

# Main guidelines of the scaling-up methodology

Industrial processes and scale-up  
Lesson #1

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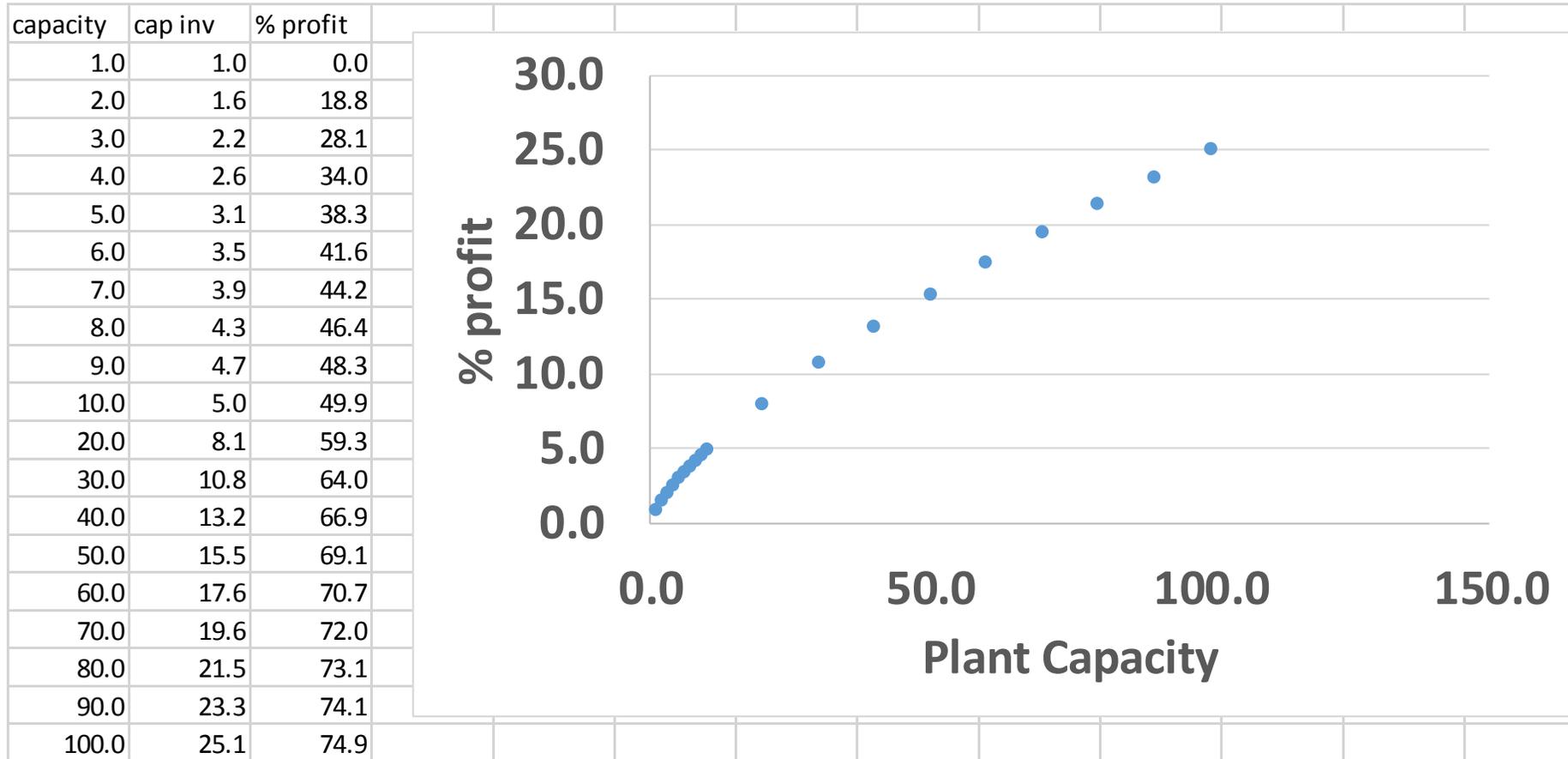
# Introduction

In view of the proliferation of scientific and technical publications one wonders why so few have been devoted to the crucial problem of scale-up.

One possible explanation is that the companies concerned consider this area as highly confidential, and that academics have neither the possibility of studying these problems or motivation to do so.

# Why large chemical plants?

- During the development of a new chemical process, one of the problem that merits close attention and often proves to be problematic is the scaling-up;
- This is especially true of the oil industry, characterized by a unique gigantism that enable it to place products on the market at relatively low cost;
- In fact, the capital investment normally required for the transformation of the raw material into a given product varies by the power of 0.7 with the capacity of the plant. For this reason the plant should be built as large as possible



$$\text{capital investment} = \text{unit capacity}^{0.7}$$

$$\% \text{ profit} = \frac{\text{capacity} - \text{cap inv}}{\text{capacity}} * 100$$

# Development and scaling-up

The development of an industrial process is a CREATIVE activity, which is aimed at finding and coordinating all the information and data required for the DESIGN, CONSTRUCTION and START-UP of a new industrial unit, in order to guarantee an ECONOMICAL PROFITABLE, SAFE and ENVIRONMENTAL FRIEND OPERATION.

The starting point generally consists of LABORATORY RESULTS that concern a chemical transformation. Process development should serve to treat quantities of raw material industrially, amounting to TONS or MILLION OF TONS, whereas only GRAMS or KILOGRAMS of these raw materials are used in the laboratory. This is the PRECISE FUNCTION OF SCALING-UP.

The problem is to REPRODUCE THE LABORATORY RESULTS by achieving the same (or better, if possible) conversion, selectivity, yield in a safe and environmental friendly way.

# Scale-up phases

Different phases are distinguished in the development of a process, BY REFERRING TO THE SCALE AT WHICH THE EXPERIMENT IS CONDUCTED:

- Bench scale
- Pilot plant
- Quarter scale
- Half scale
- Demonstration scale

These label can be different, in some way, depending on the specific Company

# Scale-up experiments

- **Laboratory-type experiments:** Certain aspects of the process are investigated, by handling relatively SMALL AMOUNTS of raw material (highly purity), in order to reduce the material constraints to the minimum;
- **Pilot-plant experiments:** The scale can change within wide proportions. All the industrial constraints are taken into account: 1) impurity in raw material; 2) operation over long periods, 3) material and equipment reliability, 4) energetic consumption, 4) tharmal problems
- **Demonstration units experiments:** construction of a first industrial units on a modest scale, about 1/10 of the size required for industrial production. This type of experiment is VERY EXPENSIVE. All the efforts made in the process development attempt to avoid this very expensive step, which delays industrial implementation by several years. In certain situation, this step may prove indispensable.

# Development methodology

This methodology employs general method for ANALYZING COMPLEX SYSTEMS.

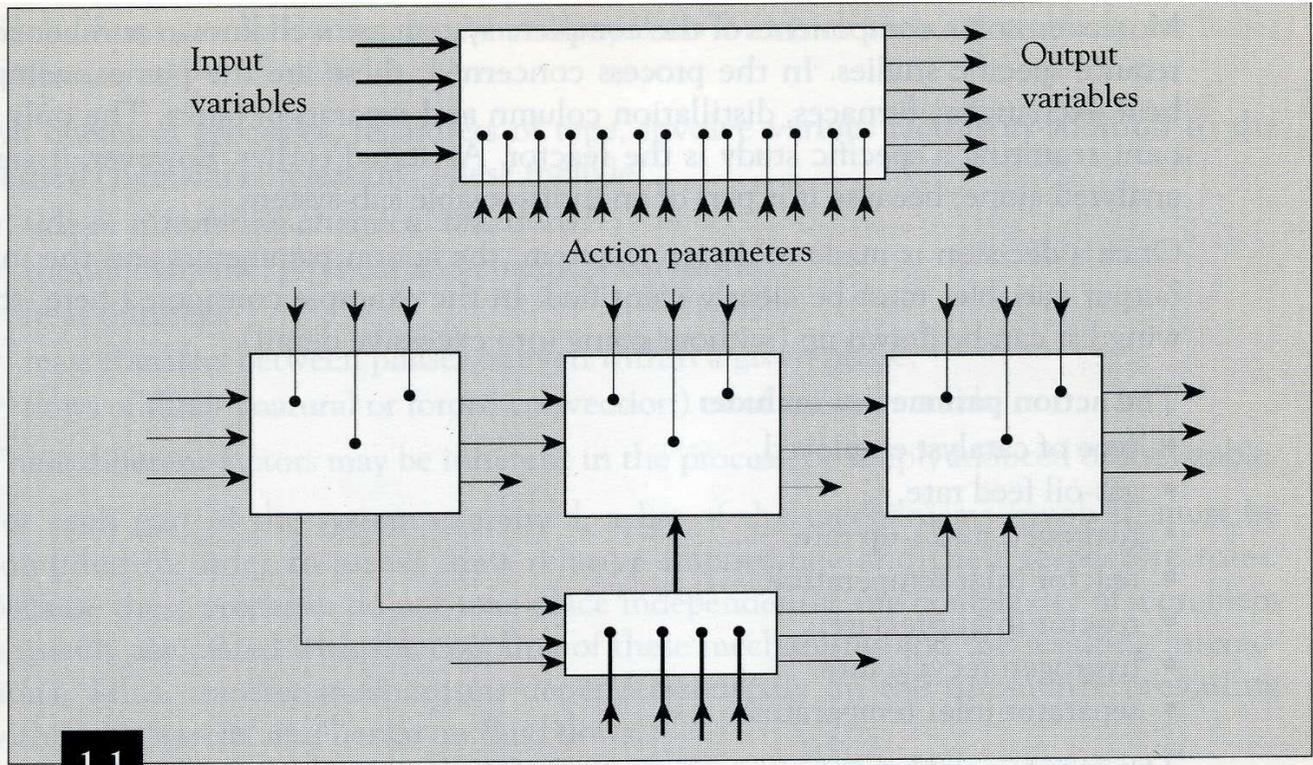
A material transformation process is typically a complex system, being formed by a LARGE NUMBER OF ELEMENTS, interconnected by many variables. They are made by a combination of elements interlinked by common flows of MATERIAL, ENERGY and INFORMATION.

Detailed characterization of a system is achieved through the variable of state (T, P, flow rate, composition) at each point of the system.

SOME OF THESE VARIABLES OF STATE PLAY A SPECIAL ROLE:

- **Input variables**
- **Action parameters which can be fixed within certain limits**
- **Output variables**

# Development methodology: sub-systems



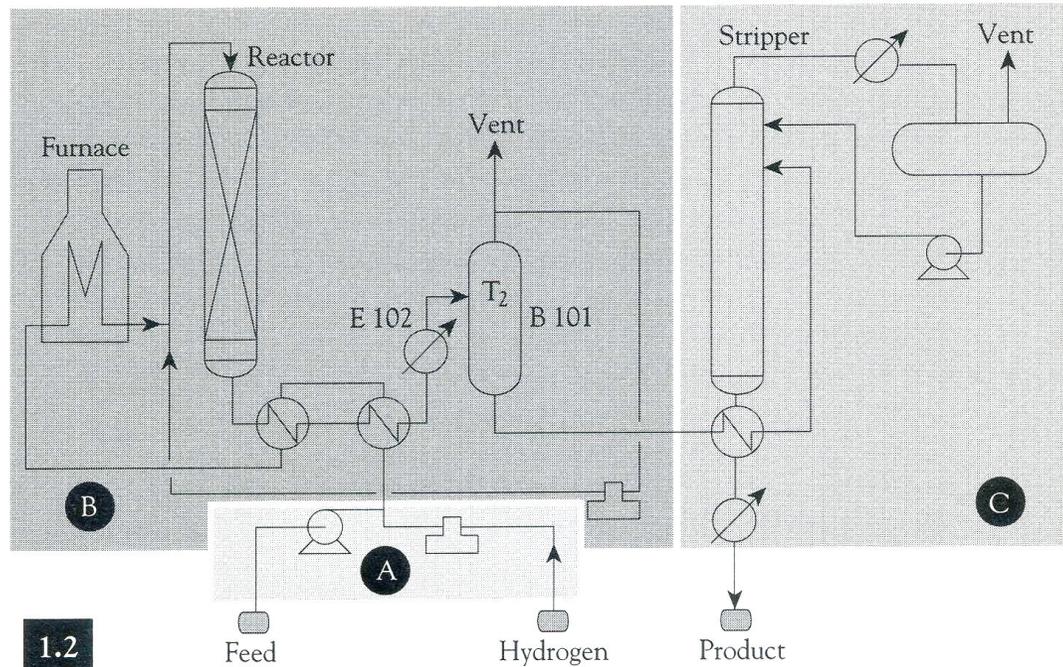
A complete system can be broken down into simpler sub-systems.

Two sub-systems are independent if the links (input variable of the system  $i$  = output variable of system  $j$ ) exists only in one direction ( $j$  to  $i$ )

For example, the existence of a RECYCLE between two components prevents a breakdown into two sub-systems corresponding to each of the components. The system must be examined as a whole, even if the analysis is more complex

# Development methodology: sub-systems

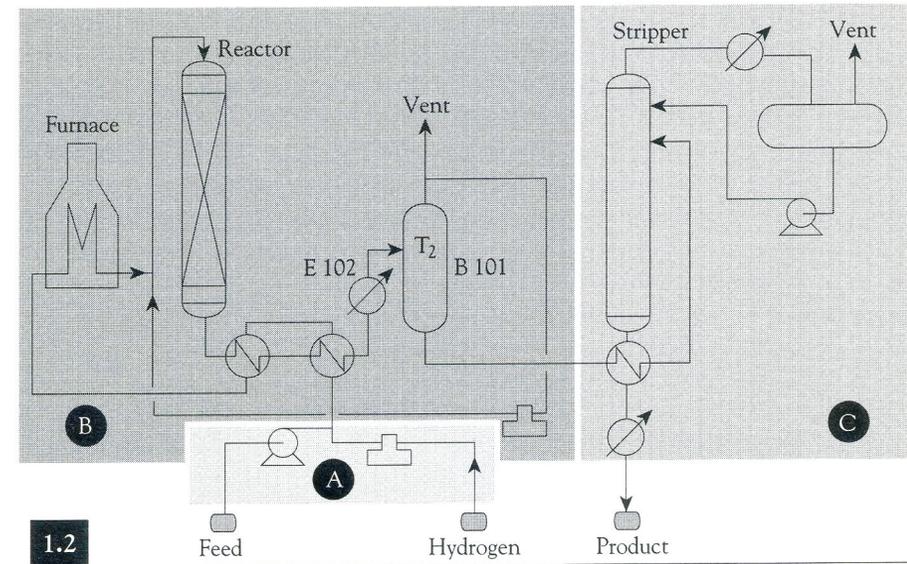
## Example: gas-oil hydrodesulfurization unit



### Components:

- Compressor
- Reactor
- Distillation column
- Separation tanks
- Heat exchangers

All the components can be combined into THREE INDEPENDENT SUBASSEMBLIES: 1) The feed section, 2) the reaction section; 3) the separation section



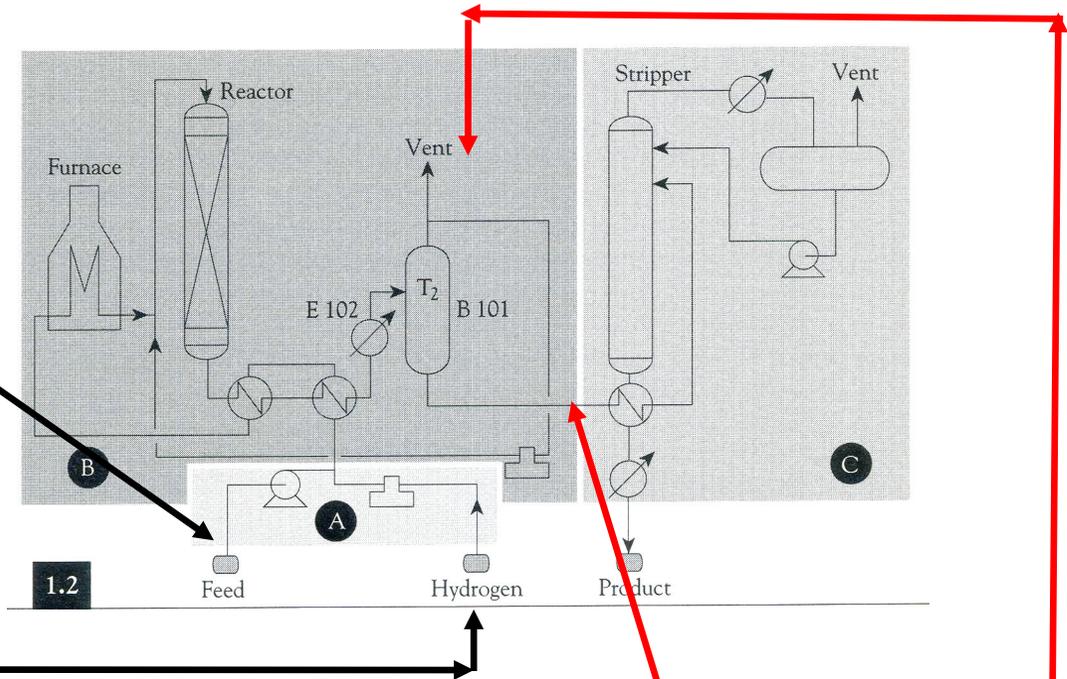
In this example, some components are well known and hence do not require specific studies: pumps, compressors, heat exchangers, furnaces, distillation columns and separation tanks.

The only component requiring a specific study is the REACTOR. The reactor can not be analyzed alone, because it is part of an indissociable sub-system. In fact, for example the heat exchangers of this system are dependent of the reactor performance.

The action parameters and the input and output variables must be clearly defined:

### INPUT VARIABLES

- Chemical composition of the gas-oil
- Purity of make-up hydrogen



### ACTION PARAMETERS

- Type of catalyst
- Gas-oil feed rate
- Hydrogen make-up rate
- Reactor inlet temperature
- Reactor inlet pressure
- Hydrogen recycle rate
- Separator inlet temperature

### OUTPUT VARIABLES

- Chemical composition of the purge gas
- Gas purge rate
- Chemical composition of the liquid effluent
- Liquid effluent fluid rate

## Observation #1:

Some components of the system perform the exclusive function of OBTAINING VALUES SELECTED FOR THE ACTION PARAMETERS. They can be replaced in the arrangement set up for the scaling-up study by any other device that help to obtain the value selected for the action parameter. This is possible if these components ARE PERFECTLY KNOWN in term of industrial technology.

For example, the furnace heated by burners (in an industrial plant) can be replaced by an electric heater, which is easier to use in the laboratory or the pilot plant.

## Observation #2:

After breaking down a complex system into independent sub-systems, these independent systems must be examined and, considering the available knowledge, the systems for which scale-up may be a problem, requiring additional experimentation, must be identified.

In our example it can be concluded that **ONLY THE REACTION SECTION REQUIRE A SPECIFIC STUDY**, because the other parts of the plant (feed and separation section) can be considered as already ready.

# Development methodology: sub-systems

The second phase of the work can now begin!

It consists of the detailed analysis of the mechanism involved in each sub-systems for which scale-up problems can arise.

All the chemical process involve various factor in addition to the desired chemical conversion:

- 1) Side or interfering chemical reactions
- 2) Thermodynamic, physical and chemical equilibria
- 3) Heat transfer
- 4) Mass transfer between phases or even within a given phase
- 5) Flows of fluid (natural or forced convection) or of granular solids

These different factors may be inherent in the process, or simply induced or inevitable.

## Development methodology: sub-systems

Because these processes do not take place independently, the complexity of a problem is usually associated with the COUPLING of these mechanisms and the resulting interactions.

For example, transfer mass mechanism depend essentially on the turbulence prevailing in the system, that is dependent from the fluid flows.

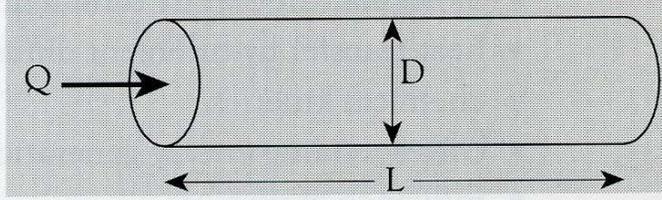
This means that the scale or size of the equipment in which the process takes place has a different effect depending on what factor of the chemical process requires to be taken into account.

## Scale-up of a system by geometrical similarity

It is possible to determine the **EFFECT OF SIZE** on a number of characteristic variable of the system, IF THE SIZE IS ESREPOLATED BY GEOMETRIC SIMILARITY, considering the generic ratio  $r$  for scale. A generic cylinder is considered, being similar to reactor (PFR, PBR ecc.), distillation column, absorption column etc....

Table  
1.1

Scale-up of a simple system by geometrical similarity



	SYSTEM 1	SYSTEM 2
Flowrate (m <sup>3</sup> /s)	$Q_1$	$Q_2 = r \cdot Q_1$
Diameter (m)	$D_1$	$D_2 = D_1 \cdot r^{1/3}$
Volume (m <sup>3</sup> )	$V_1$	$V_2 = V_1 \cdot r$
Mean residence time (s)	$\theta_1 = \frac{V_1}{Q_1}$	$\theta_2 = \theta_1 = \frac{V_2}{Q_2}$
Cross-section area (m <sup>2</sup> )	$S_1 = \frac{\pi \cdot D_1^2}{4}$	$S_2 = S_1 \cdot r^{2/3}$
Mean velocity (m/s)	$v_1 = \frac{Q_1}{S_1}$	$v_2 = \frac{Q_2}{S_2} = v_1 \cdot r^{1/3}$
Ratio: lateral area/volume (m <sup>-1</sup> )	$m_1 = \frac{4}{D_1}$	$m_2 = \frac{4}{D_2} = \frac{m_1}{r^{1/3}}$

## Principal major variables

This Table provides the principal major variables and their probable influence of the scale at which the operation is performed for each mechanism considered separately

**Table 1.2** *Influence of size on a number of key mechanisms of chemical processes*  
 (\*) T = Temperature C = Concentration P = Pressure

MECHANISM	IMPORTANT VARIABLES (*)	INFLUENCE OF SIZE
Chemical kinetics	T, C, P	None
Thermodynamics	T, C, P	None
Heat transfer	Local velocities, T, P, C	Indirect
Mass transfer within a fluid phase	Turbulence, T, C	Indirect
Transfers between phases	Relative velocities of phases, C, T, P	Indirect
Forced convection	Flow rates, geometry	Important
Free convection	Geometry, T, C, P	Determining

«Indirect» influences means that the variable influences the mechanisms that are used to obtain the specific mechanism in the chemical plants.

## Models

To analyze the behavior of the systems in detail it is necessary to construct a MATHEMATICAL MODEL describing the various aspects of interest in each system.

These models basically consist of BALANCE EQUATIONS reflecting the fundamental laws of physics

- Conversion of MASS
- Conversion of ENERGY
- Conversion of MOMENTUM

# General model equations around an element of volume $dx, dy, dz$

Table  
1.3

General balance equations around an element of volume  $\Delta V = dx \cdot dy \cdot dz$

## MOLAR BALANCE

$$\frac{\partial C_i}{\partial t} = - \left\{ v_x \frac{\partial C_i}{\partial x} + v_y \frac{\partial C_i}{\partial y} + v_z \frac{\partial C_i}{\partial z} \right\} + \left\{ D_{ix} \frac{\partial^2 C_i}{\partial x^2} + D_{iy} \frac{\partial^2 C_i}{\partial y^2} + D_{iz} \frac{\partial^2 C_i}{\partial z^2} \right\} + R_i$$

## MOMENTUM BALANCE (e. g. for x direction)

$$\rho \left\{ \frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right\} = - \frac{\partial P}{\partial x} + \mu \left\{ \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right\} + \rho \cdot g_x$$

## ENERGY BALANCE

$$\rho \cdot C_p \left\{ \frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} \right\} = k_x \frac{\partial^2 T}{\partial x^2} + k_y \frac{\partial^2 T}{\partial y^2} + k_z \frac{\partial^2 T}{\partial z^2} + S_R$$

Assumptions:  $\rho, \mu, C_p$  are constant,  
fluids are newtonian,  
viscous dissipations are negligible.

These equations take account of the following mechanism:

- Newtonian-type fluid ( $\mu$ )
- Molecular transfer by turbulent diffusion ( $D_i$ )
- Heat transfer by turbulent diffusion ( $k_i$ )
- Chemical kinetics ( $R_i$ )
- Corresponding energy generation ( $S_R$ )
- Influence of pressure ( $P$ )
- Influence of gravity ( $g$ )
- Unsteady-state character ( $t$ )

These Eq.ns must be simplified by adjusting them to the case at hand. Transient term in particular are omitted sometimes. Other simplifications can be made once the geometry of the system has been clarified.

## General model equations for multi-phase systems

Additional terms or equations must be introduced when deviating from the simple case of single-phase systems. The same equations as those in the previous Table must be written for each of the phases with, in addition, exchange terms between phases (mass and energy transfers in particular)

### General model equation: chemical mechanism

In these Eq.s, the chemical mechanism is involved in only two terms:

- 1)  $R_i$ , reflecting the chemical kinetics relative to compound  $A_i$
- 2)  $S_R$ , the production of energy associated with the chemical transformation

These two terms are, by nature, INDEPENDENT OF THE SIZE OF THE SYSTEM, and the influence of the chemical mechanism on the physical behavior of the system is often negligible, also if the thermal effect of the reaction can disturb the system, for example by introducing natural convection.

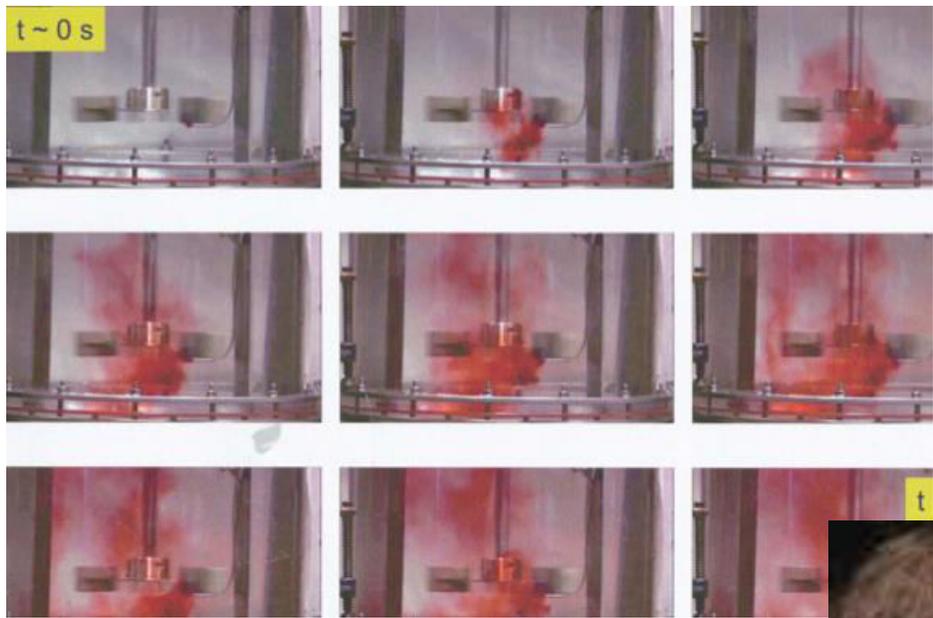
## Mock-up concept

In the scaling-up of a chemical process, it is possible to delete the two chemically-related terms from the model. Reflecting the purely physical behavior of the system. (!!!)

This part of the model will be the MOST SENSITIVE to the scale effect and could be considered separately and ADJUSTED BY CONDUCTING SPECIAL EXPERIMENTS WITH A PHYSICAL SYSTEM NOT INVOLVING THE CHEMICAL REACTION.

This leads to the concept of Mock-up.

It is important to realize the benefits of an approach that breaks down the problem into its different components.



## The experimental approaches to scale-up

The experimentation necessary to scale-up the process is split into COMPLEMENTARY parts, which belong to three categories:

1) Laboratory studies

2) Pilot-plant studies

3) Mock-up studies

## 1) Laboratories study

In the lab, a series of measurements can be taken concerning all the mechanisms that are independent of sizes.

This applies in particular to everything related to **thermodynamics** and **chemical kinetic**.

Moreover, a good number of physical quantities involved in the model, such as:

- Densities
- viscosities
- specific heats
- phase equilibria etc

can be measured and studied in the interval of operating conditions of the process.

## 2) Pilot-plant study

The typical experimentation involved in process development is still the pilot-plant experiments.

Pilot plant **MUST** be **REPRESENTATIVE**, that means with operations identical to the corresponding part in the industrial process, or transposable by using a mathematical model of this part of the unit.

The pilot plant thus appears as a tool allowing the simultaneous analysis of the physical as well as chemical mechanism. It is very important for measuring the extent of the possible interactions between these two types of mechanism.

The size of the pilot plant can be selected to minimize the total cost of operation in order to obtain useful data.

## 2) Pilot-plant study

At this stage, the term «scale-up» does not correspond EXCLUSIVELY to a change in size by multiplying the characteristic dimensions by a factor greater than one.

In fact, a TRANSPOSITION is carried out to MODIFY THE STRUCTURE OF THE SYSTEM. This approach allows to change the structure of a laboratory plant, aimed to test and verify for example a possible new reaction or separation, in a structure similar to the possible industrial configuration.

### 3) Mock-up study (or cold flow models)

These studies help to analyze separately the PHYSICAL MECHANISM that are most sensitive to size, such as hydrodynamic mechanisms (they include both flow of fluids as well as of granular solids). Mock-up studies are called sometime «cold flow models».

Mock-up simulates the physical process:

- by adopting soft operating conditions (room T and P)
- By using fluids with physical properties approaching those of the reaction fluids but also inexpensive and harmless.

This simulation makes use of dimensionless numbers that characterizes the major physical mechanism. This allows low-cost experiments that use sizes that can be varied from the pilot plant to close to the industrial units.

### 3) Mock-up study (or cold flow models)

Certain simplifications of the balance equations are accepted in constructing the ideal models often referred to PFR reactors.

Despite its ideal character (and then not realistic), this model is used as a first approximation.

Mock-up experiment are accordingly designed to indicate the prerequisite conditions for this simple model to be applicable.

In this PFR example, measurements of RESIDENCE TIME DISTRIBUTION using tracers yield highly valuable information.

# Examples

Now, we will discuss two industrial scaling-up studies, where the use of mock-ups was decisive for the satisfactory scale-up:

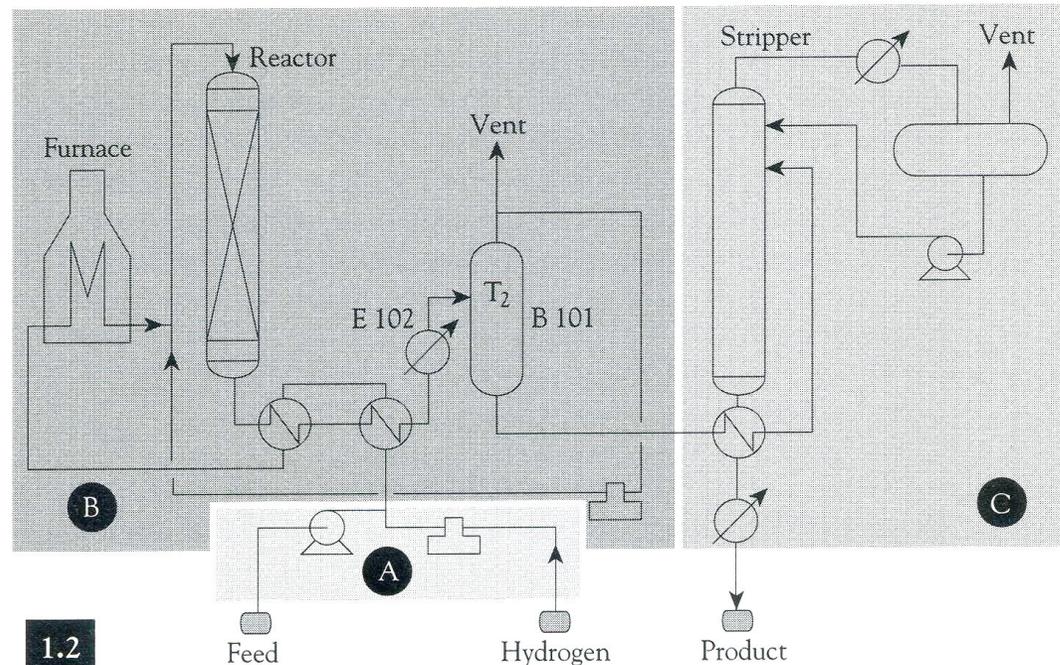
1) Hydrotreating petroleum cuts

2) Regenerative catalytic reforming

# 1) Hydrotreating petroleum cuts

The term «hydrotreating» covers all hydrogen treatment operations on a petroleum cut in the presence of a solid catalysts. Examples are hydrodesulfurization, hydrorefining, hydrocracking.

From a technological point of view, all these processes are quite similar, and the experience gained in the hydrodesulfurization (oldest process) was used in the others. First observation: all these process use the same kind of REACTOR: a fixed-bed catalytic reactor through which liquid and gas phases flow simultaneously in cocurrent downflow.



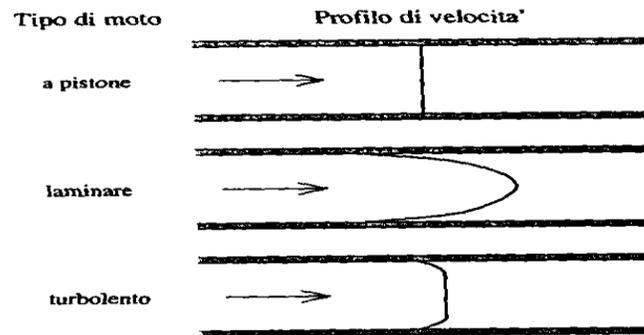
Typical flowsheet of a hydrodesulfurization unit

- Flow of liquid phase: the simplest model imaginable corresponds to PLUG FLOW.
- The problem of BACKMIXING, that when reacted chemicals combine with unreacted feed in the reactor, in the liquid phase appears negligible if the catalyst bed reaches a sufficient length (1 m)
- Differently, a problem concerns a poor liquid distribution that leads to preferential paths, with two consequences:

# Bad liquid distribution consequences:

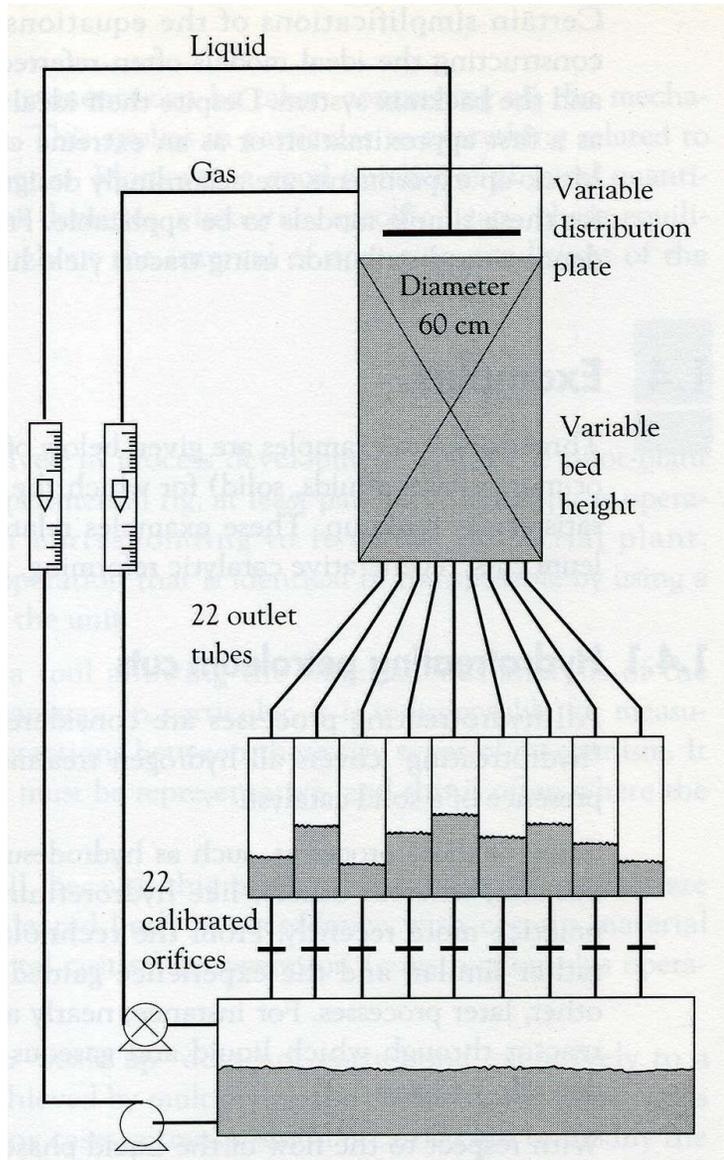
- 1) Poor use of the catalyst: some portions of the catalyst bed may not even be wetted by the liquid. Reactions may take place in the dry zones involving gas phase only, which are faster and liable to give rise to hot spot;
- 2) Broader residence time distribution, which may have a negative effect when extremely high conversion is required

It is therefore necessary to obtain liquid distribution and flow conditions in the catalytic bed which ensure that the plug flow hypothesis is valid.



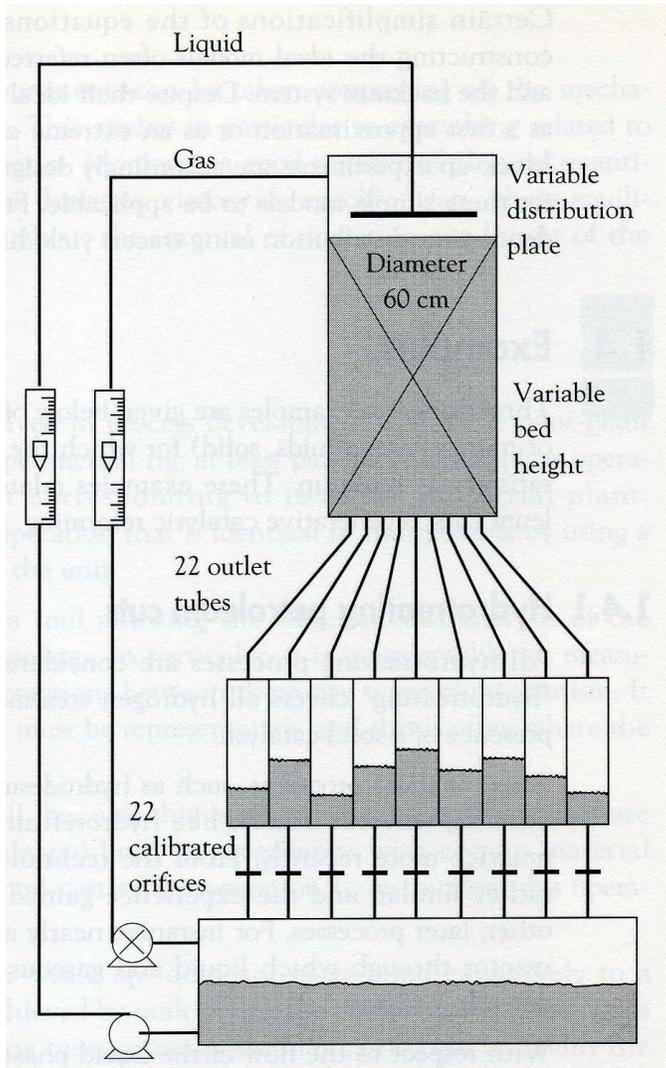
Mock-up test!

# Mock-up test:



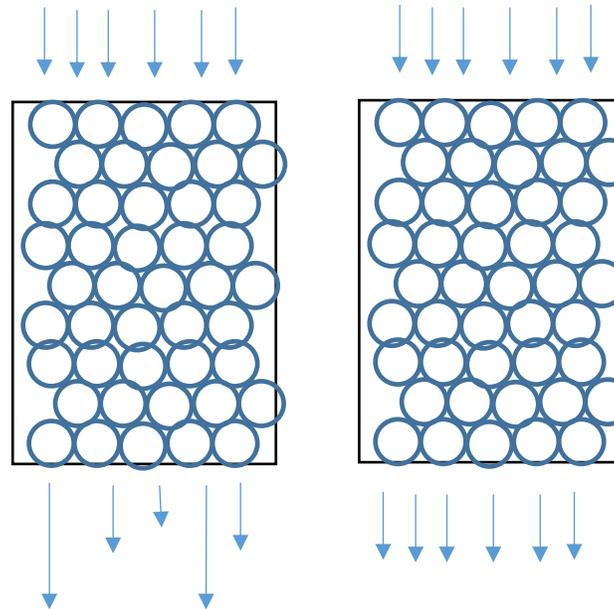
The liquid (hydrocarbon) goes into the reactor from the top and it is distributed with a variable plate, like a shower. The liquid goes down passing through the catalytic bed and exit from the bottom. If the liquid distribution was ideal, from the bottom each point will present the same liquid flow. By 22 outlet tubes and 22 cylinders collection it is possible to evaluate the uniformity of the liquid distribution.

The liquid (hydrocarbon) and gas (nitrogen) phases are RECYCLED by pumps. The catalytic bed consists of the catalyst used in the industrial process.

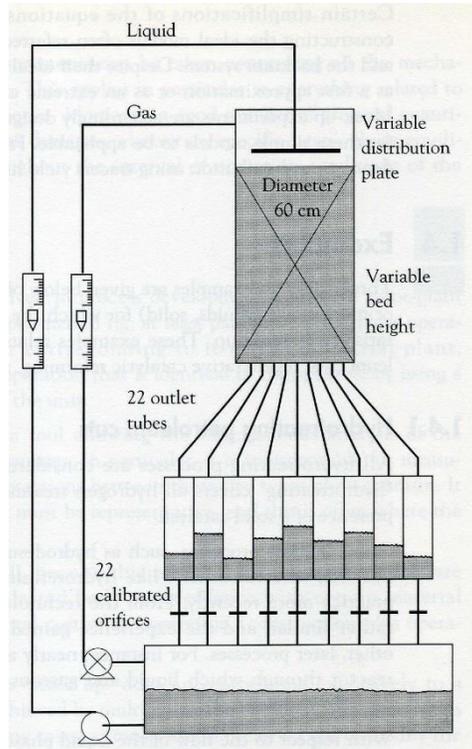


Two possible alternatives have found from these researches:

- 1) Operation with COCURRENT upflow, which obviously ensures that the catalyst bed is wetted
- 2) Downflow operation but by DILUTING THE CATALYST with INERT PARTICLES with a much smaller grain size distribution. This significantly increases the retention of the liquid phase and hence the wetting of the catalyst.



The smaller particles help the liquid homogeneous distribution inside the reactor. You can imagine golf balls in a becker and golf balls + sand. The little particles avoid for example liquid flow on the surface of the greater particles.



If the liquid distribution is good, the liquid velocity can be reduced and the reactor volume too, maintaining the same LHSV (Liquid Hourly Space Velocity) or, is the same, the residence time.

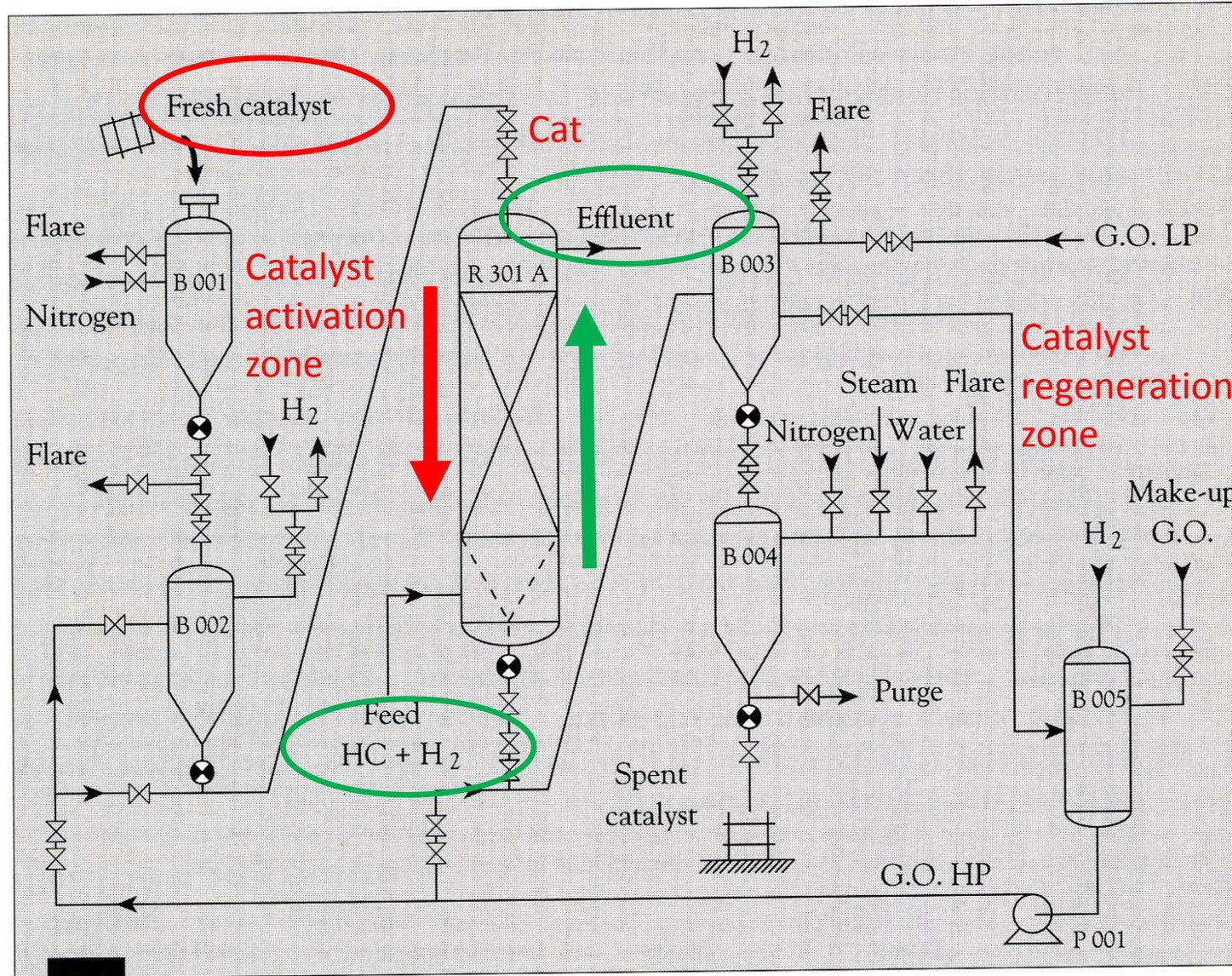
In this industrial examples the first case, the cocurrent upflow was adopted. The hydrodynamic conditions resulted compatible with the assumptions made for the model.

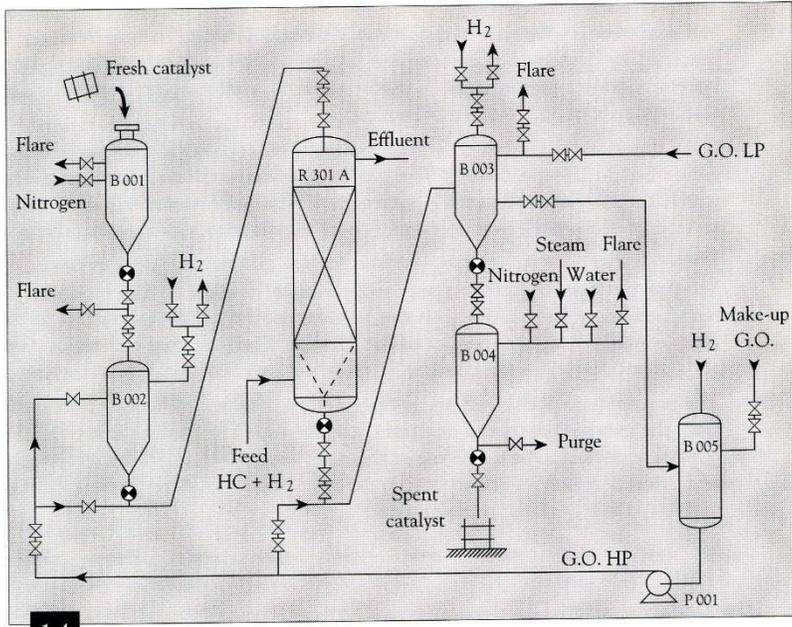
# 1) Hydrotreating petroleum cuts: another problem!!!

In this operation, if performed on packed bed reactor, the rapid CATALYST DEACTIVATION, due to the deposition of metal contained in the feedstocks, is an important problem.

The MOVING BED technology was considered and countercurrent flows appeared to offer the optimal technology.

A feasibility study was carried out using mock-ups of various sizes. The aim was to assure that the CATALYST BED COULD FLOW IN COUNTERCURRENT TO THE FLUIDS (GAS+LIQUID) AND THAT THIS GRANULAR SOLID WAS SUFFICIENTLY CLOSE TO PLUG FLOW.



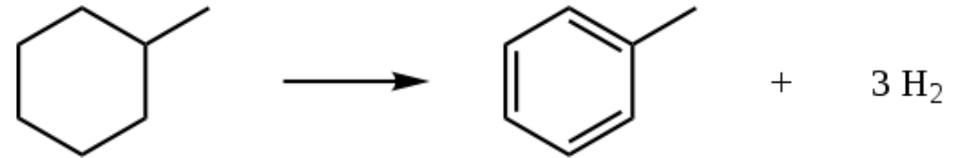


In this case, being a new technology with the RISK OF INTERFERENCE BETWEEN CHEMICAL AND PROCESS, a demonstration init is a mandatory step in process development. In this example, this was made on Asvahl complex, where a moving bed reactor (40 cm diameter, 20 m high) was operated several month to obtain sure and optimized performance, near Lyon (France).

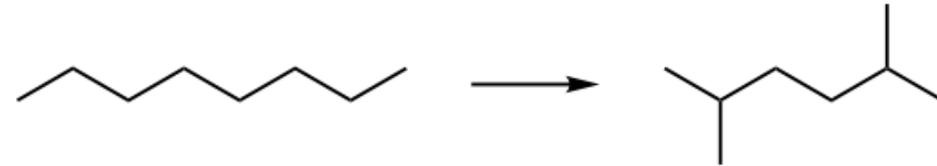
## 2) Regenerative catalytic reforming

The four major catalytic reforming reactions are:<sup>[11]</sup>

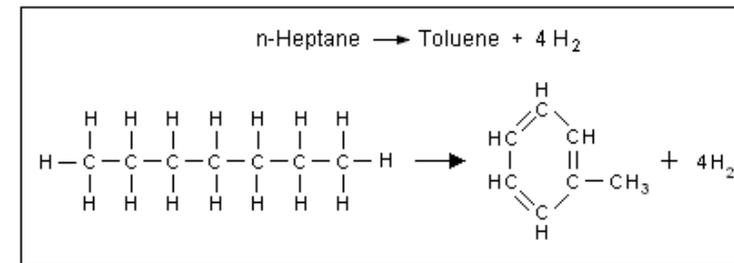
1: The **dehydrogenation** of naphthenes to convert them into aromatics as exemplified in the conversion **methylcyclohexane** (a naphthene) to **toluene** (an aromatic), as shown below:



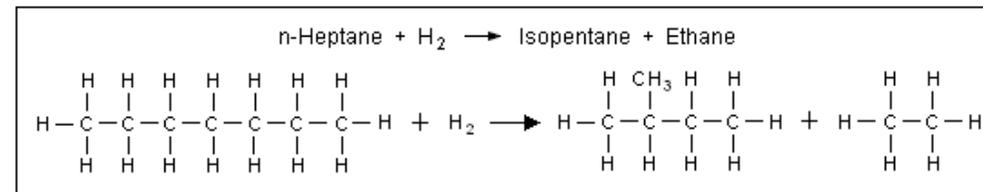
2: The **isomerization** of normal paraffins to **isoparaffins** as exemplified in the conversion of **normal octane** to 2,5-Dimethylhexane (an isoparaffin), as shown below:



3: The dehydrogenation and **aromatization** of paraffins to aromatics (commonly called dehydrocyclization) as exemplified in the conversion of **normal heptane** to toluene, as shown below:



4: The **hydrocracking** of paraffins into smaller molecules as exemplified by the cracking of normal heptane into **isopentane** and ethane, as shown below:



Remember: Catalytic reforming is a chemical process used to convert petroleum refinery naphthas distilled from crude oil (typically having low octane ratings) into high-octane liquid products called reformates

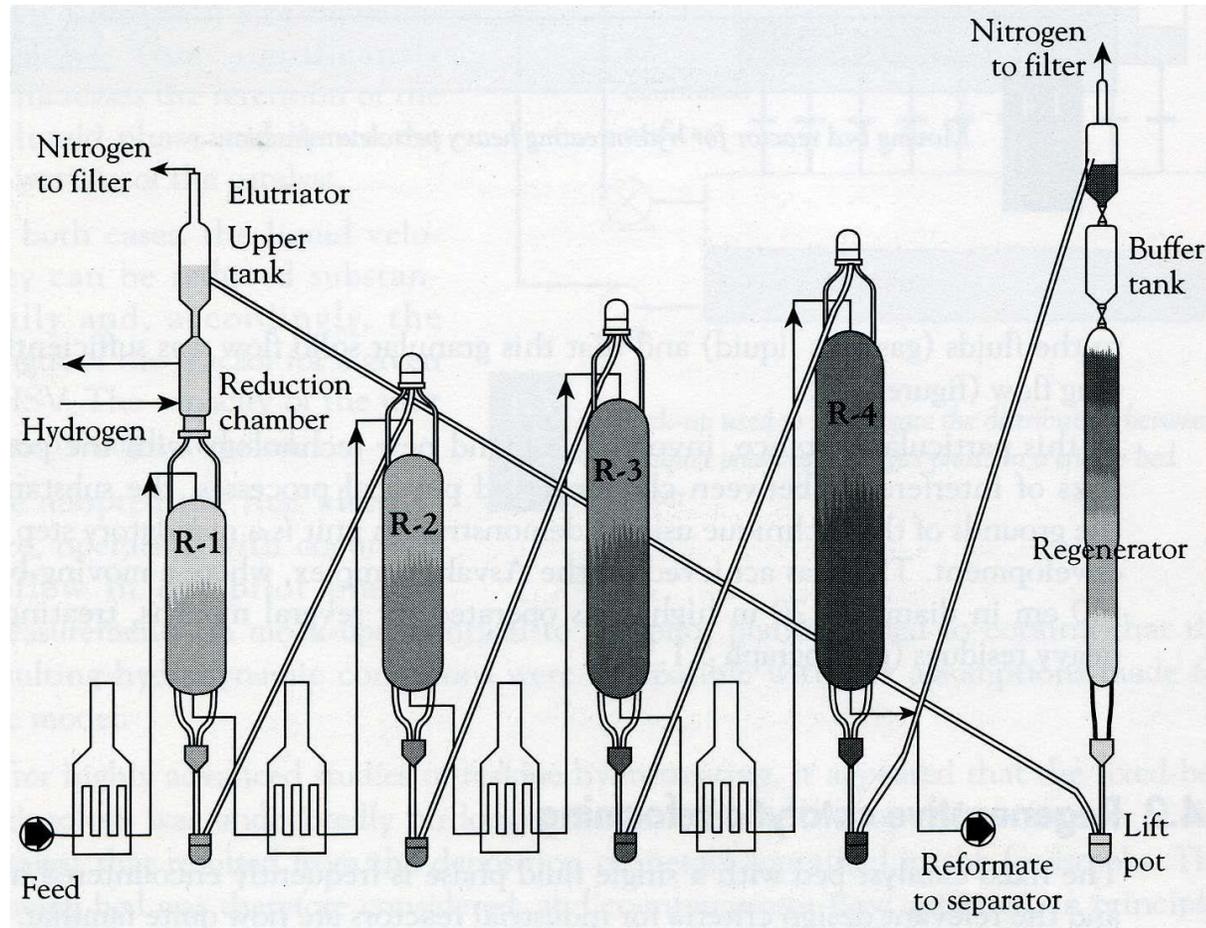
Catalytic reforming represents a complex reaction scheme for which the THERMAL EFFECT is very high during the first phase of the transformation (dehydrogenation of paraffins).

The conventional technology used FIXED BED REACTOR IN ADIABATIC CONDITIONS. In this process, three or four reactors in series are preceded by heaters that compensate the overall endothermicity of the reaction system.

Improved catalysts were discovered during the years, but the unchanged technology limited the improvement of the quality of the whole industrial process. The main problem of this process was the cycle time due to catalyst deactivation.

For this reason, MOVING-BED technology, which allows continuous or semi-continuous regeneration was developed.

## MOVING-BED technology for catalytic reforming:



After regeneration, the catalyst enters the first reactor at the top.

The catalyst is conveyed from the bottom of each reactor to the top of the next.

It passes through the reactors by gravity, and it is transferred from one reactor to the next by gas-lift.

After passing through all the reactors, it is sent to the regenerator.

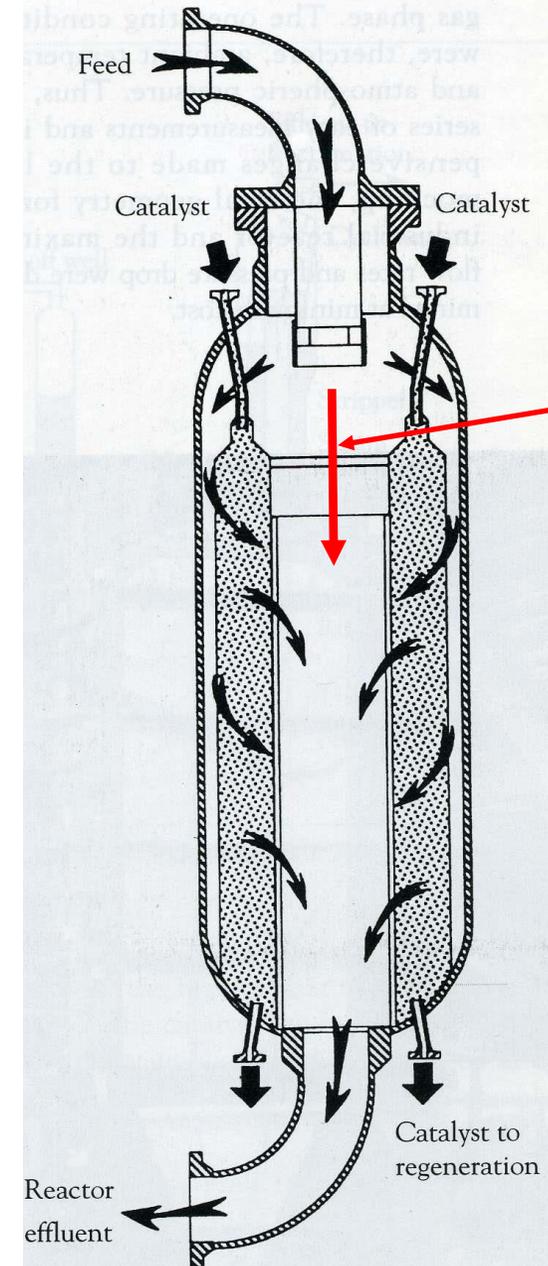
In this example, we will discuss only the design of the moving-bed reactors.

To minimize the pressure drop across the bed, a crossflow technology was adopted.

Only the studies required, among the others, to achieve the detailed design of the catalytic moving beds will be mentioned.

The catalysts flow from the top between two concentric cylinders made up of grids allowing the RADIAL PASSAGE of the gas phase.

The main risk was that the catalyst would be blocked against the grid and would no longer be able to flow. In was also necessary to obtain catalyst flow conditions approaching plug flow as closely as possible.



**Not allowed flow!!!!**



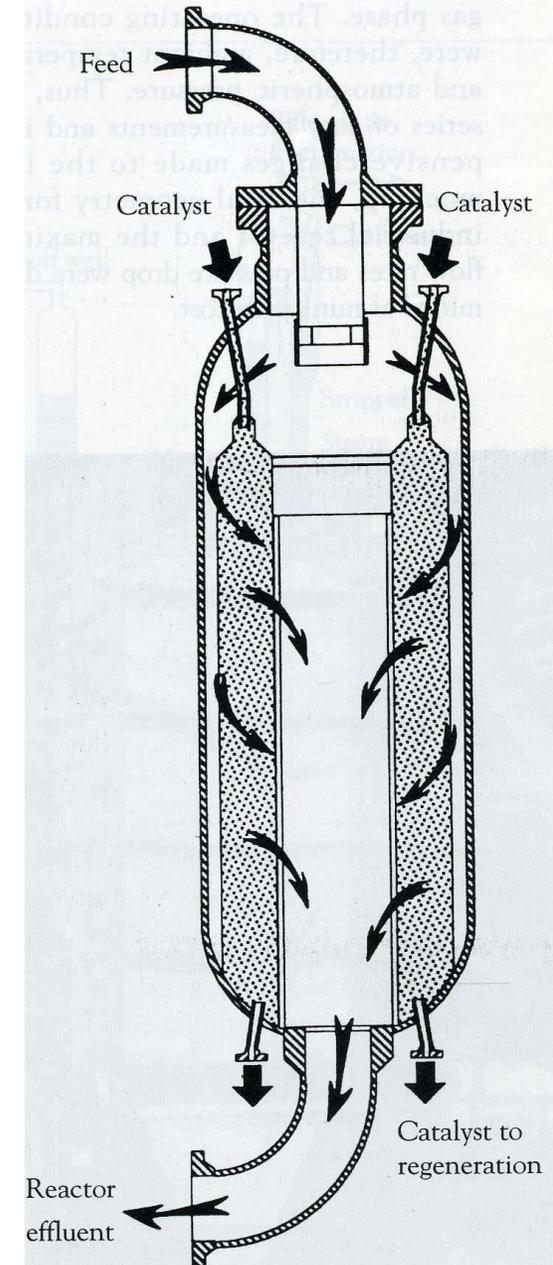
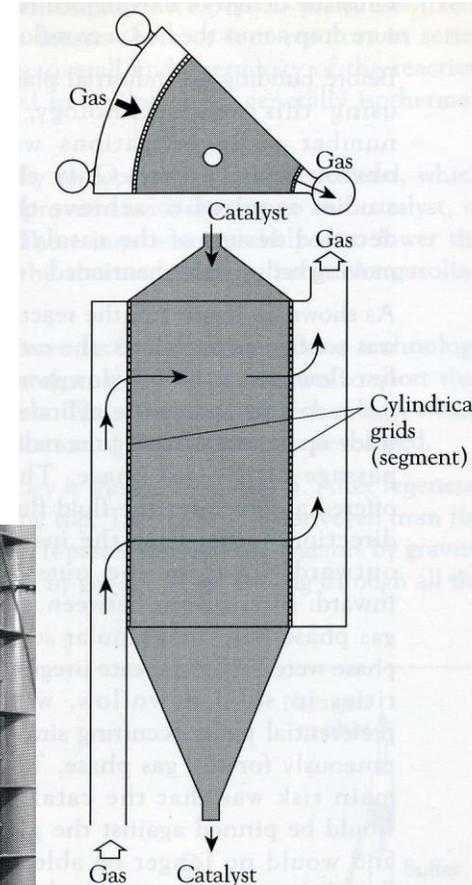
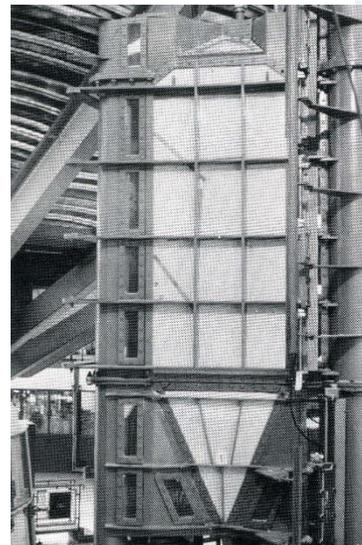
**The feed MUST pass through the catalyst!!!!**

Gas/solid interaction was investigated by using different sized mock-ups till the last with the geometry and the size of the planned industrial reactor.

Research focused on a section of the cylinder. One of the faces was MADE IN PLEXIGLAS to allow observation of the solid flow by means of tracer technique (layer of COLORED particles)

The solid used was the particles used as support for the catalyst and air as gas-phase. Room temperature and pressure.

The final geometry for the industrial reactor and the maximum flow-rate and pressure drop were determined at minimum cost.



## Final remarks

- 1) This lesson stressed the methodological aspects of scaling-up a chemical process and introduced the mock-up concept
- 2) The term «scale-up» should not be understood only in the sense of increasing the dimensions while preserving similar systems. The transposition of one system to another offers a better solution to a problem.
- 3) The construction of a right mathematical model is the most effective means for successful scale-up. «Mathematical model», does not mean a large number of complex equations. More complex is one model, the more experimental data are required to adjust it (we will discuss this point in the next lessons). A simple model, if well justified, may be the most convenient and satisfactory choice.

