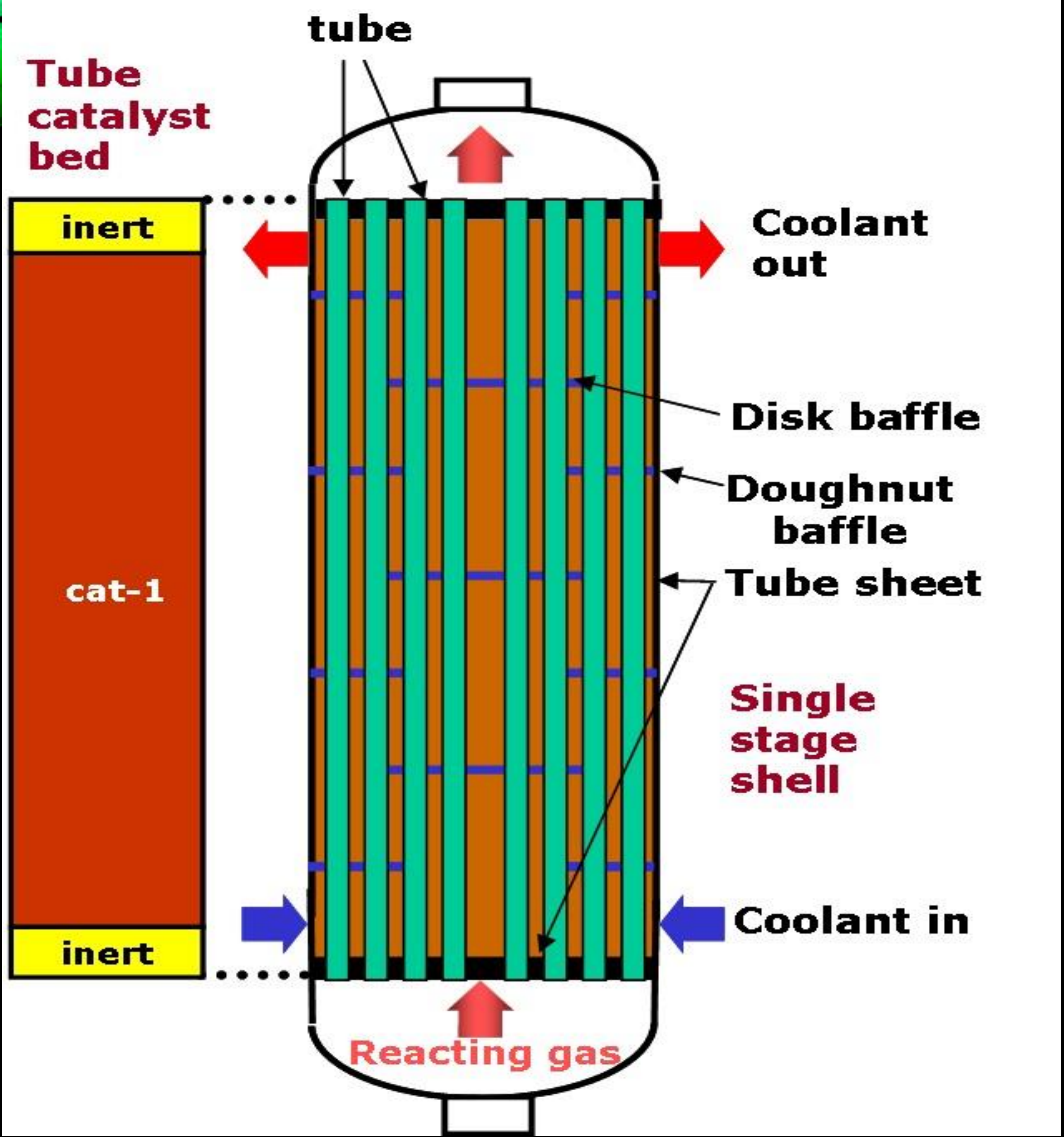
Two-Phase Flow

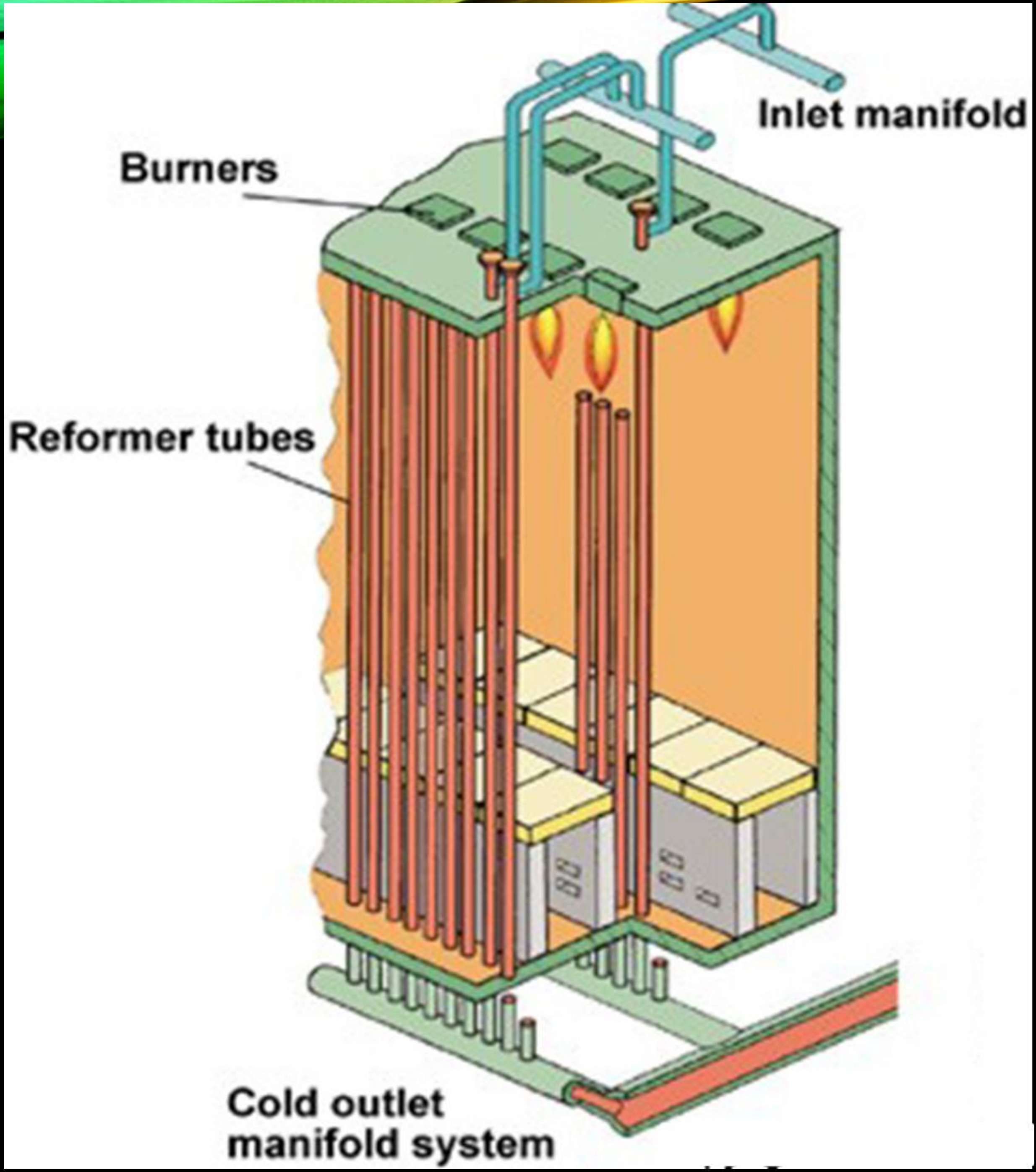
FLUID AND SOLID CATALYSIS

- Multitubular reactors
- Fluidized beds
- Fixed Bed
- Spray Tower
- Two-Phase Flow

MULTITUBULAR REACTORS

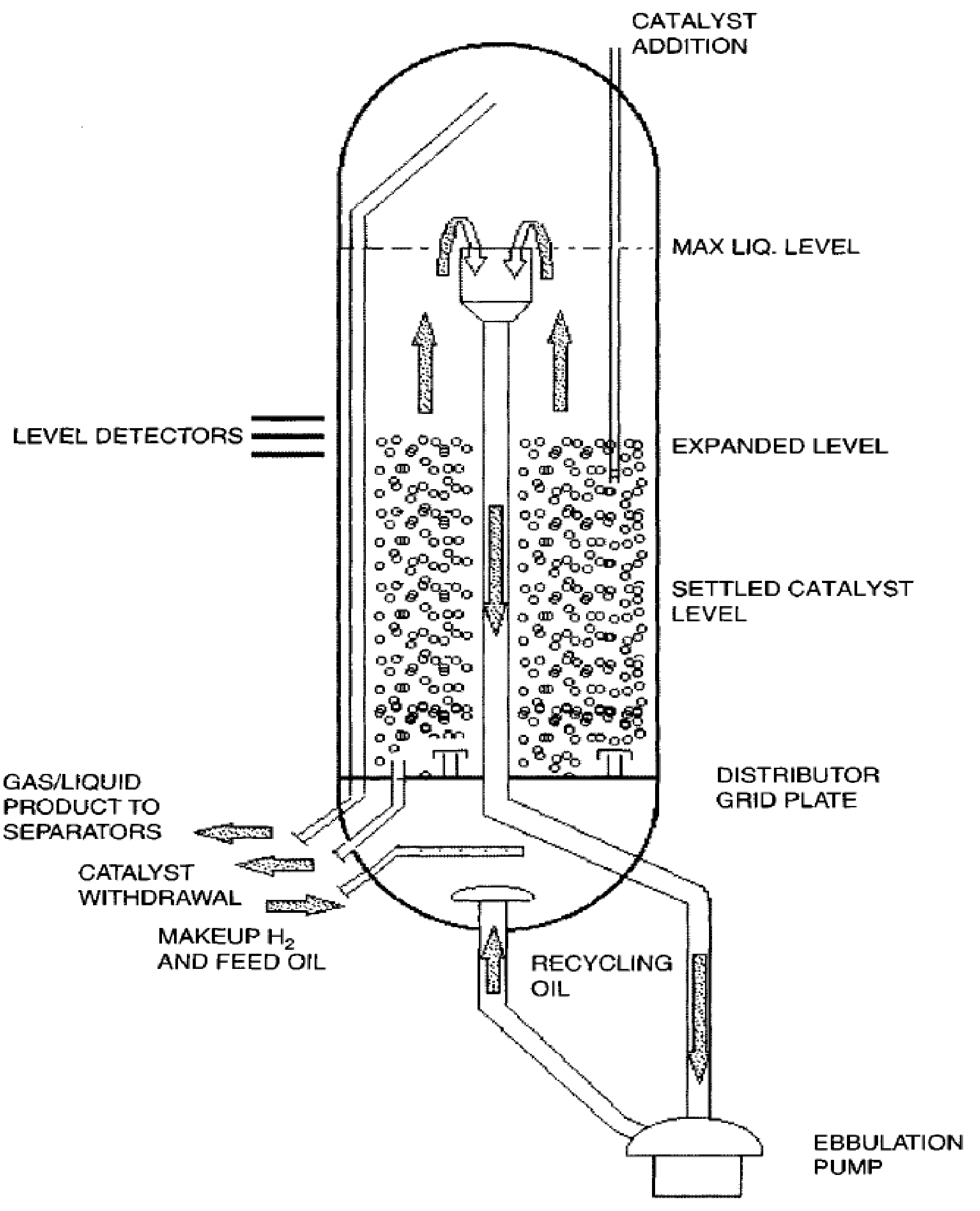
- These reactors are shell-and-tube configuration and have catalyst in the tubes.

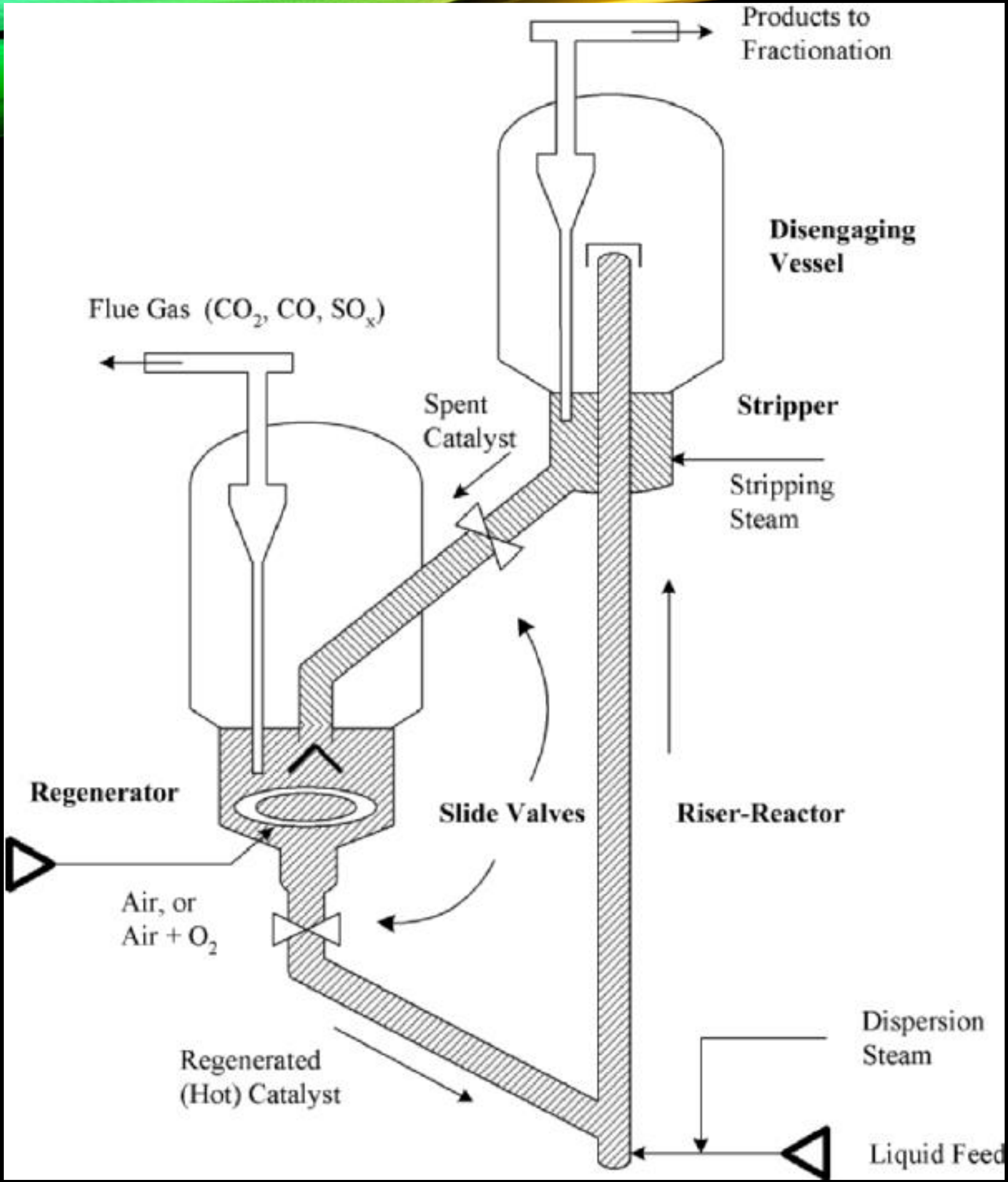

tube
Tube catalyst bed
inert
cat-1
inert
Coolant out
Disk baffle
Doughnut baffle
Tube sheet
Single stage shell
Coolant in
Reacting gas


Inlet manifold
Burners
Reformer tubes
Cold outlet manifold system

FLUIDIZED BED

- Device that can be used to carry out a variety of multiphase chemical reactions.
- A catalyst possibly shaped as tiny spheres.

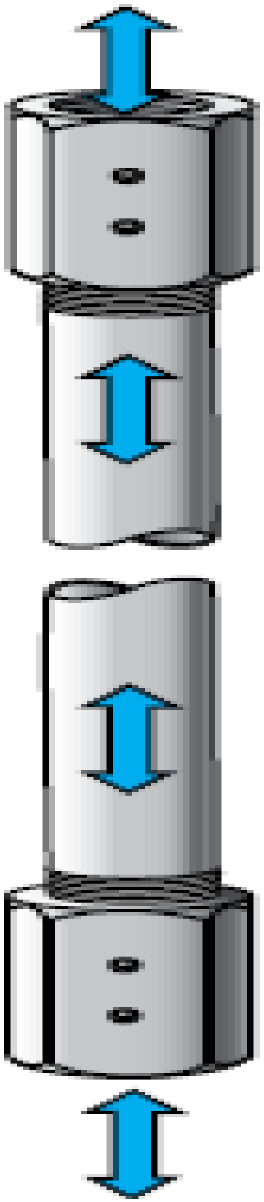

CATALYST ADDITION
MAX LIQ. LEVEL
LEVEL DETECTORS
EXPANDED LEVEL
SETTLED CATALYST LEVEL
DISTRIBUTOR GRID PLATE
GAS/LIQUID PRODUCT TO SEPARATORS
CATALYST WITHDRAWAL
MAKEUP H_2 AND FEED OIL
RECYCLING OIL
EBBULATION PUMP


Products to Fractionation
Disengaging Vessel
Flue Gas (CO_2, CO, SO_x)
Spent Catalyst
Stripper
Stripping Steam
Regenerator
Slide Valves
Riser-Reactor
Air, or Air + O_2
Dispersion Steam
Regenerated (Hot) Catalyst
Liquid Feed

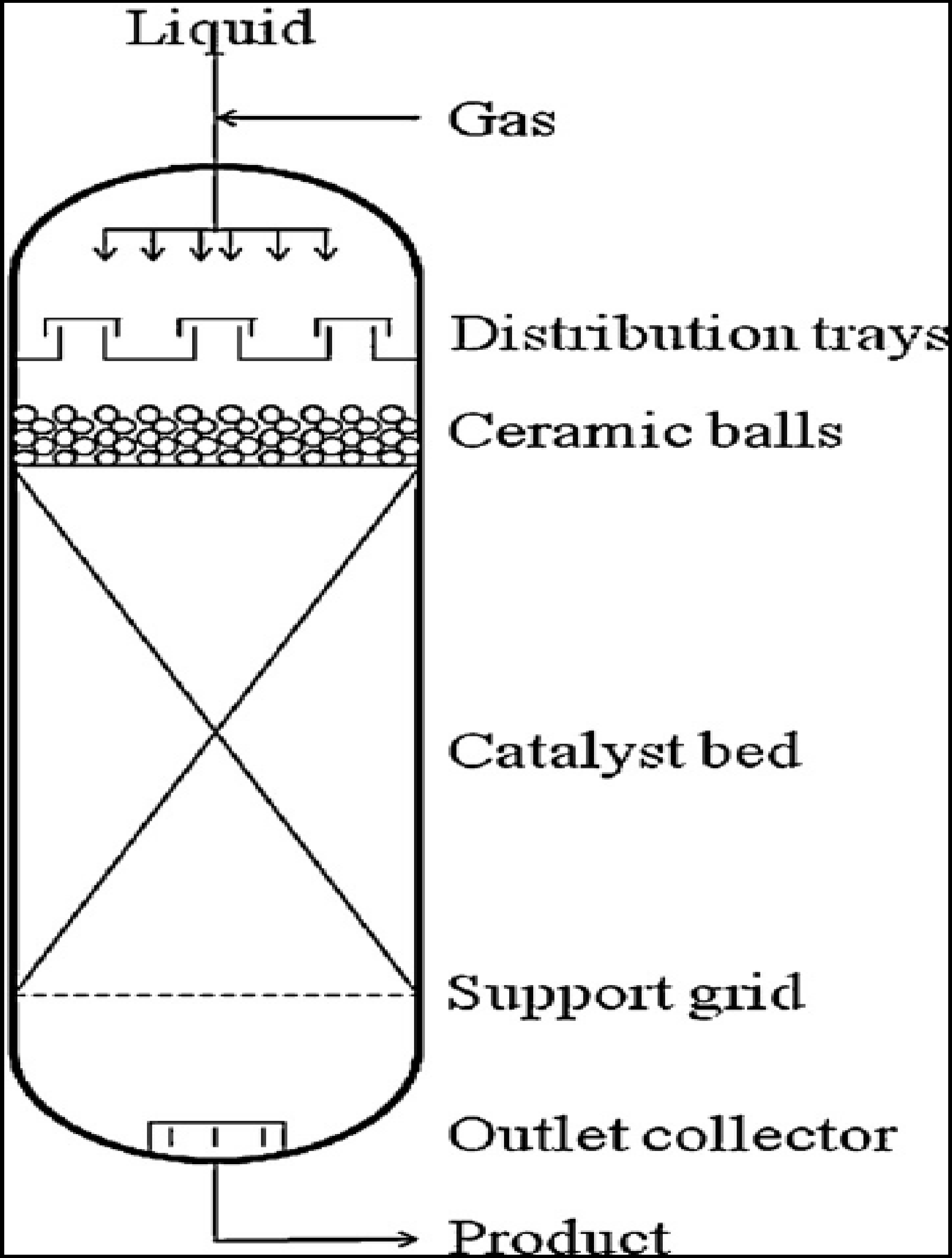
FIXED BED

- Fixed bed reactor is a cylindrical tube, randomly filled with catalyst particles, which may be spheres or cylindrical pellets.

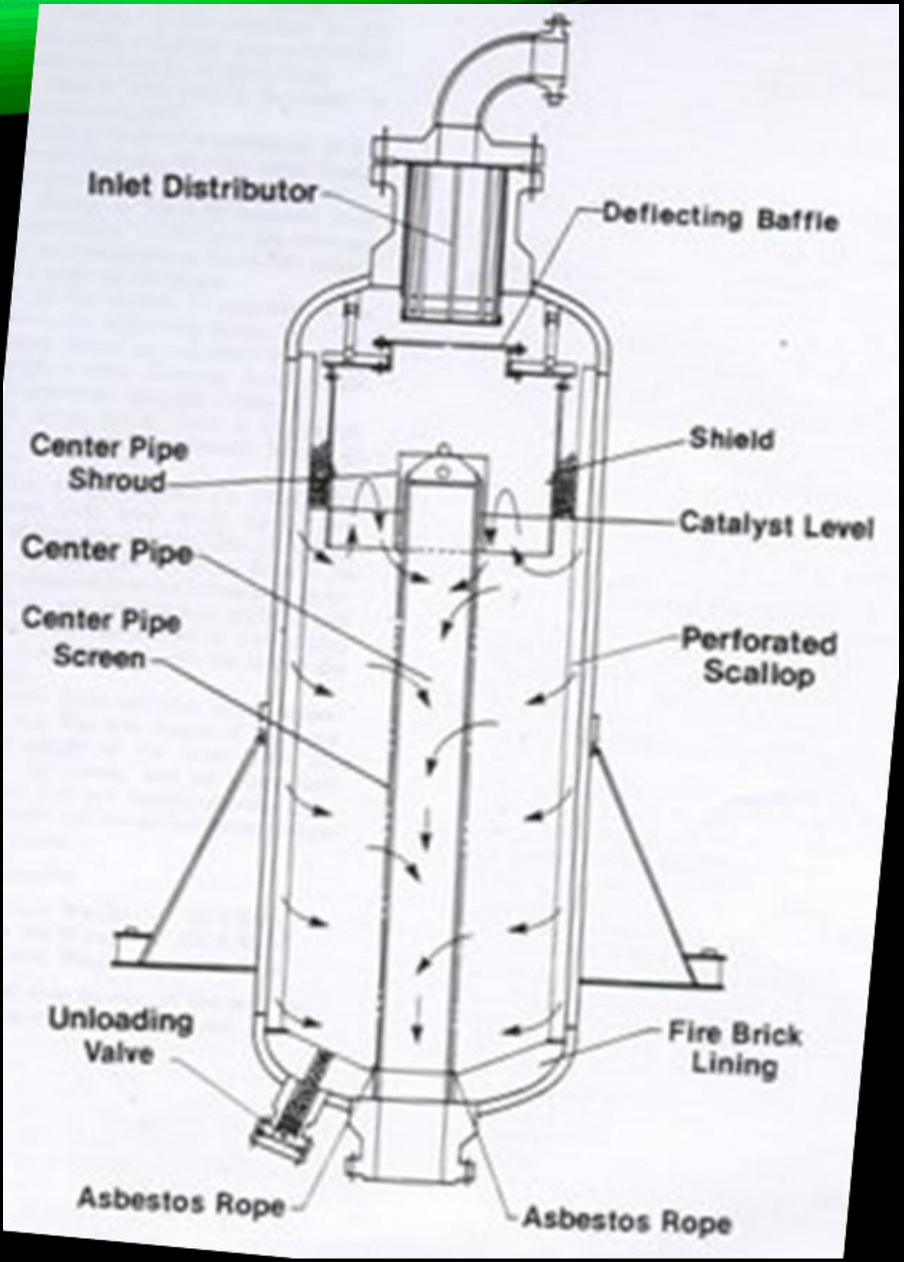
Fixed Bed (Tube) Reactors

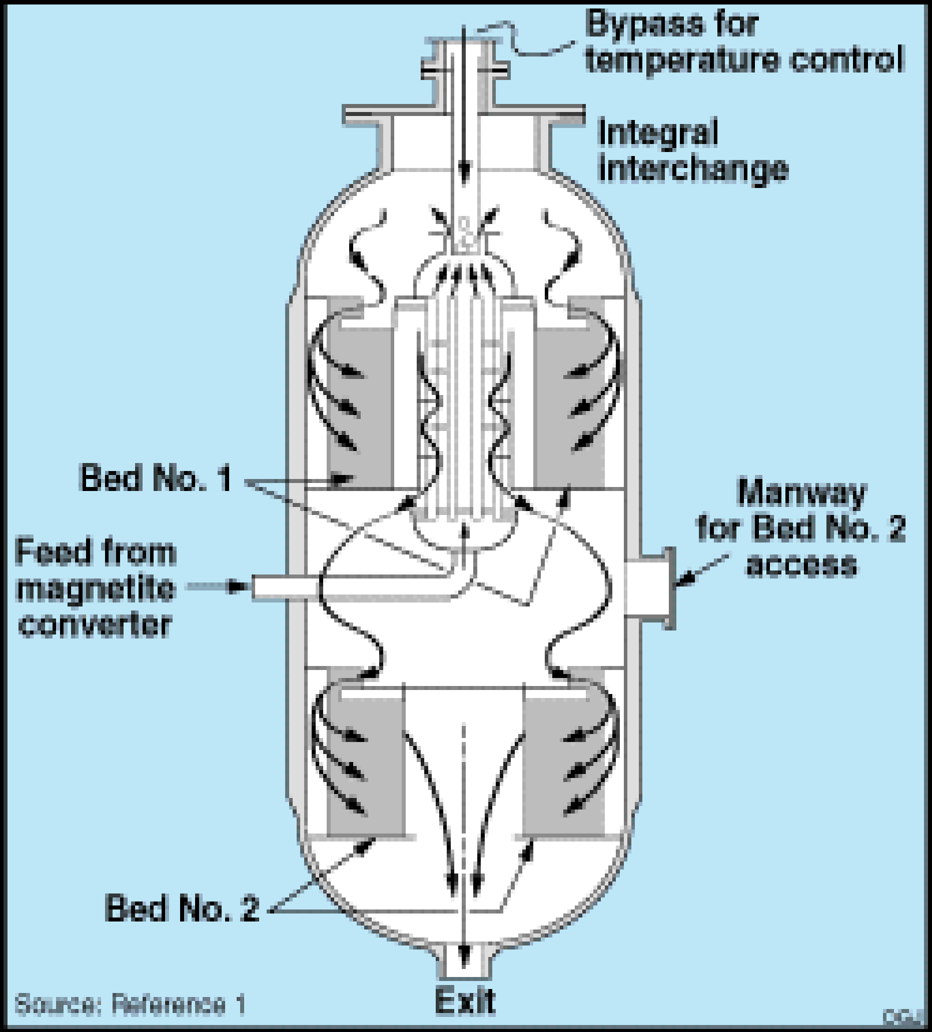


TRICKLE BED REACTOR



radial flow reactor





Source: Reference 1

SPRAY TOWER

- Are a form of pollution control technology.
- Consist of empty cylindrical vessels made of steel or plastic and nozzles that spray liquid into the vessels

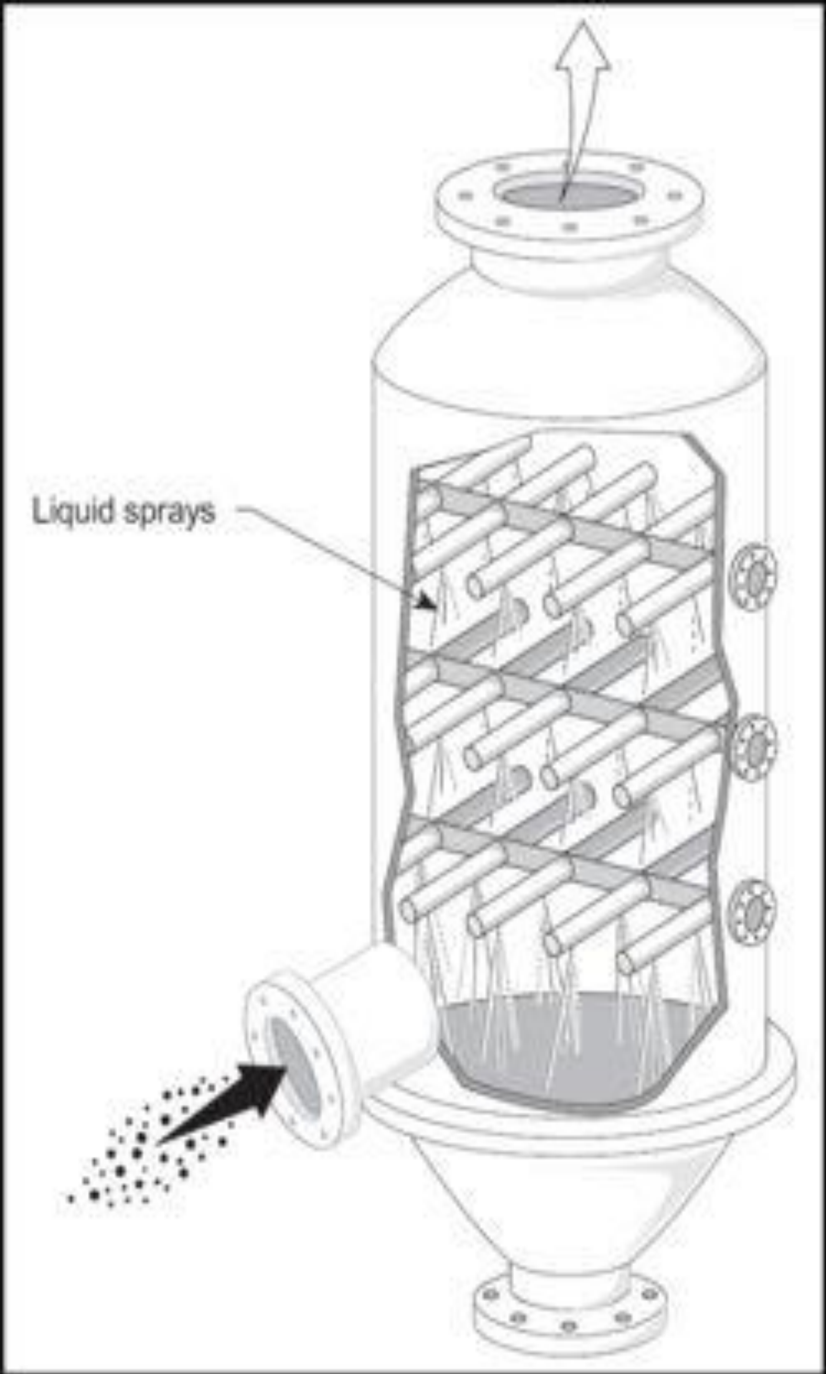
TWO TYPES OF SPRAY TOWERS

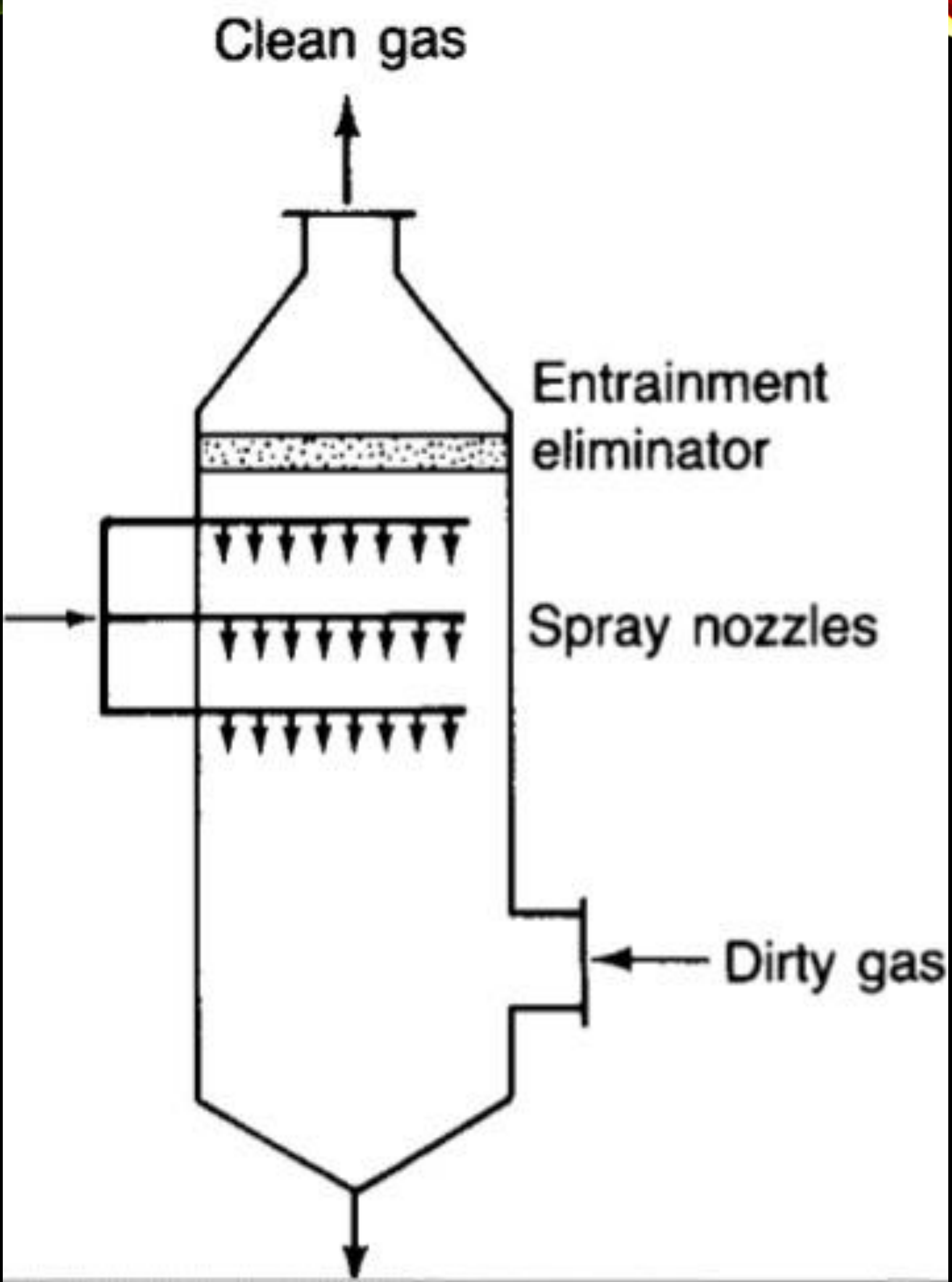
1. **Cocurrent Flow**

   -are smaller than countercurrent-flow spray towers

2. **Crosscurrent Flow**

   - the gas and liquid flow in directions perpendicular to each other.

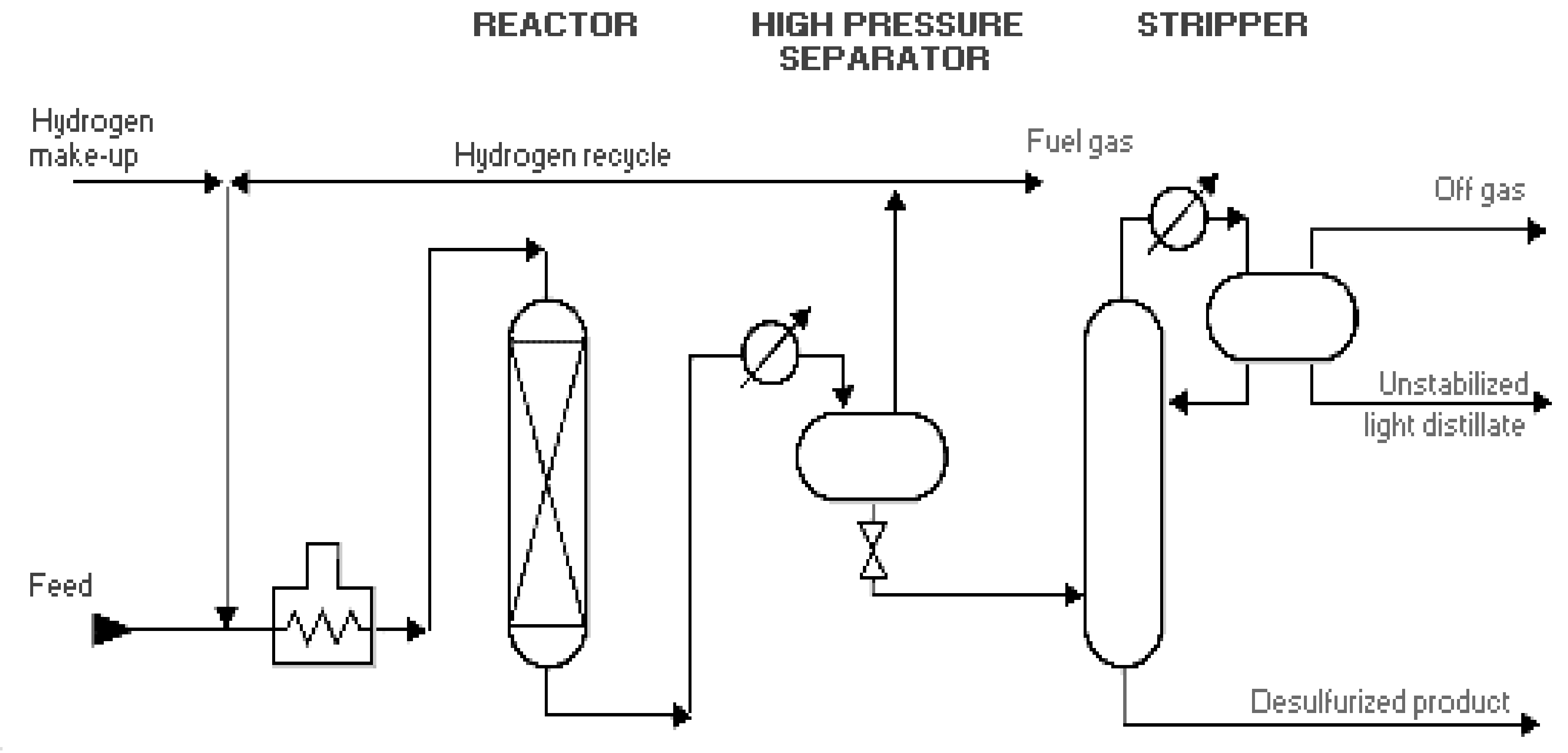

Liquid sprays


Clean gas
Entrainment eliminator
Spray nozzles
Dirty gas

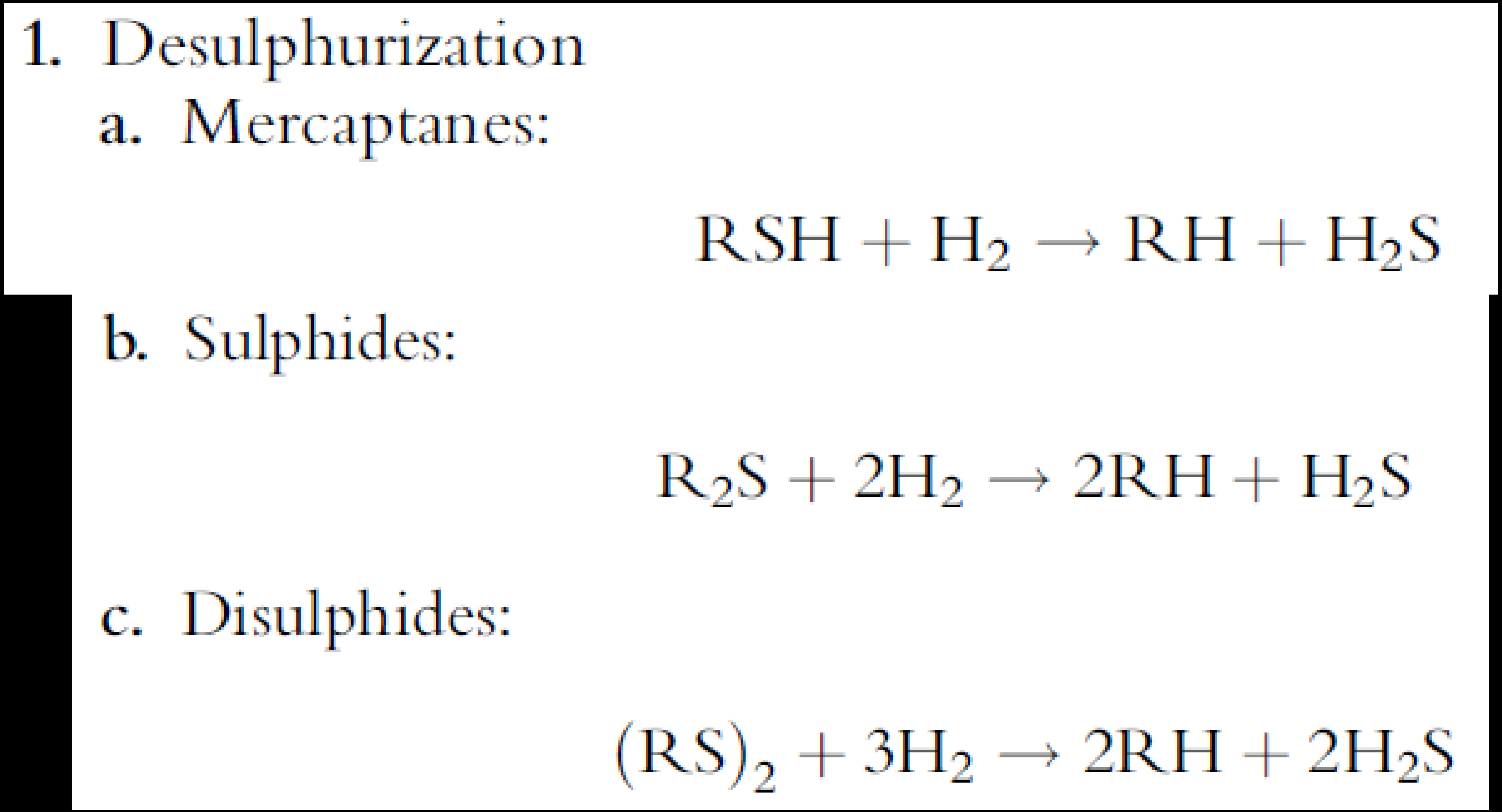
CASE STUDY

Hydrotreating and HYDROCRACKING processes


HYDROTREATING AND HYDROCRACKING PROCESSES



HYDROTREATING BASIC REACTIONS



1. Desulphurization
   a. Mercaptanes:

$$RSH + H_2 \rightarrow RH + H_2S$$

   b. Sulphides:

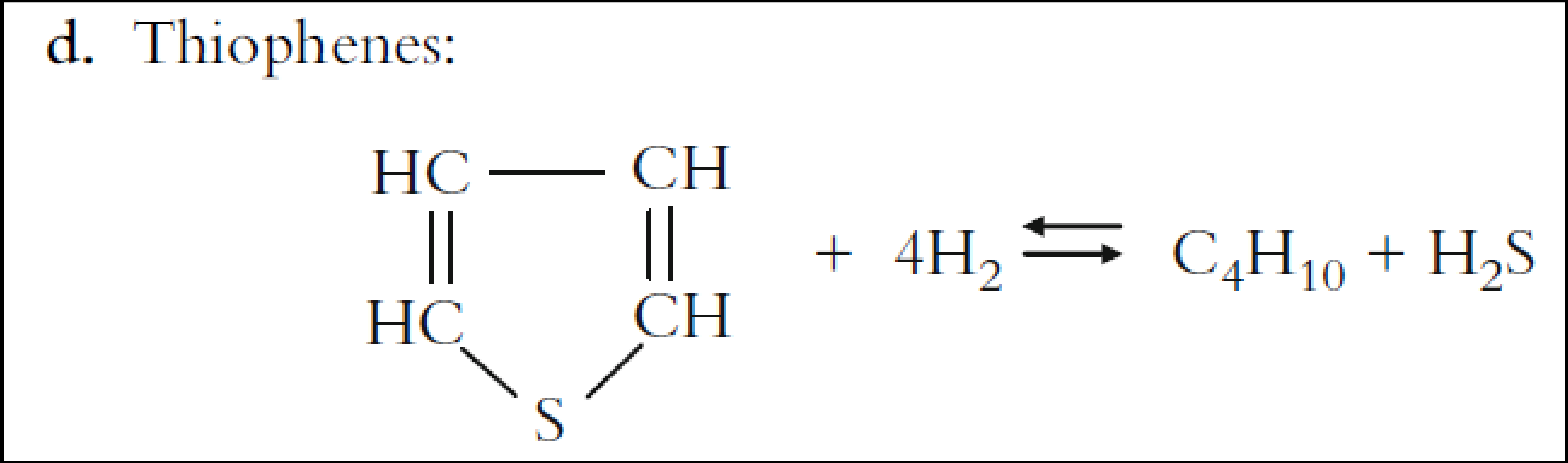
$$R_2S + 2H_2 \rightarrow 2RH + H_2S$$

   c. Disulphides:

$$(RS)_2 + 3H_2 \rightarrow 2RH + 2H_2S$$

HYDROTREATING BASIC REACTIONS

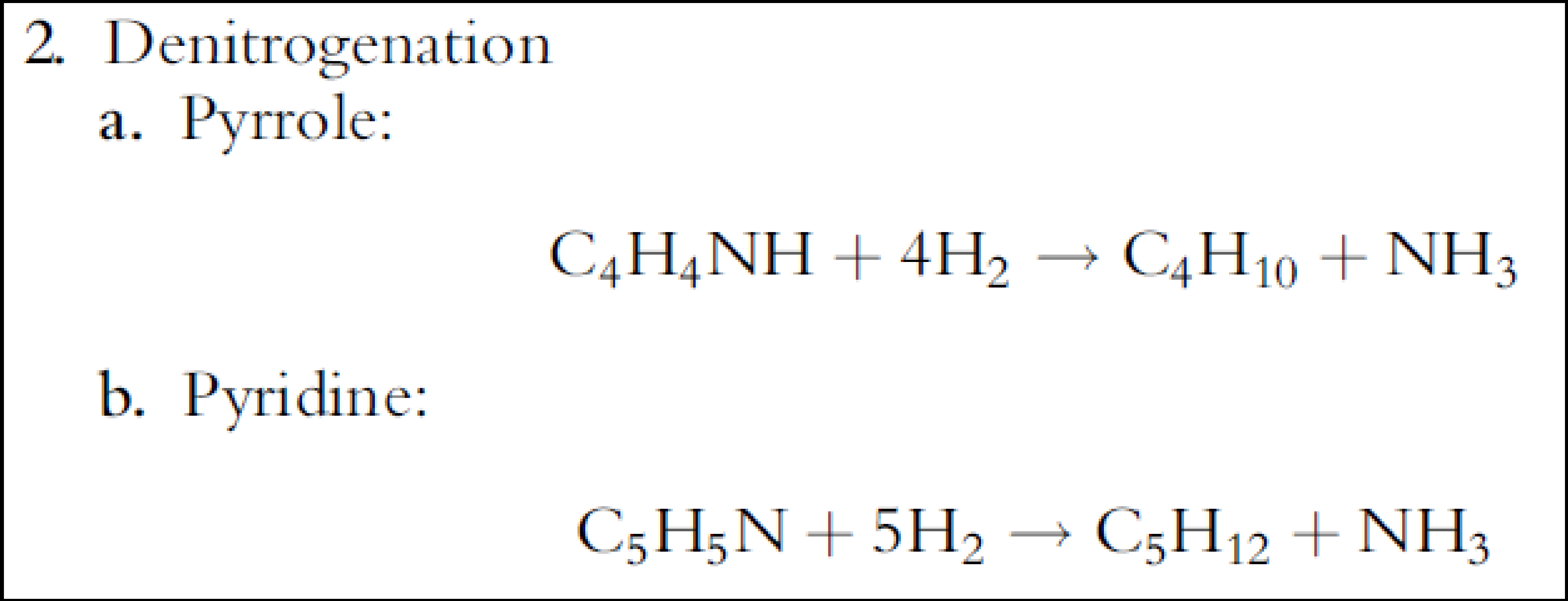
1. Desulphurization



d. Thiophenes:

$+ \ 4H_2 \rightleftharpoons C_4H_{10} + H_2S$

HYDROTREATING BASIC REACTIONS



2. Denitrogenation

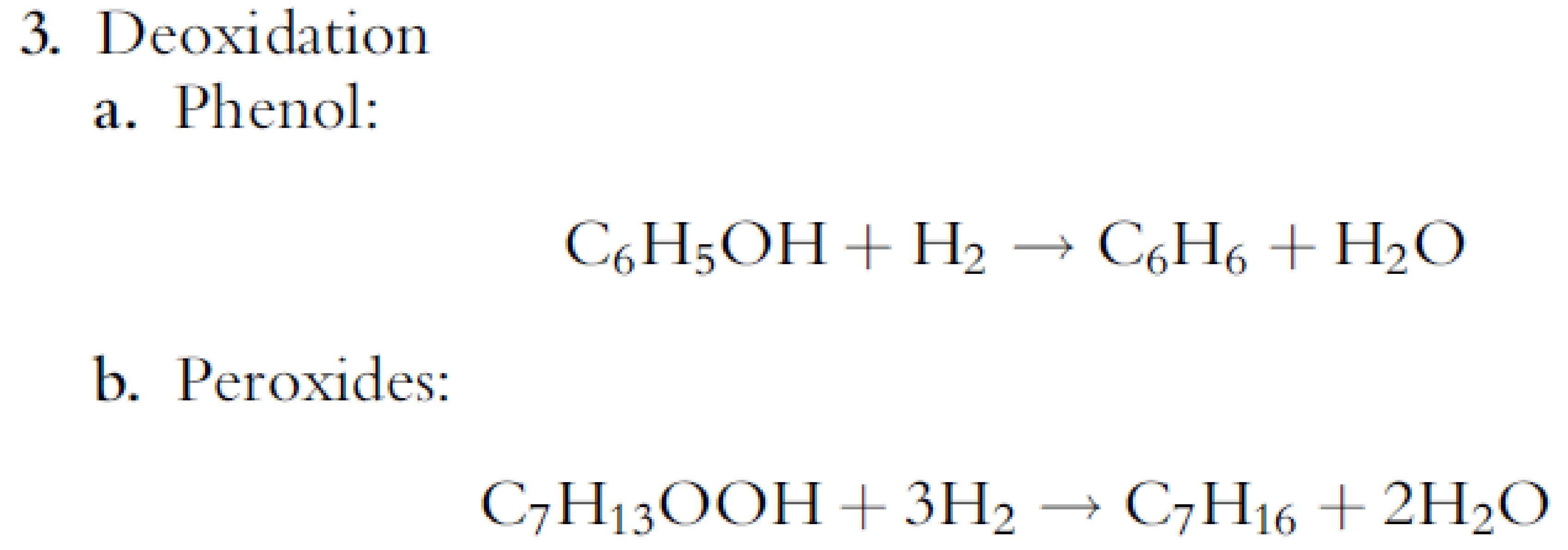
   a. Pyrrole:

$$C_4H_4NH + 4H_2 \rightarrow C_4H_{10} + NH_3$$

   b. Pyridine:

$$C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$$

HYDROTREATING BASIC REACTIONS



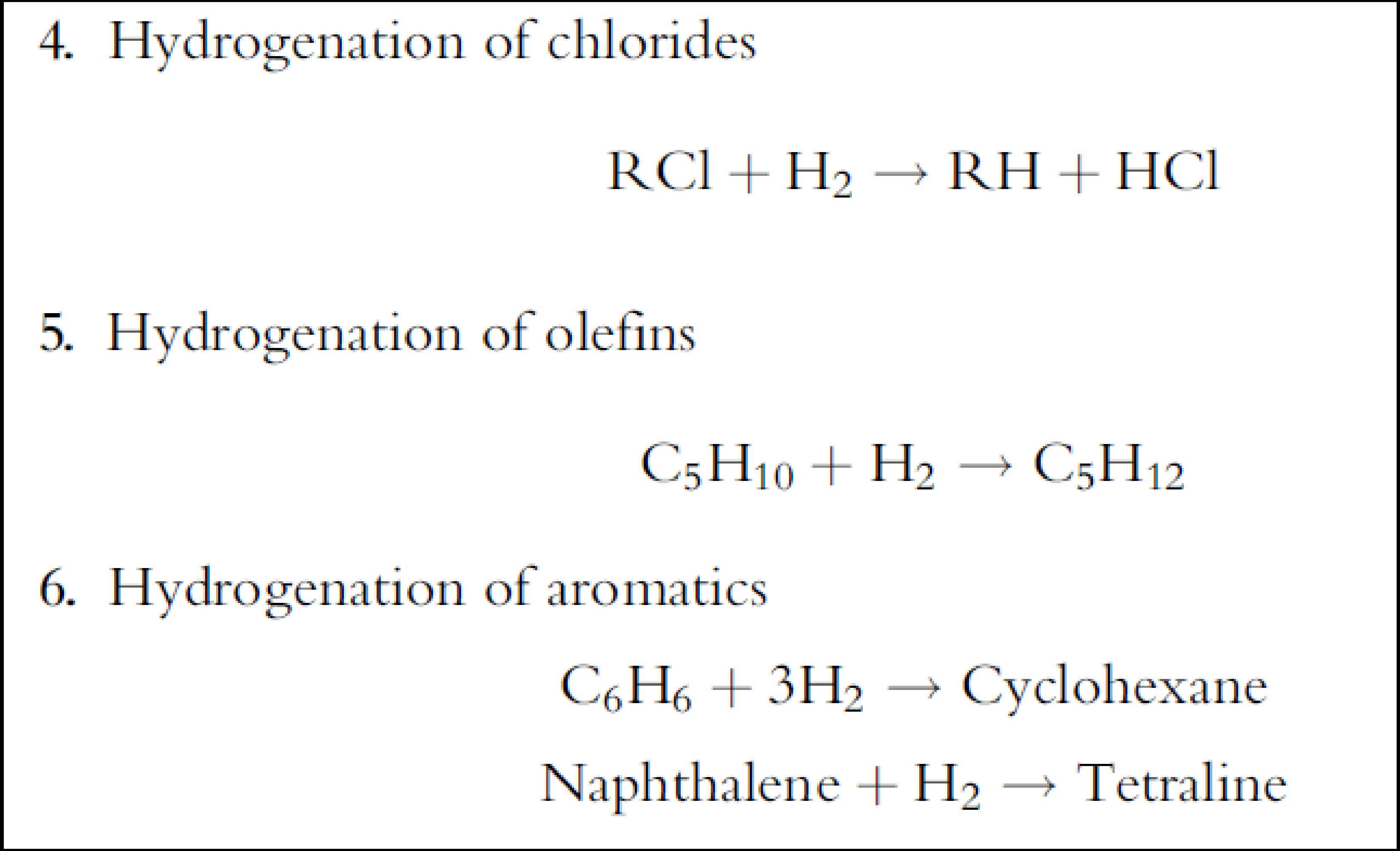
3. Deoxidation
   a. Phenol:

$$C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$$

   b. Peroxides:

$$C_7H_{13}OOH + 3H_2 \rightarrow C_7H_{16} + 2H_2O$$

HYDROTREATING BASIC REACTIONS



4. Hydrogenation of chlorides

$$RCl + H_2 \rightarrow RH + HCl$$

5. Hydrogenation of olefins

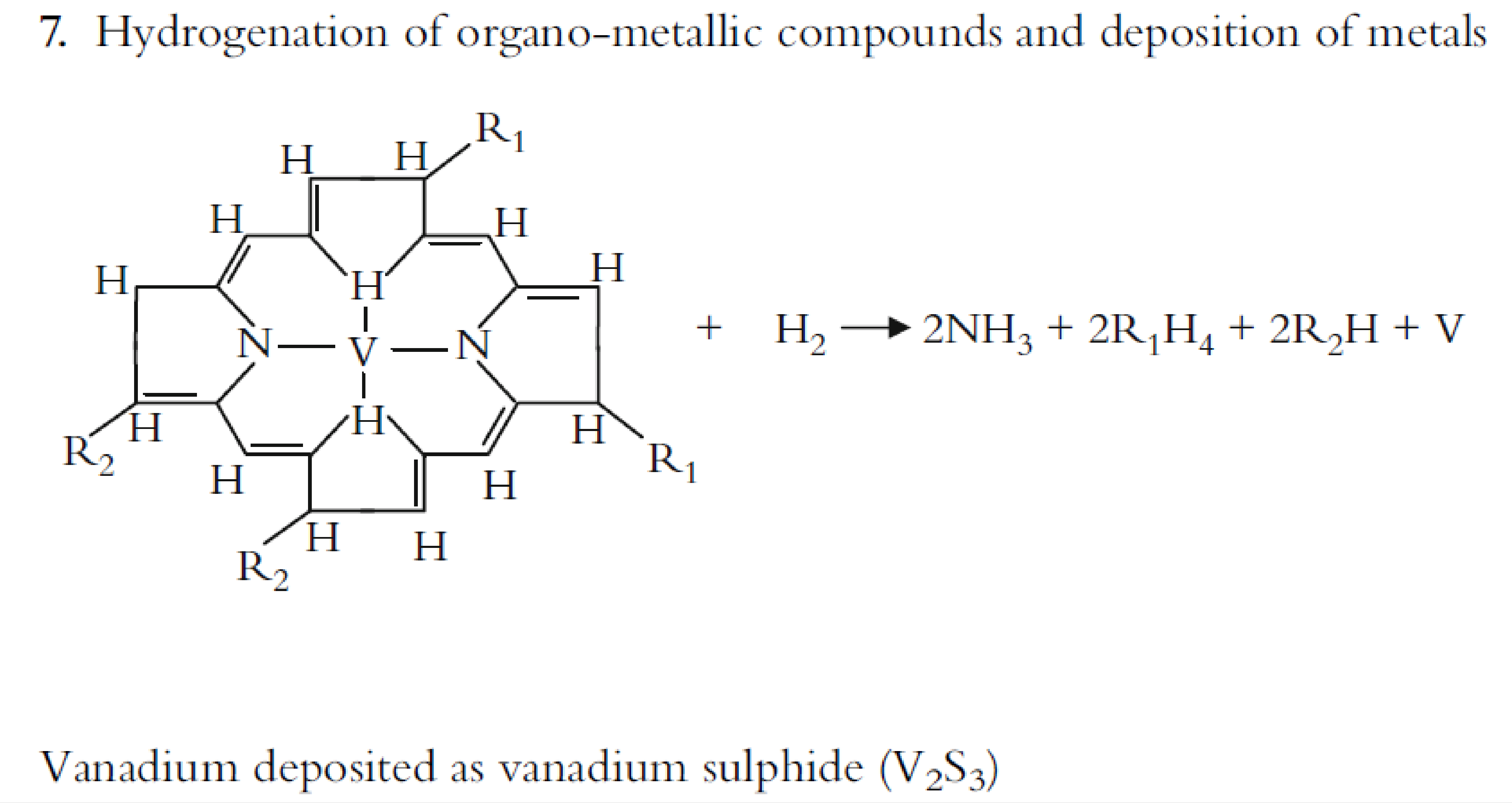
$$C_5H_{10} + H_2 \rightarrow C_5H_{12}$$

6. Hydrogenation of aromatics

$$C_6H_6 + 3H_2 \rightarrow \text{Cyclohexane}$$

$$\text{Naphthalene} + H_2 \rightarrow \text{Tetraline}$$

HYDROTREATING BASIC REACTIONS

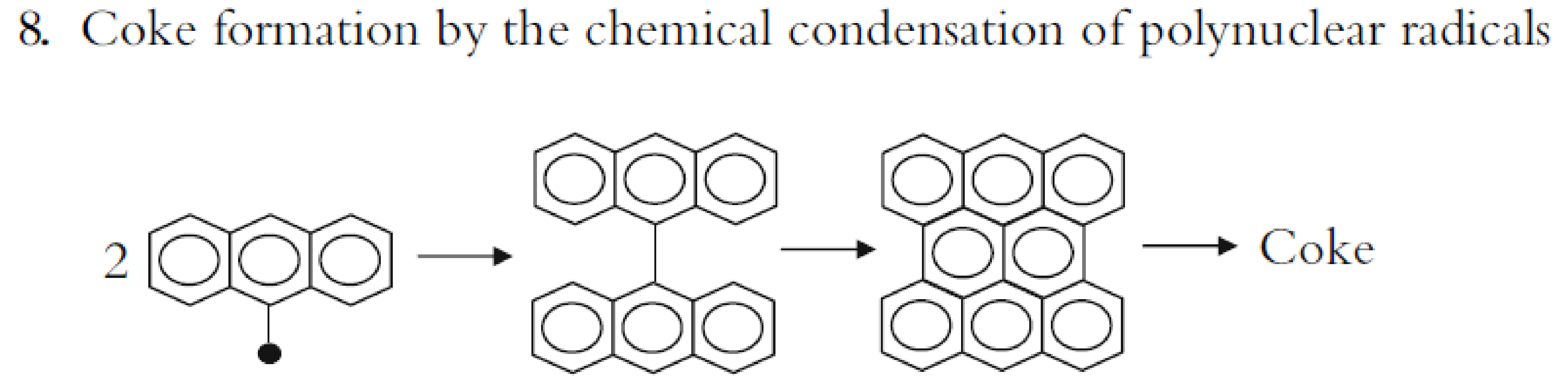


7. Hydrogenation of organo-metallic compounds and deposition of metals

$$+ \quad H_2 \longrightarrow 2NH_3 + 2R_1H_4 + 2R_2H + V$$

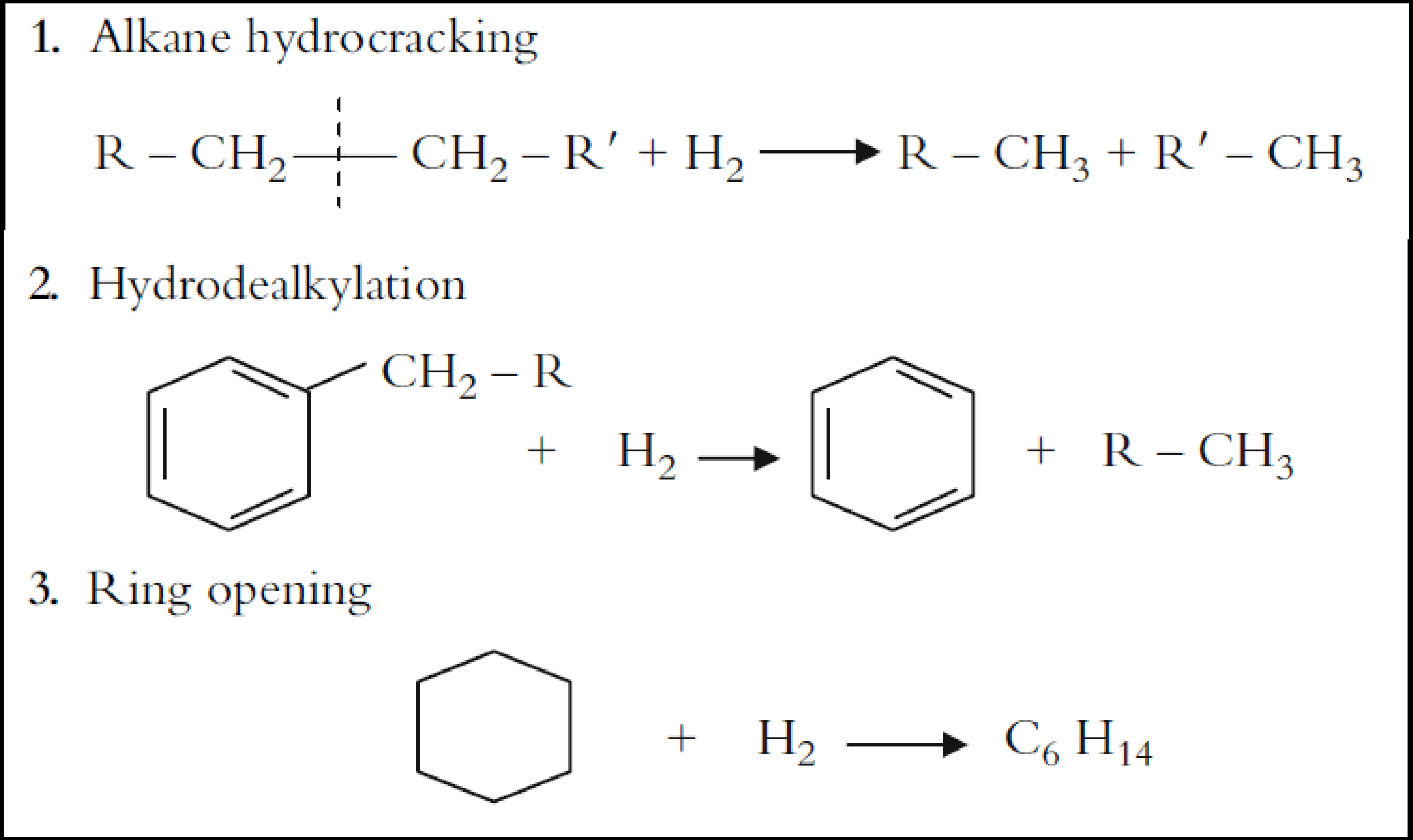
Vanadium deposited as vanadium sulphide (V_2S_3)

HYDROTREATING BASIC REACTIONS



8. Coke formation by the chemical condensation of polynuclear radicals

HYDROCRACKING BASIC REACTIONS



1. Alkane hydrocracking

$$R-CH_2 \,\vdots\, CH_2-R' + H_2 \longrightarrow R-CH_3 + R'-CH_3$$

2. Hydrodealkylation

CH_2-R

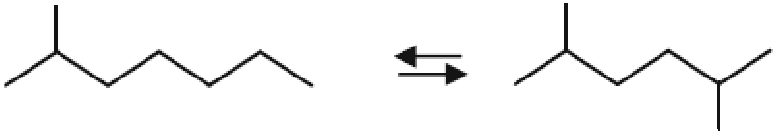
$+ \; H_2 \longrightarrow \; + \; R-CH_3$

3. Ring opening

$+ \; H_2 \longrightarrow C_6H_{14}$

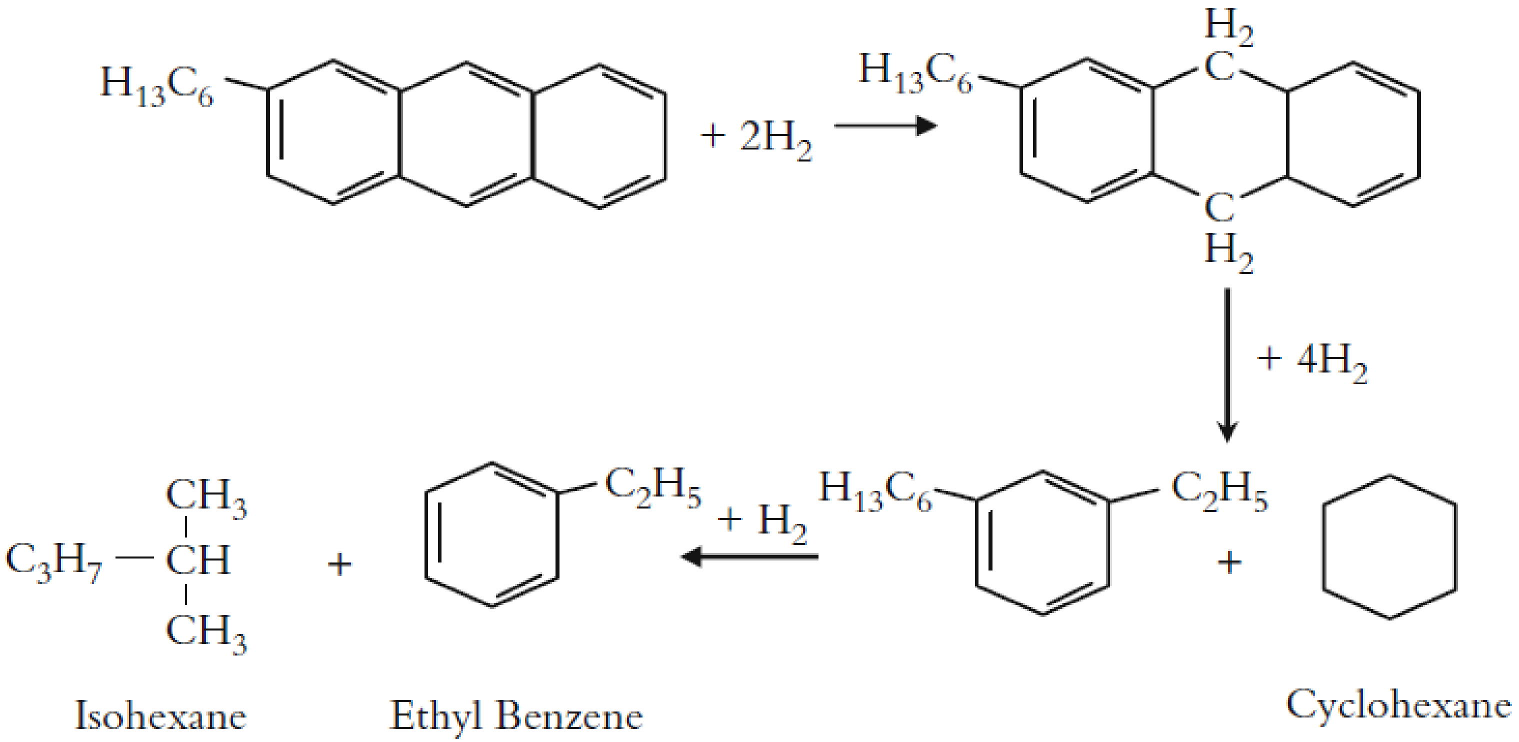
HYDROCRACKING BASIC REACTIONS

4. Hydroisomerization



HYDROCRACKING BASIC REACTIONS

5. Polynuclear aromatics hydrocracking



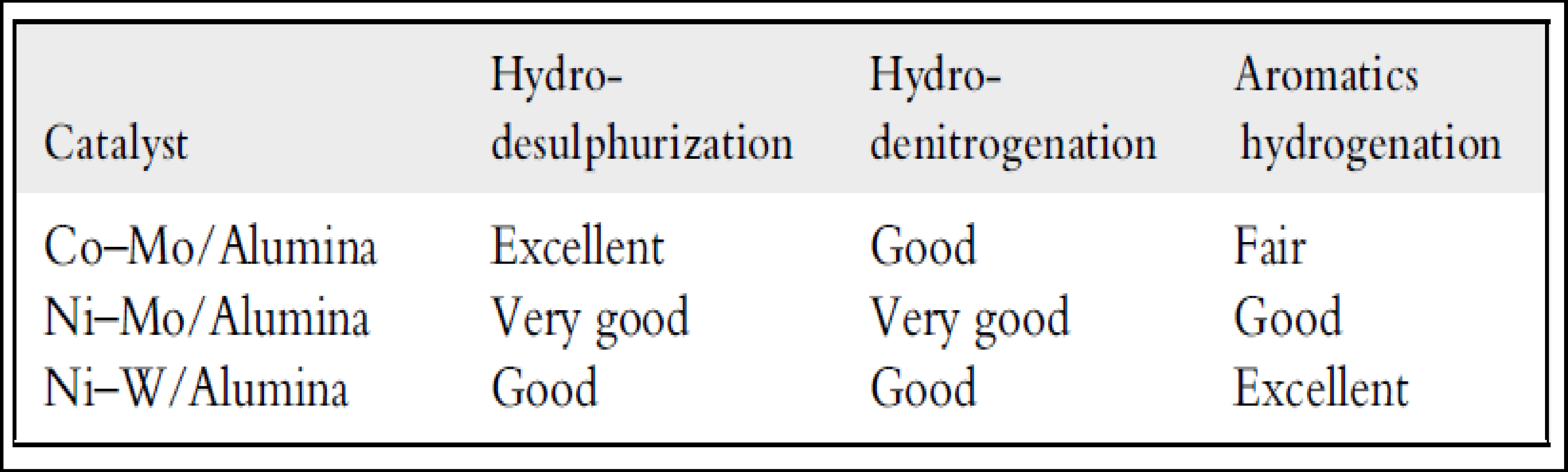
HYDROTREATING CATALYSTS

- The catalyst consists of two parts, the catalyst support and the active elements. The support consists of solid substances with high porosity and able to withstand the temperature, pressure.
- The support utilized by the HDS catalyst is alumina in the form of balls. The active elements are the metals deposited on the support in form of oxides.
- Before operation, the catalyst is sulfided in order to moderate activity.

HYDROTREATING CATALYSTS

- The principal types of catalyst used in the HDS service are
    - Cobalt (molybdenum on alumina support). This is the general catalyst for HDS service.
    - Nickel (molybdenum on alumina support). This is used especially for denitrification.
    - Cobalt (molybdenum and other metals on neutral support). The neutral support prevents the polymerization of the olefins. This catalyst for olefinic feeds.
    - Ni–W tungsten catalysts are chosen only when very high activity aromatic saturation is required

HYDROTREATING CATALYSTS



Catalyst	Hydro-desulphurization	Hydro-denitrogenation	Aromatics hydrogenation
Co–Mo/Alumina	Excellent	Good	Fair
Ni–Mo/Alumina	Very good	Very good	Good
Ni–W/Alumina	Good	Good	Excellent

HYDROCRACKING CATALYST

- Hydrocracking reactions can be divided into two groups:
    - Desulfurization, denitrification are favored by the hydrogenating function of the catalyst (metals).
    - hydrodealkylation, hydrodecyclization, hydrocracking, and hydroisomerization reactions are promoted by the acidic function of the catalyst (support). The support function is affected by the nitrogen content of the feed.

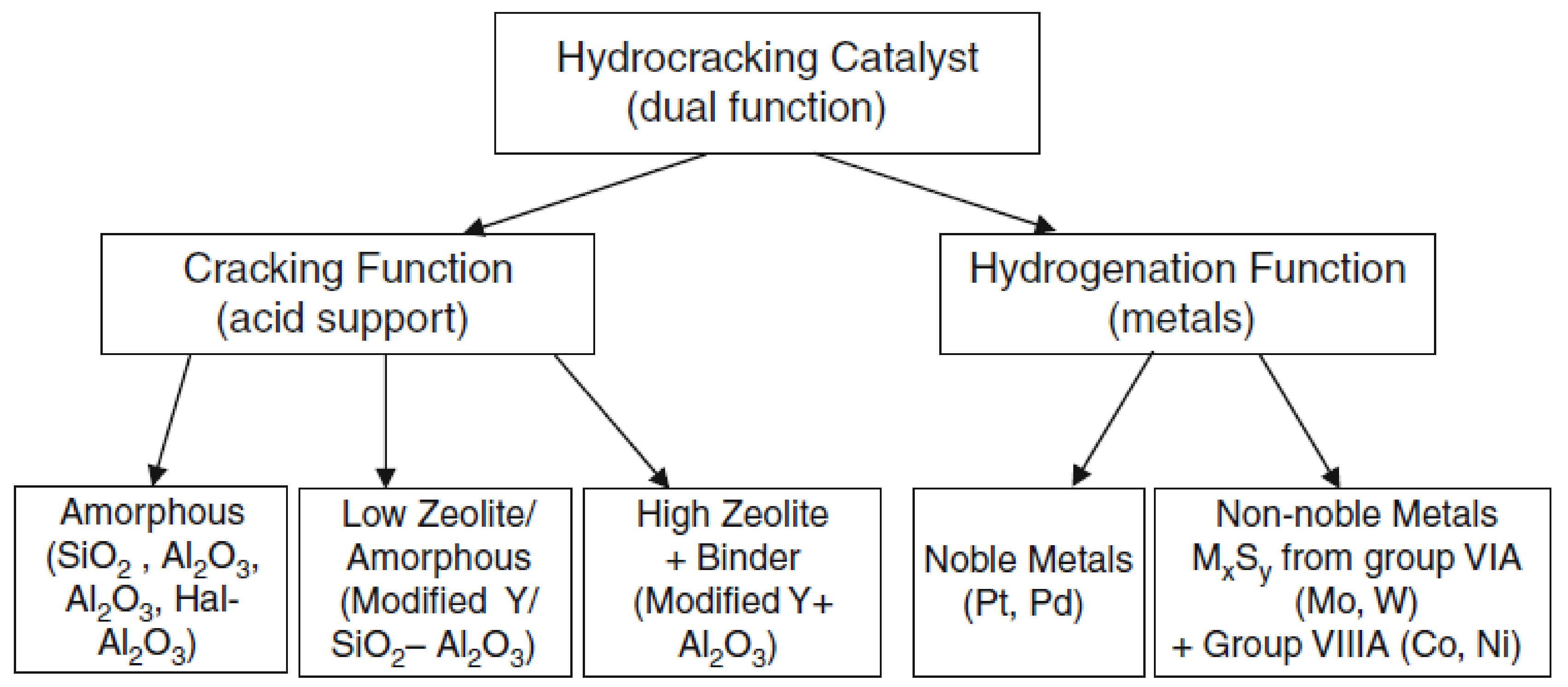
HYDROCRACKING CATALYST

- The catalyst employed in hydrocracking is generally of the type (Ni-Co-Fe), (Mo-W-U) on a silica/alumina support.

W : Tungsten   U : Uranium

HYDROCRACKING CATALYST

- The ratio of alumina to silica is used to control the degree of hydrocracking, hydrodealkylation, hydroisomerization, and hydrodecyclization.
- Cracking reactions increase with increasing silica content of the catalyst.
- The choice of catalyst system depends on the feedstock to be treated and the products required.
- The hydrocracking catalyst is very sensitive to certain impurities, such as nitrogen and metals.



Hydrocracking Catalyst (dual function)

Cracking Function (acid support)

Hydrogenation Function (metals)

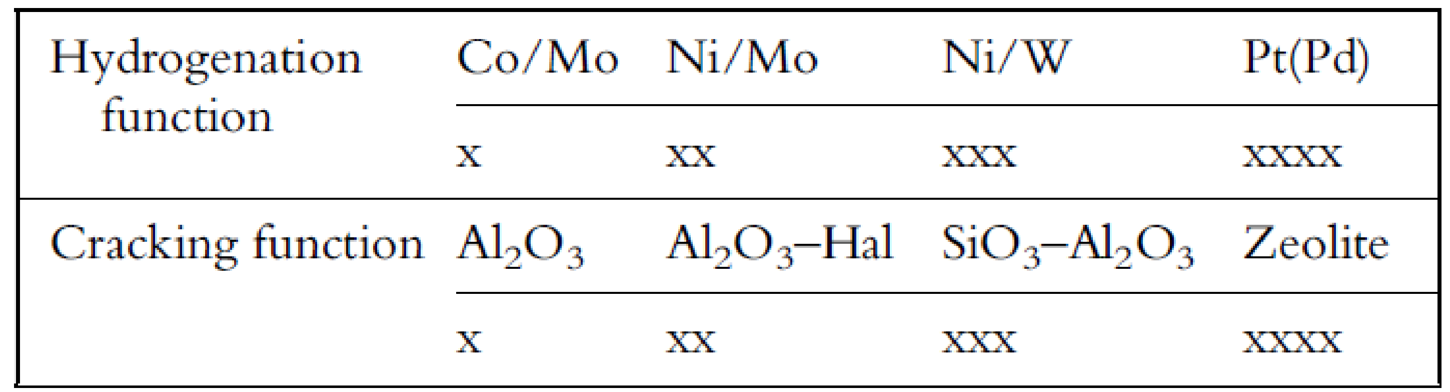
Amorphous (SiO_2 , Al_2O_3, Al_2O_3, Hal-Al_2O_3)

Low Zeolite/ Amorphous (Modified Y/ SiO_2– Al_2O_3)

High Zeolite + Binder (Modified Y+ Al_2O_3)

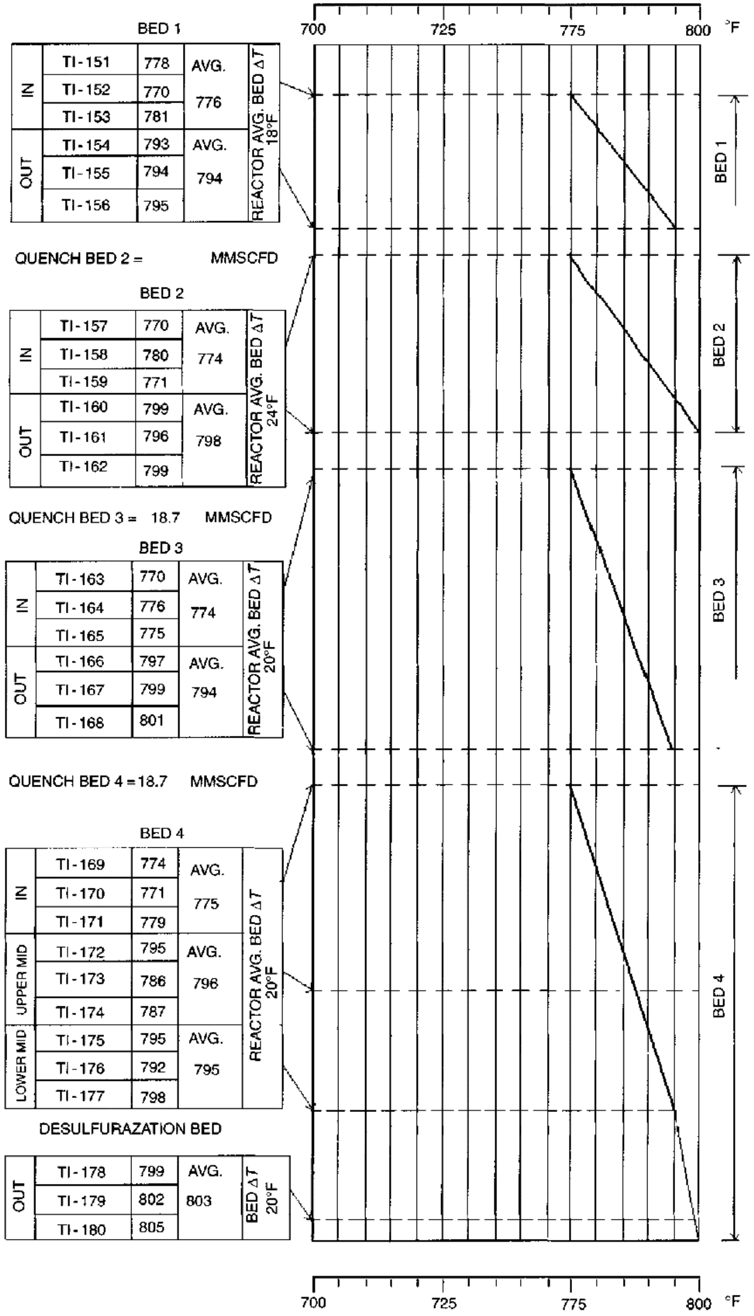
Noble Metals (Pt, Pd)

Non-noble Metals M_xS_y from group VIA (Mo, W) + Group VIIIA (Co, Ni)



Hydrogenation function	Co/Mo	Ni/Mo	Ni/W	Pt(Pd)
	x	xx	xxx	xxxx
Cracking function	Al_2O_3	Al_2O_3–Hal	SiO_3–Al_2O_3	Zeolite
	x	xx	xxx	xxxx

HYDROCRACKER REACTOR TEMPERATURE PROFILE



BED 1

IN	TI-151	778	AVG. 776	REACTOR AVG. BED ΔT 18°F
	TI-152	770		
	TI-153	781		
OUT	TI-154	793	AVG. 794	
	TI-155	794		
	TI-156	795		

QUENCH BED 2 = MMSCFD

BED 2

IN	TI-157	770	AVG. 774	REACTOR AVG. BED ΔT 24°F
	TI-158	780		
	TI-159	771		
OUT	TI-160	799	AVG. 798	
	TI-161	796		
	TI-162	799		

QUENCH BED 3 = 18.7 MMSCFD

BED 3

IN	TI-163	770	AVG. 774	REACTOR AVG. BED ΔT 20°F
	TI-164	776		
	TI-165	775		
OUT	TI-166	797	AVG. 794	
	TI-167	799		
	TI-168	801		

QUENCH BED 4 = 18.7 MMSCFD

BED 4

IN	TI-169	774	AVG. 775	REACTOR AVG. BED ΔT 20°F
	TI-170	771		
	TI-171	779		
UPPER MID	TI-172	795	AVG. 796	
	TI-173	786		
	TI-174	787		
LOWER MID	TI-175	795	AVG. 795	
	TI-176	792		
	TI-177	798		

DESULFURAZATION BED

OUT	TI-178	799	AVG. 803	BED ΔT 20°F
	TI-179	802		
	TI-180	805		

Hydrocracker reactor temperature profile.

MECHANISMS OF DEACTIVATION

- Prevention of catalyst degradation poses substantial challenges in the design and operation of a large-scale, catalytic process. There are many paths for catalyst decay.
- For example, a catalyst may be poisoned by any one of a dozen contaminants present in the feed; its surface, pores and voids may be fouled by carbon or coke produced by cracking/condensation reactions of hydrocarbon reactants.

MECHANISMS OF DEACTIVATION

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions

MECHANISMS OF DEACTIVATION

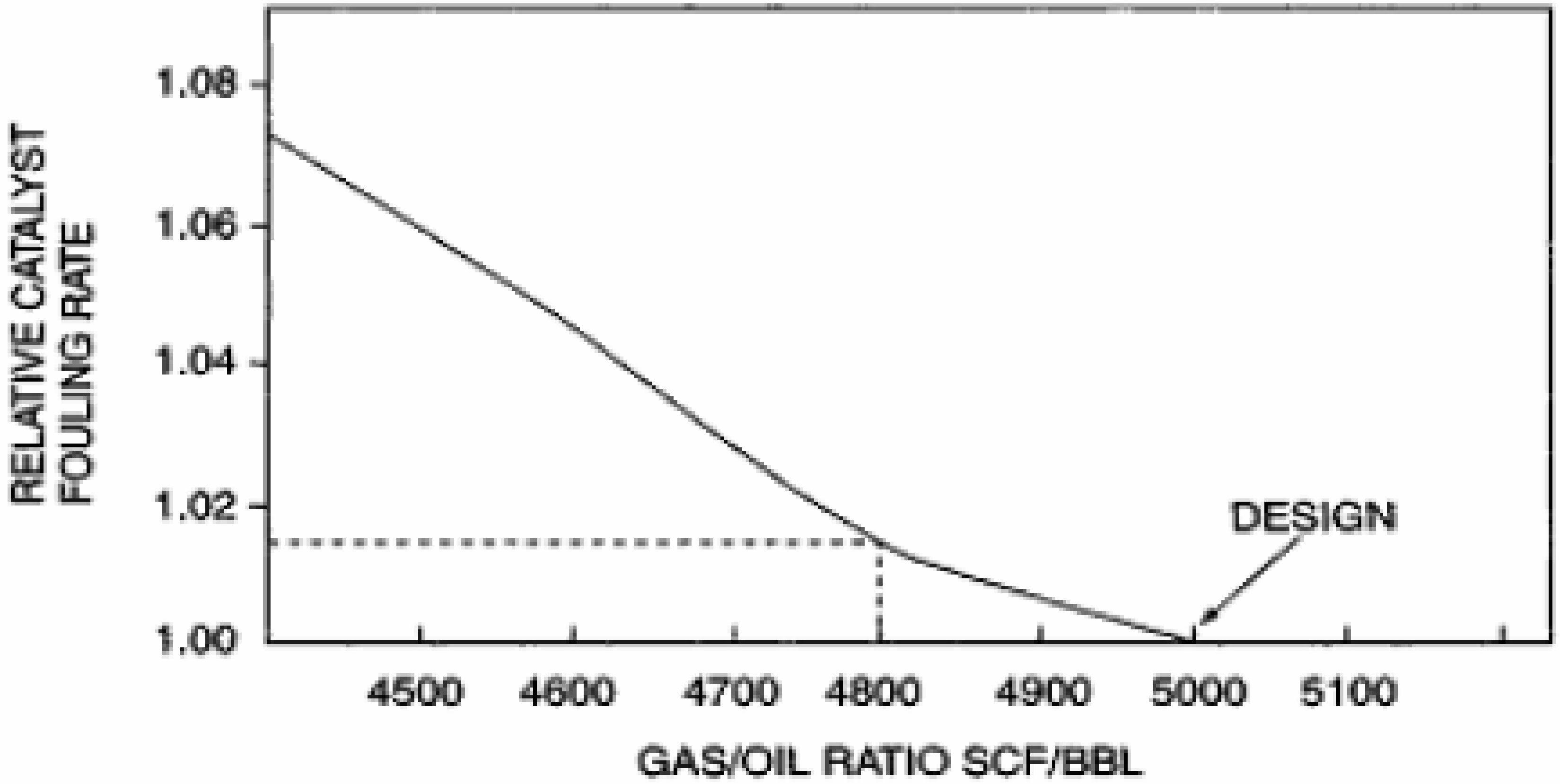
Mechanism	Type	Brief definition/description
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and solid–solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
Attrition/ crushing	Mechanical	• Loss of catalytic material due to abrasion • Loss of internal surface area due to mechanical-induced crushing of the catalyst particle

CATALYST FOULING RATE

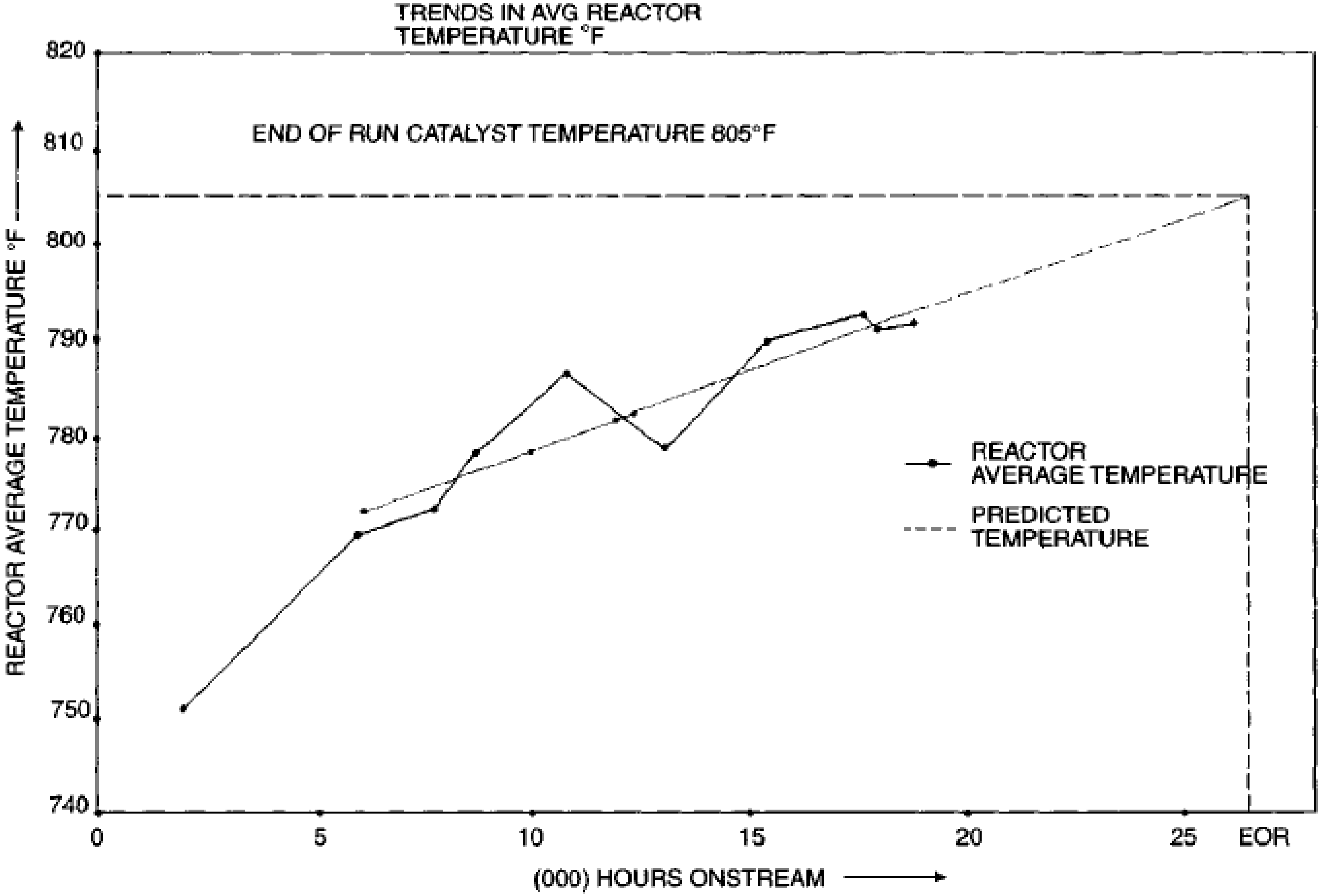
- The design of a hydrocracker unit is based on a specified conversion rate of the feed and a specified catalyst life, usually 2-3 years between catalyst regeneration.
- During the course of the run (COR), the activity of the catalyst declines due to coke and metal deposits, and to maintain the design conversion rate, the temperature of the catalyst has to be increased.

CATALYST FOULING RATE

- The rate of increase in average reactor catalyst temperature (to maintain the design conversion rate) with time is called the catalyst fouling rate. It is an important parameter, used to make an estimate of time when the EOR conditions are likely to be reached.



The effect of the gas/oil ratio on the catalyst fouling rate.

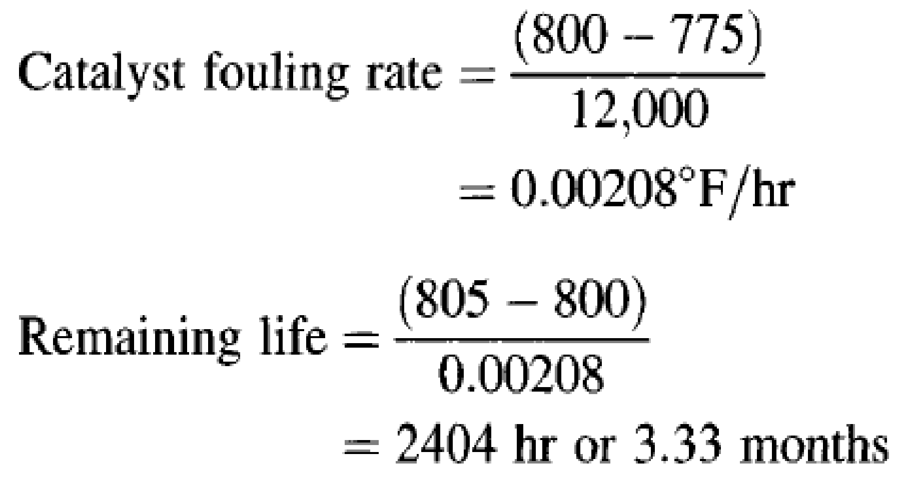


Estimating the remaining catalyst life.

CATALYST FOULING RATE

- EXAMPLE :

The design start of run (SOR) temperature of a hydrocracker reactor is **775 °F**. After the unit is on stream for **12,000 hours**, the CAT (weighted average bed temperature) is **800 °F.** Estimate the remaining life of the catalyst if the design EOR temperature of the catalyst is 805 °F :



$$\text{Catalyst fouling rate} = \frac{(800 - 775)}{12{,}000}$$

$$= 0.00208°\text{F/hr}$$

$$\text{Remaining life} = \frac{(805 - 800)}{0.00208}$$

$$= 2404 \text{ hr or } 3.33 \text{ months}$$

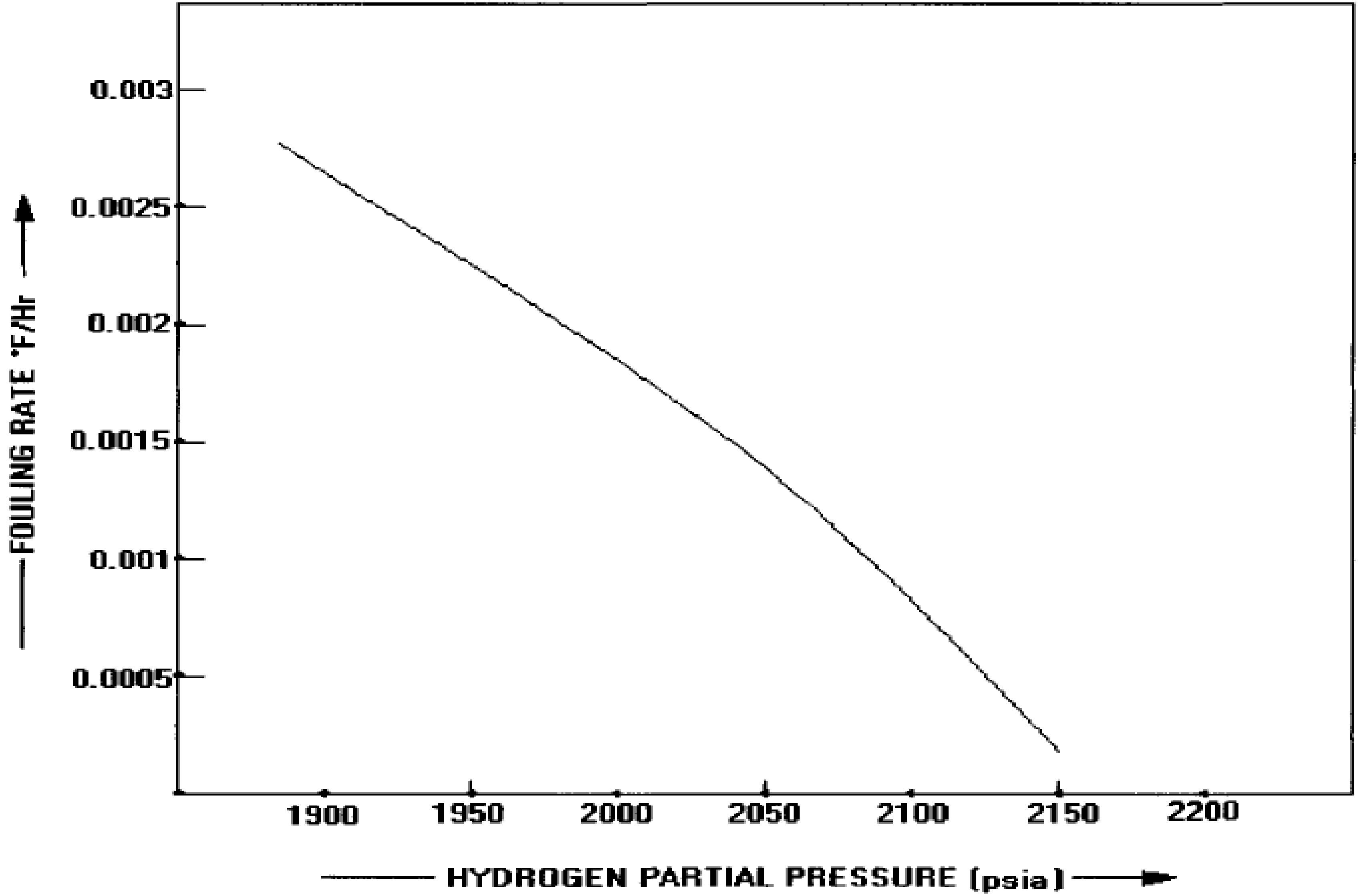
HYDROGEN PARTIAL PRESSURE

- Hydrogen partial pressure provides the driving force for hydrocracking reactions.
- An increase in the hydrogen partial pressure serve to suppress the catalyst fouling rate, maximized to operate the unit at the lowest possible temperature. This increases the run length and minimize light ends production.

HYDROGEN PARTIAL PRESSURE

The factors affecting hydrogen partial pressure are

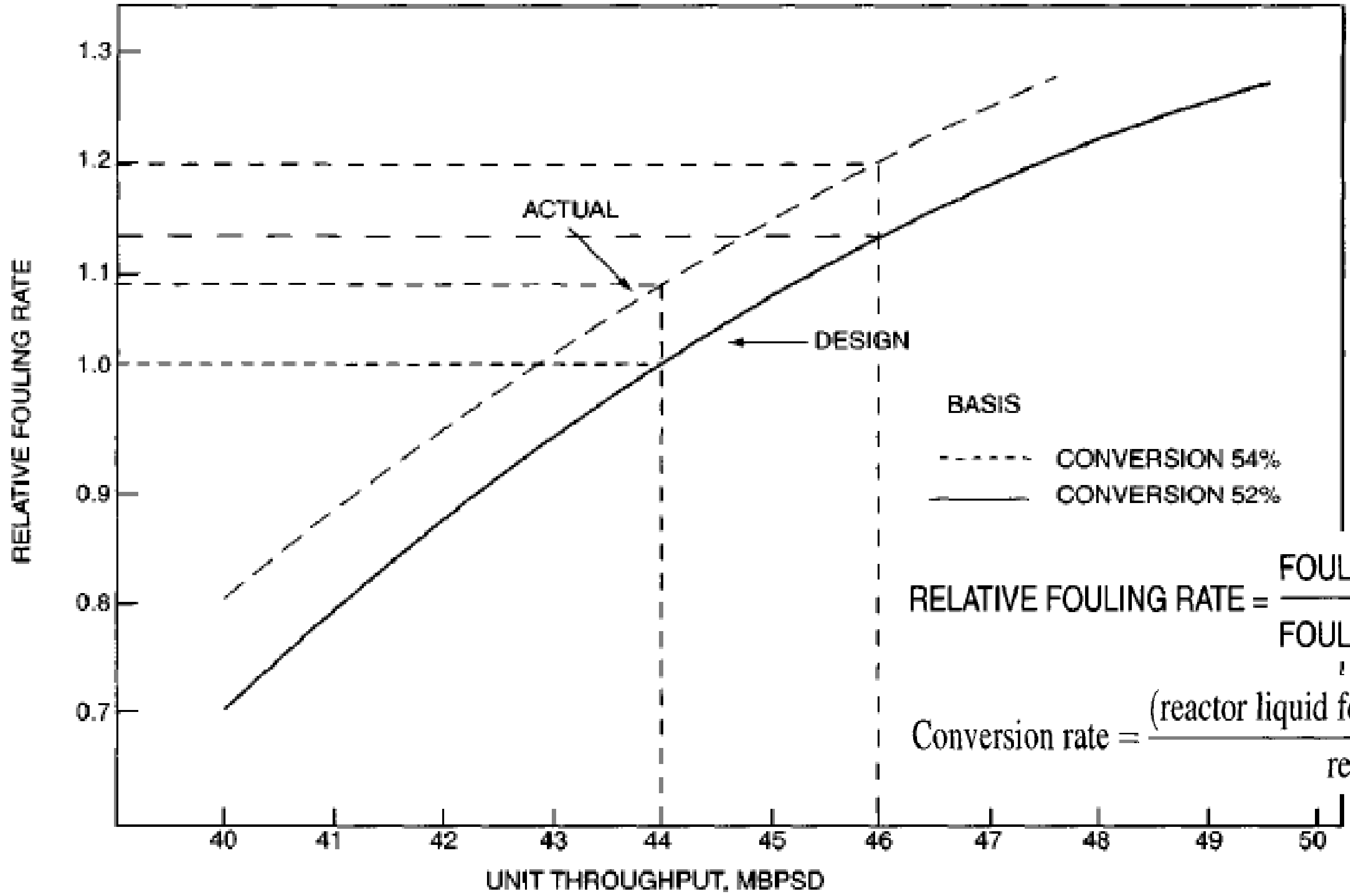
- Total system pressure.
- Makeup hydrogen purity.
- Recycle gas rate.
- HP gas bleed rate.
- HP separator temperature.



Effect of H_2 partial pressure on catalyst fouling rate (schematic).

FEED RATE

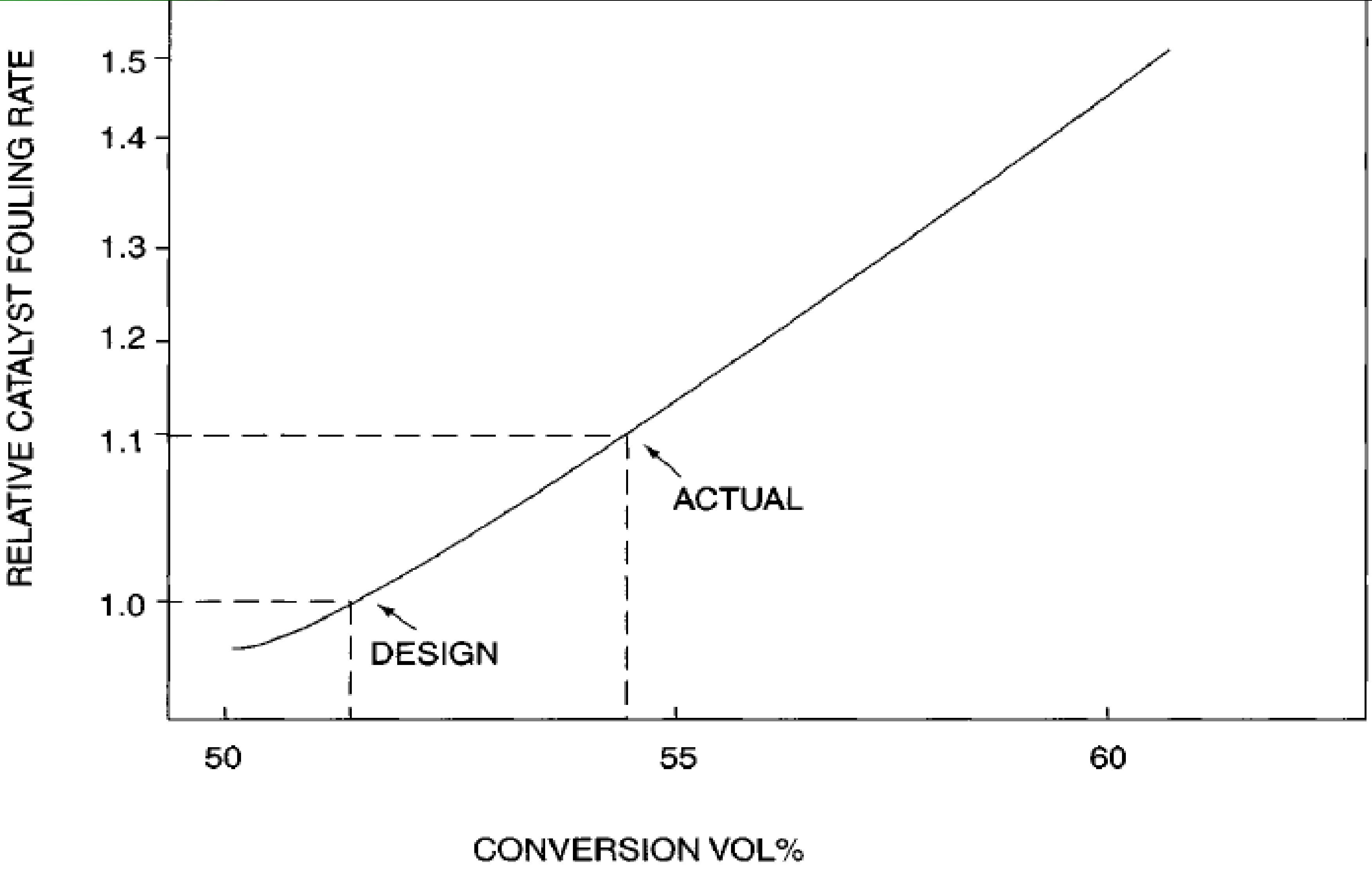
- Increasing the feed rate requires an increase in average catalyst temperature to maintain the required feed rate conversion.
- The increased feed rate also causes an increase in the catalyst fouling rate and the hydrogen consumed.
- A heavier feed, as characterized by the ASTM DI160 weighted boiling point, requires an increase in average catalyst temperature to maintain the desired level of feed conversion. An increase in the catalyst fouling rate also occurs.



$$\text{RELATIVE FOULING RATE} = \frac{\text{FOULING RATE AT ACTUAL CONDITION}}{\text{FOULING RATE AT DESIGN CONDITION}}$$

$$\text{Conversion rate} = \frac{(\text{reactor liquid feed rate} - \text{fractionator bottom rate})}{\text{reactor liquid feed rate}}$$

. The effect of the feed rate on the catalyst fouling rate (schematic).



The effect of conversion on the catalyst fouling rate (schematic).

CATALYST SULFIDING AND UNIT STARTUP

- Sulfiding is the injection of a sulfur-containing chemical such as dimethyl sulfide into the hot circulating gas stream before the introduction of liquid feed.
- The reactor inlet is heated to 500-525 oF, this temperature is held until the temperature is 450 oF at reactor outlet.
- At 300 psig, the hydrogen is introduced slowly, through the makeup compressor and pressure increased to 700 psig at reactor inlet.

CATALYST SULFIDING AND UNIT STARTUP

- Sulfiding chemical is then added into gas stream at the reactor inlet.
- Addition of a sulfiding agent causes two temperature rises in the reactor, first due to reaction of hydrogen with the sulfiding chemical to form H2S, which occurs at the reactor inlet, and second due to reaction of the sulfiding chemical with the catalyst, and this moves down through the catalyst bed.

CATALYST SULFIDING AND UNIT STARTUP

- The catalyst temperature is closely monitored during sulfiding, and it is not allowed to exceed 600 oF.
- After the sulfiding temperature rise has passed through the reactor, the H2S concentration of gases out of the reactor begin to rise rapidly.

CATALYST SULFIDING AND UNIT STARTUP

- When 0.1% H2S is detected in the effluent gas, the recycle gas bleed is stopped and sulfiding continued at a low injection rate until the concentration of H2S in the circulating gas is l-2 mol%.
- When the reactor system has remained steady at the design pressure, at reactor inlet/outlet temperature of 560/530 oF and H2S concentration of 1-2 mol%, for 2 hours, sulfiding is complete.

CATALYST SULFIDING AND UNIT STARTUP

- The reactor is slowly cooled by reducing inlet temperature and adding quench between the catalyst beds until reactor temperature reaches about 425 °F.
- The startup temperature is next approached by increasing the reactor inlet temperature to 450-475 oF and outlet temperature to 425-450 oF , the quench temperature controller is set at 450 °F.

CATALYST SULFIDING AND UNIT STARTUP

- The recycle gas rate is set at the design rate. Also the HP separator pressure is set at the design value. Condensate and polysulfide injection at the design rate is started.
- The reactor is now ready for introduction of the feed. The feed pump starts pumping with slowly increasing oil flow rate.

CATALYST REGENERATION

- In the regeneration process, the coke and sulfur deposits on the catalyst are burned off with a dilute stream of oxygen.
- During the combustion phase, sulfur oxides are liberated because the sulfided catalyst is converted to the oxide form.
- During the combustion phase, a dilute caustic quenching solution is mixed with reactor effluent to neutralize the SO2/SO3 present that cause damage to the catalyst and equipment corrosion.

CATALYST REGENERATION

- The reactor/effluent gases are cooled then flows to the high-pressure separator to separate out the vapor and liquid phases.
- A portion of the inert gas from the separator is bled to the atmosphere and the reminder recirculated. The dilute caustic quench solution then flows to the low-pressure separator.

CATALYST REGENERATION

- The burning or oxidation consists are : three burns
  1. After the regeneration burn has started and the recycling gas stream is free of hydrogen, The concentration of O2 is kept at 0.5%. The reactor inlet temperature is 650 °F or less.
  2. the reactor inlet temperature is increased to 750 °F and O2 is 0.5 vol% at the reactor inlet.
  3. the temperature at reactor inlet is raised to 850 °F ± 25°F and the O2 content is slowly increased to 2% by volume. This condition is maintained at least for 6 hours or until the oxygen consumption is essentially nil.

CATALYST REGENERATION

- No point in the reactor should be allowed to exceed 875 °F.

CATALYST LOADING

- There are two methods of catalyst loading sock loading and dense loading. Sock loading is done by pouring catalyst into a hopper mounted on top of the reactor and then allowing it to flow through a sock into the reactor. Dense loading or dense bed packing is done with the help of a mechanical device. Catalyst loaded by sock loading will have a higher void fraction than catalyst that was dense loaded.
- Dense loading and the resulting higher pressure drop provides a more distribution of liquid in a trickle flow which is the flow regime for most hydrocracker applications.

CATALYST LOADING

- If diffusion limitations are negligible, dense loading is desirable in order to maximize the reaction rate per unit reactor volume. The other advantage of dense loading is that it orients the catalyst particles in a horizontal and uniform manner. This improves the vapor/liquid distribution through the catalyst beds & liquid mal distribution or channeling is eliminated. Catalyst particle orientation is important especially for cylindrically shaped extruded catalyst in vapor/liquid reactant systems. The great majority of units worldwide are dense loaded.

CATALYST RECLAMATION

- Even though noble-metal hydrocracking catalysts contain only small amounts of Pd or Pt, these metals are so expensive that recovering is more cost-effective than throwing them away.
- Reclamation companies convert these materials into salable products using different combinations of oxidation, pyrolysis, and dissolution in acid or alkali, precipitation, extraction or ion exchange.

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