

Chapter 5

Foundations of Process Industrialization

5.1. Introduction

Process development aims to transpose an idea, resulting from research conducted mostly in a laboratory, into an industrial innovation, which consists of a new reliable process, economically profitable and having an environmental impact as low as possible. Process development is based on multidisciplinary scientific skills, several scientific and technological barriers will be removed during this phase, and it usually takes several years. Any process development is associated with a risk of failure, which must be integrated into the development strategy.

The transition from laboratory experimentation to industrial implementation is a fundamental step in the development of a technology or a product. This step determines the value and industrial credibility of an innovation.

The industrialization process of a method can be divided into two phases: a “study” phase followed by an “engineering” phase.

The first phase consists of carrying out studies (development phase) such as: laboratory research, pre-study of the possible variants of the process, selection of process flow diagrams to develop, acquiring basic data through development of experimental tools, technologies, simulation steps of the process units, and simulation and optimization of a typical scheme of the process. This phase leads to the development of a process file, which contains all of the scientific bases (design criteria, models, etc.), which will enable industrialization, that is to say, the sizing of an industrial unit.

The second phase includes engineering studies: process engineering (editing the process book), basic engineering (development of FEED (Front End Engineering Design) which assesses the investments precisely), and detailed engineering after an investment decision is made. After this phase, the production unit is built on the industrial site and can be commissioned.

This chapter deals with the first phase, that is to say, process development: the foundations of industrialization.

Three main objectives are pursued in this first phase of studies leading to the basic process guidelines:

- feasibility: imagine, build, and develop experimental tools to acquire the basic data that are necessary for the development process;
- reliability: ensure that the process can continue in the long-term (even in the case of fits and starts or incidents caused) without irretrievable drift or loss of control, and without major degradation of product quality while maintaining the profitability of production;
- extrapolability: ensure the conversion of research results to an industrial scale.

Methodologies of process development have evolved over time, with the aim of improving the process to minimize the development time and associated costs, while maintaining a very good management of risks related to extrapolation.

5.2. The various stages of process development: from research to the foundations of industrialization

The creation of the process guidelines containing the basics for the industrialization of a process can be divided into three stages, whose relative importance depends on the degree of innovation: a significant improvement of existing technology or development of a new technology, even a break away from the existing technology.

The three major phases that structure the development of a process are as follows:

- the pre-study (or pre-development) of the process is the first step which is based on the results of the laboratory research (new reaction, new catalyst);
- the developmental stage leading to the process guidelines containing the basics of industrialization;
- the establishment of process guidelines, foundations of industrialization, which brings together all the elements relating to the process guidelines.

5.3. The pre-study (or pre-development process)

The preliminary study builds a consistent and rigorous development approach. It also acts as a support tool for decision-making. Indeed, process development starts with the analysis of the potentials and techno-economic feasibilities of the idea resulting from the research work. So, depending on the increase in level of difficulty of the scientific and technical barriers and on the potential market of the process, it is decided whether to continue the development process that will implement the idea on an industrial scale or not. This comprehensive approach of pre-study alone helps in judging the value of a new idea at a given time.

The process begins with the first design of a process flow diagram of the new concept (a simplified illustration is given in Figure 5.1), starting from a limited amount of data from the first laboratory tests, the first calculations, or using data from literature in order to identify the key points and any other possible barriers to be removed later in the development.

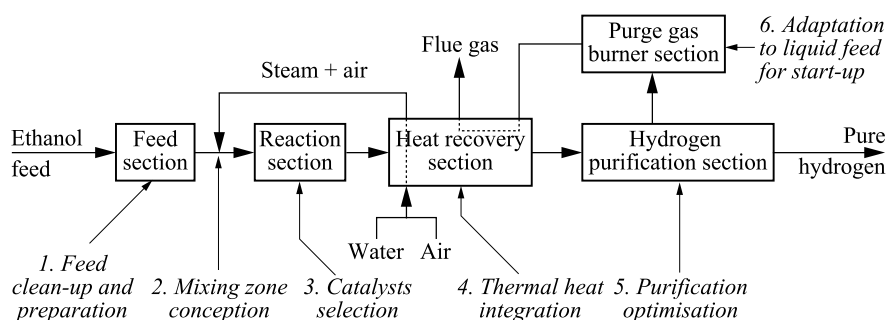


Figure 5.1. Example of a process flow diagram established in a preliminary study of a process for hydrogen production (source: IFP energies nouvelles)

Finally, we must estimate the technical and economic performances of the process: this study is made from strong hypotheses, especially by assuming the removal of technological barriers identified in the design of the diagram. This pre-estimation will enable us, by comparing the expected performance of the process with respect to the performance target related to the setting up of the marketing process, to validate or not the viability of the concept and, if necessary, switch to the development phase of the process if the research and development effort assessed is consistent with the issue.

In parallel, an analysis of the patent literature is required to stand out from the competition and to ensure the freedom to operate. This analysis aims to establish an industrial property: protecting innovative diagrams from the beginning by acquiring the data necessary for patent drafting.

In general, the completion of technical and economic preliminary studies also requires making strong hypotheses, as it is necessary to develop the methodologies that help to make these preliminary studies reliable.

The design and development of a process are primarily based on the material and energy assessments obtained by simulation. However, environmental constraints (resource use, environmental pollution) are increasingly present and do not appear directly in this analysis, because the pollutants are, in general, several orders of magnitude below the primary products, hence they are not taken into consideration in the simulations. Currently, we must also add the environmental impact of processes at the pre-development phase. The technical and economic preliminary studies have become technical, economic and environmental preliminary studies [POR 10]. Integrating the environment when the technical possibilities are at maximum, is the whole point of the eco-design process.

However, there is no guarantee that the process developed from just the material and energy assessments will be economically viable. The integration of economic and energy constraints has led to the birth of a new method: thermo-economic analysis [TOC 10]. This method integrates both the operational and economic aspects of the process and even seems to be able to guide the design and optimization of complex systems.

The first design of a process flow diagram is an opportunity to highlight the technical difficulties and possible barriers that will have to be removed later in the development of the process.

Barriers are the key points of the process, which, if not removed can lead to the discontinuation of the project; for example, barriers can include:

- unknown effect of recycling (accumulation of impurities in trace amounts and having a strong impact on the catalytic performances);
- need to develop a new piece of technological equipment, whose extrapolation rules are unknown;
- need for a catalyst whose shaping is not controlled, for example, in some cases it can be very difficult to produce a catalyst in the form of beads of high mechanical resistance;
- the cost of separation steps;
- dealing with any process discharges.

Various configurations are studied and assessed at this stage on a technical, economic and environmental basis: different types of reactors, defining a first fractionation flow diagram of effluents, identification of possible recycling, and so on. This pre-development approach can also specify the additional experimental data

that are required. These data will be acquired on dedicated experimental tools (studies of chemical reactions, acquiring thermodynamic data, and study of transport phenomena). This study will also be fueled by the results of the study of process modeling which is carried out in parallel, in order to optimize the pre-development process.

Once a process flow diagram is selected, the new data and models developed will be integrated throughout the development phase of the process, in order to update it based on the technical, economic, and environmental simulation and evaluation.

Beyond the technical and economic preliminary studies conducted within the boundaries of a process, it is interesting from the pre-development phase to study its impact on the performance of the industrial site in which it operates. This can be achieved by using linear programming. Linear programming is a methodology to find an optimum (maximum or minimum) by considering a certain number of constraints (material balances, quality and composition of a mixture, maximum capacity of a plant, demand for a particular product, etc.). This tool is used in operational research (deciding making) and in various fields such as air transport (rotation of crews), petroleum refining (procurement, manufacturing, and distribution), the food industry (defining mixtures), the metal industry (definition of alloys), and so on.

Tools and methodologies used in pre-development are as follows:

- process schemes are studied using commercial simulation software. These tools perform the calculations of thermodynamic equilibrium but can be enriched with kinetic models of varying complexity for the reactive sections of the process;

- optimization of heat integration can be achieved, for example, by using the pinch method which determines the objectives of consumption of utilities, calculates the pinch temperature of the process and estimates the quality of the commodities required (low steam, medium or high pressure, cold boxes, etc.). This method provides evidence that can guide the process engineer in the design of heat integration and locate the places where heat is exchanged inefficiently in terms of energy. Then it is up to the developer to accept these inefficiencies, justified by other reasons (constraints on loss of load, start up constraint, flexibility or security constraints) or to rectify them;

- tools for sizing major equipment (pumps, compressors, heat exchangers, reactors, etc.);

- different methods of technical and economic evaluation can be used, among them we will discuss the method developed by A. Chauvel [CHA 01] at IFP Energies nouvelles;

– experimental tools to acquire kinetic data, which help us to develop a simplified kinetic model of the reactions;

– reactor modeling tools (kinetic modeling, modeling of mass and heat transfer phenomena), based on the kinetic data acquired to develop the first performance models that are included in the overall process flow diagram.



Figure 5.2. Example of a reactor using a heterogeneous catalyst in a fixed bed for the hydrogenation of fuels © IFPEN

At this stage of development, it is often necessary to define the technology of the reactor, which is one of the key pieces of equipment of the process; Figures 5.2 and 5.3 are illustrations of industrial reactors using a fixed bed of catalyst within a large volume reactor (Figure 5.2), and a moving bed of catalyst within several reactors in series (Figure 5.3).



Figure 5.3. Reactors of the catalytic reforming process for light fuels, radial bed technology © IFPEN

5.3.1. Experimental tools for acquiring kinetic data

In the pre-study phase, it is necessary to acquire the experimental data when they are not available in the literature. It is absolutely necessary to have experimental equipment that helps us to acquire the required information in a reasonably short time (e.g. a few months). These data are used first through kinetic models that will make it possible, through reactor designs, to assess the possible choices for reactor technology, and also to set the targets in terms of performance for the development of the catalyst.

The goal is not to cover the whole field of operation of the process envisaged, but to target the minimum data necessary to develop the first model that will enable us to choose the technology of the reactor (fixed bed, fluidized bed, circulating bed, etc.).

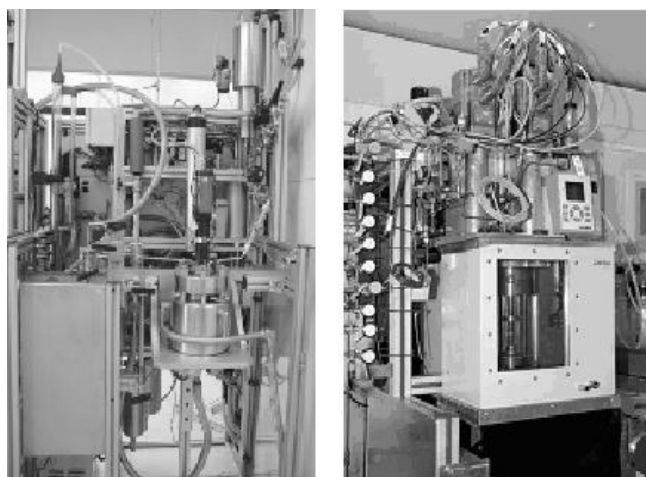


Figure 5.4. Pilot plants with a perfectly stirred reactor used to acquire kinetic data in the pre-development process © IFPEN, © P. Chevrolat

Acquiring kinetic data can be done on a pilot plant, operated continuously or discontinuously, in a fixed bed or in a perfectly stirred reactor, and whose configuration is not necessarily indicative of what the reactor(s) of the industrial unit will be. Taking into consideration the small volume of this type of reactor, in general from 50 cm³ to 500 cm³ of reactive volume (Figures 5.4 and 5.5), the isothermal conditions are met.

To determine the intrinsic kinetics, it is necessary to model the reactor, taking into account the transport transfer, and diffusion phenomena that can alter the performance of the catalytic system.

In the case where the catalyst is solid and the reactants and reactive products are in gaseous form, the flow of the gaseous phase within the reactor can be described by a piston dispersion model to consider the non-ideality of flow via an axial dispersion coefficient characterizing the degree of retro-mixing.

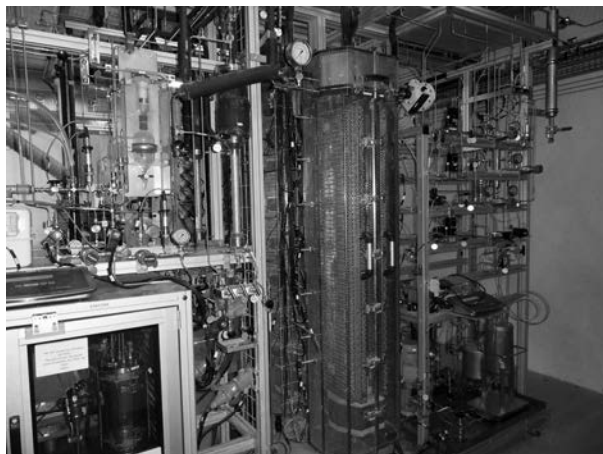


Figure 5.5. Pilot plant with a fixed bed reactor used to acquire kinetic data in the pre-development process © IFPEN, © P. Chevrolat

The external gas/solid transfer will be taken into account by writing a material balance at the level of laminar film of catalyst external transfer. The transfer coefficient of gas/solid will be determined by correlation. A model of particules in spherically or cylindrically coordinates, including the diffusion (characterized by an effective diffusion coefficient depending on the porosity and tortuosity of the particle), adsorption and reaction, will also be implemented to consider the possible diffusional limitations.

The coupling of flow models, external transfer, and diffusion in the particles enables us to determine the intrinsic kinetic parameters of the reactions.

Only this kinetics is directly extrapolable to other types of reactors because it depends only on the nature of the support and the active phase of the catalyst. Considering the physical and chemical phenomena is required in the pre-development phase in small pilots, so as to ensure high reliability in the scale-up studies in this pre-development phase.

Knowledge of the kinetic data intrinsic to the reactive system, coupled with the knowledge of transfer phenomena, helps us to choose the most suitable reactor technology; the first technical and economic evaluations are thus based on this reactor technology.

The choice of reactor technology also includes a first assessment of the stability of the catalytic system. Indeed, if a heterogeneous catalyst is used, then the choice of reactor technology will be directly related to the rate of deactivation, that is to say, the loss of catalyst activity over time.

This loss of activity may be due to several phenomena, including:

- the presence of impurities in the feedstocks (inhibiting or poisonous effect);
- an inhibiting effect of one of the products of the reaction;
- the loss of active sites (extraction of the active site in operating conditions of the reaction), or degradation of the catalyst support;
- build up of polymers or coke on the catalyst surface.

This knowledge is based on bibliographic studies in relation to similar reactive systems, and dedicated experimental tests aimed at identifying the main causes of deactivation of the system studied. To do this, we may, for example, harden the operating conditions to accelerate deactivation phenomena, for example by using higher reactor temperatures in order to accelerate the rate of coke building up. An initial deactivation model is then developed.

In the event that the main cause of deactivation is related to the presence of impurities in the products to be processed, it can be done using a purification section (e.g. mass capture to remove metals such as mercury and arsenic), special washing, or even dedicated reactors for purification by selective hydrogenation, for example, if these polyunsaturated components present may lead to polymers building up in the main reactor.

In the case where the cause of deactivation is related to a secondary reaction, and it is not possible to change the operating conditions to minimize such a reaction, the reactor technology proposed must consider this parameter, and this must be integrated into the preliminary technical and economic evaluation. There is not always only one technological solution to solve the phenomenon of rapid deactivation. Indeed, within the framework of a chemical transformation performed in the presence of a heterogeneous catalyst and whose deactivation rate is about 24 hours, two solutions are possible:

- the use of multiple reactors operated in “swing” mode, one of the reactors is in production, and the other reactor is in regeneration (or rejuvenation) mode. A periodic swing from one reactor to another is performed in order to maintain continuous production;
- the use of a single reactor, with a continuous or discontinuous flow of the catalyst within it, a regeneration zone being located in immediate proximity of the

reactor and the catalyst circulating between these two zones to be regenerated continuously (Figure 5.6). Such a mode of operation may appear to be more complex, however, it ensures a constant quality of the final product, and manages transitional situations that generate fits and starts of deactivation by accelerating the rate of the catalyst circulation in a more flexible manner.



Figure 5.6. *Industrial unit using a technology of continuous regeneration of the catalyst (catalytic reforming process by moving radial bed for production of base fuels with a high octane number) © IFPEN*

These technological choices are to be carried out at the pre-development stage, in order to clearly identify the scientific and technical barriers so that development will rise, such as the development of a catalyst adapted to the conditions and constraints of its implementation in the industrial unit: mechanical resistance (during the transport phases), catalyst shape (to minimize the process drops), accessibility of the active phase, and so on.

In the fields of chemistry, and the petrochemical and oil refining industries, chemical transformations are often carried out in large capacity reactors (a few cubic meters to 100 cubic meters). The reactions carried out can be highly exothermic, and the elimination of the heat of reaction is an important criterion to be considered, at least to preserve the quality of the manufactured products, the stability of the catalyst system, and especially to ensure safe operation of the industrial plant.

The inclusion of this criterion in the first stage of the process development is part of the pre-development phase, because it also guides us toward the choice of technologies related to the elimination of the reaction heat (exchanger reactors, using quench boxes, recycling the reaction products to limit the temperature increase by dilution of reactants, partial vaporization of the products within the reactor, etc.).

The pre-development phase also addresses the management of products and, in particular, the by-products and possible discharges of the process. These can be of various kinds, gaseous for example, if nitrogen oxides are formed, liquid or even solid.

At the end of the pre-development stage, teams responsible for the development of the process have the elements necessary for “Go/Don’t Go” decision-making to launch the development phase of the process. The development phase of the process is detailed in section 5.4.

5.4. Development stage of the process

5.4.1. Introduction

Process development aims to establish the basic data necessary for industrialization, that is to say all the necessary scientific data (models, design criteria, catalysts, optimized process flow diagram, etc.). It is executed around the technological barriers identified during the pre-studies carried out in the pre-development phase.

As the research progresses on these critical points, the engineers update the technical and economic studies and possibly redirect the studies.

The development phase is also an opportunity to protect the concepts via the patenting of process flow diagrams, formulation of catalysts, or technological solutions.

This is a complex process whose success is largely connected to the control of project management methods by the project manager, who is responsible for this development.

Scale-up factors between the tools used to acquire the basic data of the process and the industrial unit are often very high, as is illustrated in Figures 5.7 and 5.8. The quality of the experimental data, which constitute the basic data of the process, as well as models developed will guarantee the reliability of scaling up.

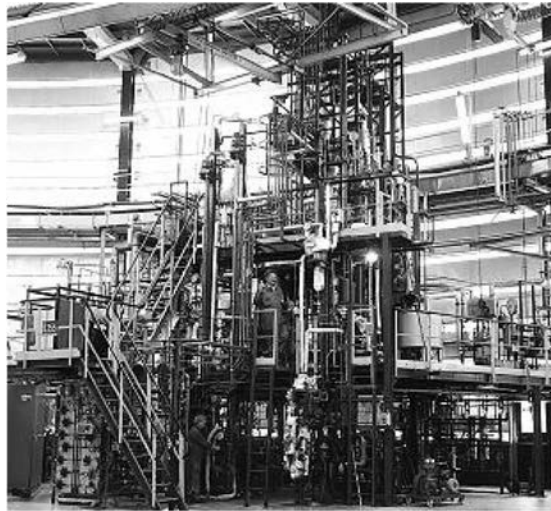


Figure 5.7. *Pilot plant used in developing a process for hydrotreating petroleum with a fixed catalyst bed* © IFPEN, © P. Chevrolat



Figure 5.8. *Industrial unit for hydrotreating petroleum in a fixed catalyst bed* © M. Roussel, ScOpimag

5.4.2. Data acquisition process

The team responsible for developing the process develops a strategy to acquire the experimental data required for the scale-up of the process; these data are used to develop a set of models which enables scale-up: choosing the best technology for

the reactive section, sizing key equipment, and selection of the process flow diagram, optimization, and heat integration. There are many books that deal with the design of chemical reactors, and readers can refer to [LIE 98, SCH 01, TRA 02, VII 93] for more information.

The main data to be acquired in this step are as follows:

- kinetic measurements, thermicity of the reaction (amount of heat exchanged with the reactor);
- measures in relation to the mass and heat transport phenomena;
- thermodynamic data;
- data related to the product quality obtained;
- impact of impurities on the deactivation of the catalyst(s);
- regeneration conditions.

The main deliverables of this stage of development are as follows:

- the reactor models which enable scale-up (prediction of performance of beginning of the cycle and deactivation);
- criteria for sizing key technological equipment;
- thermodynamic models that enable sizing the separation equipment (distillation, decantation, etc.), compression equipment, and heat exchange equipment (heat exchangers and furnaces).

Different experimental tools are used at this stage of process development: pilot plants to acquire data in representative reaction conditions and mock-ups to study the transport phenomena of mass and the technologies (filtration, gas/solid separation, fluid distribution, etc.).

The pilot plant is an experimental device that helps us to ensure the transformation from a feedstock into its desired product(s) and continuously over time.

The experimental conditions to be studied are set at the end of the pre-developmental stage. The pilot plant operates mostly on a continuous basis over time (24h/24h) and for periods up to several months in order to be able to quantify the stability and reliability of the process, to determine the lifetime of the catalyst, and also to produce sufficient quantities of finished product to verify the quality. The size of a pilot plant is significantly greater than that of the laboratory equipment; it is usually located in dedicated areas equipped with all the safety measures required.

A cold mock-up is a piece of equipment used for the study of technologies and is considered to be “cold” to the extent that there is no chemical transformation in it. Mock-ups help us to test the possibility of certain functions. They are usually operated in the absence of reaction and the presence of simple fluids (nitrogen, water, air, etc.); they help to test different technologies, to validate or calibrate models, such as the one developed by CFD (Computational Fluid Dynamics) which is the study of fluid dynamics by the numerical solution of the equations responding to it [WIL 05].

5.4.2.1. *Experimental acquisition of chemical kinetic data*

Acquisition of chemical kinetic data is a key step, because it determines the choice of reactor technology to be kept, as well as the main variables related to its size (volume, temperature, pressure, residence time, etc.).

In the preliminary study, a first simplified kinetic model has been developed based on the main reaction mechanisms involved. In the development phase, a comprehensive kinetic model will be developed, which will integrate a complete set of reactions and will cover a domain of operating conditions wider than that covered by the simplified model. The methodology of acquisition of intrinsic kinetic data is however similar to that used in the pre-study.

Data acquisition of reaction kinetics requires the availability of experimental tools whose hydrodynamics is well characterized so that we can separate the mass transport phenomena, and therefore access the intrinsic reaction kinetics of the system considered. Once the intrinsic kinetic data is acquired and mass transport phenomena are known, different reactor configurations can be calculated using models, their performance can therefore be compared, and hence the choice of the best technology will be established.

In general, kinetic models are established in operating conditions corresponding to regimes of stable operation of the catalyst, that is to say, without significant change in catalytic activity and selectivity with the time stream of the catalyst. The kinetic model developed is then a *Start Of Run* model, the engineer must develop in parallel by means of dedicated experimental data related to the stability of the catalyst in the case of a heterogeneous catalytic system, or with the consumption of catalyst in the case of a homogeneous or heterogeneous catalyst system in specific cases.

This approach is not always possible because some catalytic systems have a high or even very high deactivation rate. The catalytic activity therefore changes rapidly with time, the loss of activity could be complete within a few hours or a few days. A deactivation kinetic model of the catalyst must be developed to account for all observed phenomena. This model will help us to choose the best reactor technology

to be used to compensate for this loss of activity over time and thus ensure a constant production over time.

To acquire kinetic experimental data, continuously functioning pilot plants are most often used.

The pilot plant is not usually a small scale representation of the industrial reactor; however, the key operating conditions of process will be replicated.

Intrinsic kinetic data are directly accessible when the unit is operating under chemical kinetics conditions; in other cases, we use a model of the reactor of the pilot plant to extract from it the intrinsic kinetic data that will be used to develop the reactor models for scale-up.

5.4.2.1.1. The sizing of catalytic reactors for pilot plants

The sizing of pilot plants units has been discussed in many publications. For example, Sie and Krishna have reviewed the methodology that is used to intrapolate and extrapolate fixed bed reactors by demonstrating the limitations on the use of small size fixed bed reactors [EIS 98].

Two criteria must be considered to size a laboratory reactor:

- conservation of surface velocities of fluids with respect to those of the industrial reactor considered (speed of fluid flow in m/s within the reactor);
- conservation of the hourly space velocity of reagents injected into the reactor (flow rate of reagent in m³/h by reactor volume in m³ and by unit of time).

The first criterion helps us to ensure that the fluid dynamics is substantially identical between the reactor of the pilot plant and the future industrial reactor. This criterion is often difficult to achieve because in practice, the fluid velocities are lower at the scale of pilot unit reactors.

This reduction in fluid velocities can lead to the existence of external diffusional limitations to catalyst particles, due to too low mass transport outside the catalyst particles. This should be taken into account when using the experimental data to determine the intrinsic kinetic constants that will be used to select and size the industrial reactor.

In the second criterion, conversion of reagents and product selectivity is potentially the same, provided there are no mass transfer limitations.

Another important effect in the reduction of scale of a reactor is the effect of the reactor walls. Near the walls of the reactor, the particle distribution is different from that inside the bed. The average porosity near the walls being greater than the porosity within the bed, a radial velocity profile appears in the catalytic bed. This effect is negligible for industrial-scale reactors but grows when the diameter of the reactor is reduced: the deviation from ideal plug flow increases due to a disparity in the local velocities. In addition, the existence of preferential passages is probable.

Finally, because of very low flow rates, the wetting of the particles may not be uniform during downward flow of fluids. Currently, a frequently applied solution that helps us to improve the wetting, is to increase the local velocities of fluid and therefore to improve the mass and heat transfer. For this, we proceed to fill the bed with small particles to increase its porosity.

The use of these particles also reduces the axial dispersion, by limiting the preferential passages, and helps to dissipate heat, by reducing the radial temperature profiles using inert particles having a coefficient of high thermal conductivity.

For highly exothermic and very fast reactions, as for example, selective hydrogenation, a good thermal control becomes very difficult and limitations to external mass transfers are more important and can become insurmountable to evaluate the catalytic performances on pilot unit reactors with fixed beds. These problems are worsened with the development of new generations of more active catalysts.

As a conclusion, various effects influence hydrodynamics and external mass transfers during the scale reduction of a reactor. By filling the porosity of a pilot reactor with small inert particles, we can improve the wetting, local velocities, mass and heat transfers, and axial dispersion.

Technologies implemented within the pilot plants have evolved over the past 20 years, with the following objectives: reducing the cost of data acquisition, reducing development time, and obtaining more accurate measures. The development of advanced analytical techniques was carried out in parallel with the development of online analysis (analyzers being an integral part of the pilot plant), and online microanalyzers to obtain the analytical information with low quantities of products.

Progress achieved on analytical methods helped to provide more detailed information on the products, due to better identification of the set of molecules, which enabled the development of more detailed kinetic models and therefore more representative of reality and consequently safer extrapolation models.

In the field of oil refining and the petrochemical industries, studies on size reduction of pilot plants have helped to move from reactor volumes close to 1 liter to

a few cubic centimeters, while preserving the quality of results (Figure 5.9). This has the advantage of requiring smaller amounts of catalyst, and having facilities equipped with several reactors in parallel, in order to multiply the number of experimental points in the same duration, which helps us to reduce the cost and duration of this phase of the development process.

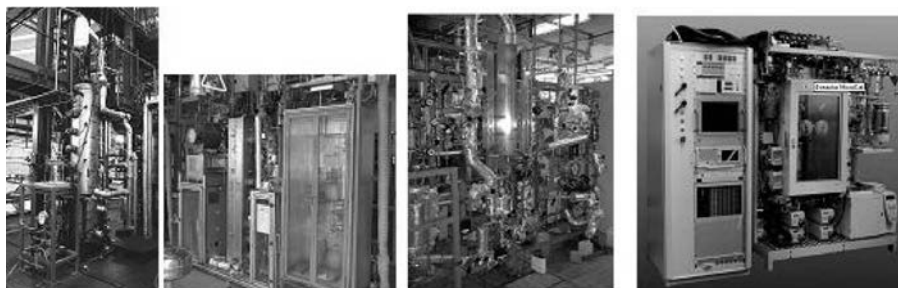


Figure 5.9. Pilot units equipped with fixed bed reactor with volume decreasing from left to right (1,000, 200, 50, and 5 cm³) used to acquire data on a process for hydrotreating petroleum fractions © IFPEN, © P. Chevrolat

The most frequently chosen criterion in downscaling is the preservation of the hourly space velocity (HSV). The maintenance of HSV in conventional pilot units is often accompanied by low-velocity flows of fluids. Indeed, the height/diameter ratio of reactors of pilot units is generally lower than that in the industrial reactors.

At these velocities, external mass transfer to particles can become limited with respect of reaction rates, especially for fast reactions like hydrogenation.

In this context, a new geometry of the reactor has been developed to intensify the mass and heat transfer and to increase the velocity of fluid flow: the “string” reactor (Figure 5.10). This is a reactor with a diameter equal to or close to that of the catalyst particles with a very high height (or length) to diameter ratio, which increases the fluid velocities by a factor of 10–100 compared to the conventional reactors. It is expected that the flow of fluids in the reactor allows a very good gas/liquid mass transfer. As the diameter of the reactor is very small, the ratio of external surface/volume is more considerable and thermal control is better. Another advantage of this type of reactor is to allow testing with catalyst particles similar to the commercial catalysts (extruded or beads), which helps us to represent the internal potential limitations existing in the operation of a commercial reactor.

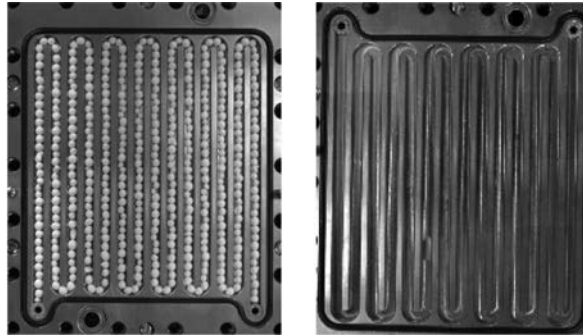


Figure 5.10. Reaction section of a string reactor: catalyst-filled on the left and empty on the right © IFPEN, © P. Chevrolat

		Industrial reactor	Traditional pilot reactor	Wired reactor
Reactor diameter (mm)		1,500–8,000	10–20	2–4
Height (mm)		1,500–15,000	100–500	4,000–10,000
P (bar)		20–150		
T (°C)		30–300		
Liquid	VVH (h^{-1})	1–20		
	ρ_L (kg/m^3)	600–800		
	μ_L (cP)	0.1–2		
	uLs (mm/s)	1–100	0.03–3	1–50
Gas	ρ_G (kg/m^3)	15–30		
	μ_G (cP)	0.02		
	uGs (mm/s)	10–200	0.5–10	10–200

Table 5.1. Operating conditions of typical industrial reactors in the petroleum and chemical industry, of conventional pilot plants and wired reactor

5.4.2.2. Development of kinetic models

Kinetic modeling is based on theoretical tools to describe the phenomena from what is available. This description constitutes the model.

A model includes a number of variables including parameters that are necessary to estimate from experimental or measured data [CON 10]. The model with its set of

parameters enables us to generate the data that are to be compared with available experimental data (all or part). To estimate the set of parameters that will best describe the reality, a quantification of the adequacy of the model is necessary. This quantification is a criterion which is expressed mathematically by an objective function to be optimized (usually minimized).

The acquisition of experimental data, parameter estimation, and the analysis of results obtained are the stages of the modeling process and implement methods whose effectiveness we have to be aware of and manage.

In the context of developing a kinetic model, which will be integrated within a reactor model, the initial phase of developing specifications is essential.

The specifications are a document prepared in collaboration between an engineer in charge of developing the model and the project manager who makes it possible to specify the performance and goals of the model:

- definition of values to be predicted, application domain (reactants, operating conditions, performance, product quality, etc.), and accuracy of the model;
- defining the conditions for validation of the model.

The objectives of a model are thus clearly defined and collected in the specifications written in collaboration between the members in charge of developing the model of the reactor and the project manager who is responsible for coordinating the various tasks that are necessary for the development of the process. It is very much apparent that an engineer in charge of developing the model has to analyze whether the goals set are achievable, for example, in terms of the model development time or adequacy of the information required about the model predictions and information available during the acquisition phase of the experimental data.

The system that we need to model can be approached in two ways. Either by including the available knowledge based on chemistry and physics, which will build a phenomenological model, also called a knowledge model (e.g. material balance, energy balance, momentum balance, etc.), or by considering only the input–output behavior without worrying about the “reality” of the model which helps us to build a behavioral model, also called as representation model (e.g. correlations).

A basic classification of models can be made by taking into account the qualitative properties of descriptions [WAL 94]. These classification criteria, often dichotomous, correspond to a classification of resolution methods, so it is useful to specify the type of concerned or desired models, for example:

- phenomenological or behavioral;
- linear or non-linear;

- continuous time or discrete time;
- deterministic or stochastic.

5.4.2.2.1. Phenomenological or behavioral

The phenomenological models have a concrete meaning that enable us to interpret them as the variables and parameters. They take a long time to implement because they require an understanding of the phenomena hence a certain expertise in system to be modeled. The computing time can be long or even prohibitive for certain applications. However, they are more reliable, especially in extrapolation.

Behavioral models are often based on a mathematical technique available *a priori*, independent of the application domain of the model. They are fairly easy to implement, they can be very effective in interpolation and low computing time, but have many drawbacks: low predictability outside the domain of validity, sensitivity to parameters, which, in general, we prefer among the phenomenological models when they are available.

5.4.2.2.2. Linear or non-linear

Dependence of models on the parameters is a very important point in the classification of models. The chemical models are often non-linear, through the intervention of the activation energy of the reaction (denoted by E_a) in an exponential in the expression of the rate constant ($k = k_0 e^{-E_a/RT}$). However, we must first ensure that the model dealt with is non-linear because, on the contrary, linear models benefit from the existence of powerful mathematical tools and are accurate for both the offline and online identifications. In particular, the calculation of the gradient during the optimization and the calculations of uncertainty about the parameters (confidence intervals) can be done at low cost and accurately.

5.4.2.2.3. Continuous time or discrete time

The equations of the model can be formulated as continuous equations with respect to independent (differential equations) or discrete variables (equations with differences). This is a classification of equations independent of the resolution type (numerical, analytical, etc.).

In the context of ordinary differential equations encountered in most cases, the continuous formulation is used, whereas in the case of differential equations with partial derivatives or boundary conditions, discretization (orthogonal collocations on finite elements) is preferred. In the latter case, we can find a hybrid form with the method of lines found in discretizing with respect to one of the variables and can be continuous with respect to the other (e.g. a discrete on space variable and a continuous time variable).

5.4.2.2.4. Deterministic or stochastic

Most models are deterministic: the same inputs lead to the same outputs. Stochastic models [JAV 08] can, however, be used in many cases to:

- model an unmeasured interference (analysis error, etc.);
- simulate a system of differential equations;
- describe a distribution.

The first point is very useful for the study of uncertainty and discrimination of models. The second is more anecdotal in nature; the deterministic methods of differential integration have proved it. As for the third, it is especially used in the load reconstruction algorithms.

5.4.2.2.5. Kinetics

The main objective of this section is not to present the way of establishing the equations that govern kinetics, but to put forward some concepts. Readers may refer to works cited in [LIE 98, SCH 01, TRA 02, VII 93] for more details.

5.4.2.2.6. Rate of reaction

The rate of a chemical reaction is defined as the amount of material processed per unit of time and per unit of extensity which depends on the volume set: volume, mass, surface, and so on. Rate therefore measures of a specific rate of chemical transformation [VII 93].

In a control volume, it demonstrates an accumulation of product that has no place in the steady-state applications and for which there is still a chemical reaction. This notation can be confusing and therefore we prefer to take r as the rate of chemical reaction, whereas the concept of speed is not related to a temporal evolution.

5.4.2.2.7. Reaction mechanisms

Let us take a set of N chemical reactions of index i , described by the following equation:

$$\sum_j \nu_{ij} A_j = 0 \quad [5.1]$$

where ν_{ij} are the stoichiometric coefficients of the reaction (positive for a product and negative for a reagent) and A_j are the numbers of moles of each i species.

The net flow of formation of component j , R_j , is given by the following equation:

$$R_j = \sum_i \nu_{ij} r_i \quad [5.2]$$

where r_i is the rate of reaction i .

5.4.2.2.8. Approximation of quasi-stationary states and reduction of mechanisms

In the case of complex mechanisms, the number of equations can become very important.

In order to simplify the equations, we often carry out a reduction of the mechanism that does not show the intermediate species.

The reduction of a kinetic diagram often involves one of the following two principles:

- approximation of quasi-stationary states;
- approximation of the limiting step.

The approximation of quasi-stationary states is the most rigorous step. Its application involves the intermediate species and requires:

- the existence of intermediate species whose formation rates are almost zero;
- intermediate species in a negligible amount.

The approximation of the limiting step is to identify the slowest rates of reaction, which govern the overall kinetics and assume the other invariants in time. The rate of evolution of each of the reagents is then expressed as the amount of rate limits to which they are connected by the kinetic network.

The approximation of quasi-stationary states is considered to be a special case of approximation of the limiting step.

5.4.2.2.9. Intra- and extra-particle diffusion

So far, it has been considered that the concentration of reagents inside and outside the catalyst particle was the same. This is not always the case and we may observe external and/or internal diffusional limitations.

There are various mathematical and experimental criteria to ensure the domain in which there may be the presence or absence of diffusion.

In the case where we cannot experimentally escape diffusional limitations, they must be taken into account in the model. In addition to mass transfer, they can also affect the heat transfer, that should also be considered.

The development process of kinetic models has undergone many changes since the 1960s. Thus, there is generally a continuous increase in complexity over time resulting from the development of new analytical tools providing access to more detailed information at the molecular compositions level as well as to improving the understanding of the physicochemical phenomena observed.

In fact, one of the major difficulties encountered during the construction of a model is the representation of the inlet and outlet flow of the material(s). Usually, these flows are described by their molecular composition, that is to say by the relative quantification of different chemical species that constitute them. In the oil domain, the flows are mixtures that are too complex to be represented in this way. For example, a commercial diesel can have up to several million different components.

Historically, the difficulty was circumvented by grouping the components with similar properties shared by a common family based on the type of process being studied: these are called lumping models. In the field of non-reactive thermodynamics, as oil components have a low polarity, they are grouped by family of increasing volatility called pseudo-components. With a description of the oil flows and with the help of a dozen pseudo-components and an appropriate thermodynamic model, it is possible to develop reliable models for a multistage distillation, a process of heat exchange, and so on.

In the field of reactive (and often catalytic) process models, the family lumping remains an art that depends on analytical techniques and the computing power of computers available at the time of development of the model. For example, models of catalytic cracking of petroleum residues have changed from a description in the form of 3 lumps of molecules in 1970 to 10 lumps in 1976, and to 18 in 1994. Once the lumps are defined, a kinetic network helps to show the relations of different families among them.

The models are then based on a kinetic module that helps to track the changes in the quantity of different families either over time if the reactor is agitated and closed, or along the reactor if it is open. The advantage of these models is in their ease of development and use. Their main disadvantage is that they are often dependent on the type of feedstock (mixing formed by the reactants and recycled products feeding the reactor) used in the process and the type of catalyst used if it is a catalytic process. The second drawback is that the number of parameters of the models increases, at least, in proportion to the number of lumps describing the flow.

On the contrary, other models have been developed from a molecular description of reactive flows and a network of basic steps. Several teams have worked on this type of approach: the team of M.T. Klein [KLE 91, KOR 94] based on the kinetic theory LFER (*Linear Free Energy Relationships*) and teams of G. Froment and

G. Marin that worked on the theory of single events [VYN 91]. Reconstruction methods have been developed so that they can generate a mixture of molecules (100–10,000 molecules) whose composition is optimized in such a way that the overall properties of the mixture obtained will be identical to those accessible by the analytical techniques [HUD 04, PYL 09, VAN 07, VER 10].

The advantage of mechanistic models is that the number of parameters of the model is relatively low and the parameter values are independent of the type of feedstock. Their main disadvantage is that it is necessary to have access to the molecular details of the feedstock which is possible only on the mixtures of molecules that are clearly identified, either on petrochemical feedstock or on light fuel-type petroleum fractions. For heavier petroleum fractions, it is necessary to use the “posterior lumping” to get to a level of analytical detail. A second problem concerns the reactive network whose size increases exponentially with the number of components present in the flow.

Theoretically, prediction models of processes should be mechanistic models based on fundamental kinetic theory. In practice, the difficulties in characterizing the feedstock associated with management difficulties regarding the size of the reaction networks lead to the consequence that the models usually remain combination models, even if they become more complex with an increasing number of groupings. The models then introduce an increasing number of parameters and the experimentation required for their optimization finally becomes more restrictive.

5.4.2.3. *Data acquisition for the sizing of technological equipment*

The objective is to measure, understand, and describe the hydrodynamics and transfers (mass, momentum balance, and heat) in the common operations of process development and to establish the scale-up rules of technological equipment.

The necessary experimental tools are as follows:

- cold mock-ups;
- instrumentation for the acquisition of comprehensive measures: concentration measurements of liquid/solid transfer (denoted by L/S) and gas/liquid transfer (denoted by G/L), and local measures, such as determining local *hold-up* L/G/S by gamma tomography;
- imaging techniques (colorimetry, MRI, etc.).

Modeling of phenomena at different scales is used in addition to the acquisition of experimental data:

- dimensional models: these are “conventional” models of the discipline, such as the development of hydrodynamic models of pressure drop and hold-up;
- multidimensional models: modeling based on the CFD (Computational Fluid Dynamics) which enables us to design technological equipment.

The data obtained as well as the transfer models developed help to extrapolate by predicting the performance of the industrial system and by coupling of thermodynamics, intrinsic kinetics, hydrodynamics, and heat and mass transfer through a reactor model. This reactor model (or a simplified version) will be then introduced into a process simulator to study the overall performance of the system.

The experimental tools used for this data acquisition can be large pieces of equipment, and the acquired data can then be used with great reliability during the scale-up process.

Two illustrations of mock-ups are shown in Figure 5.11.

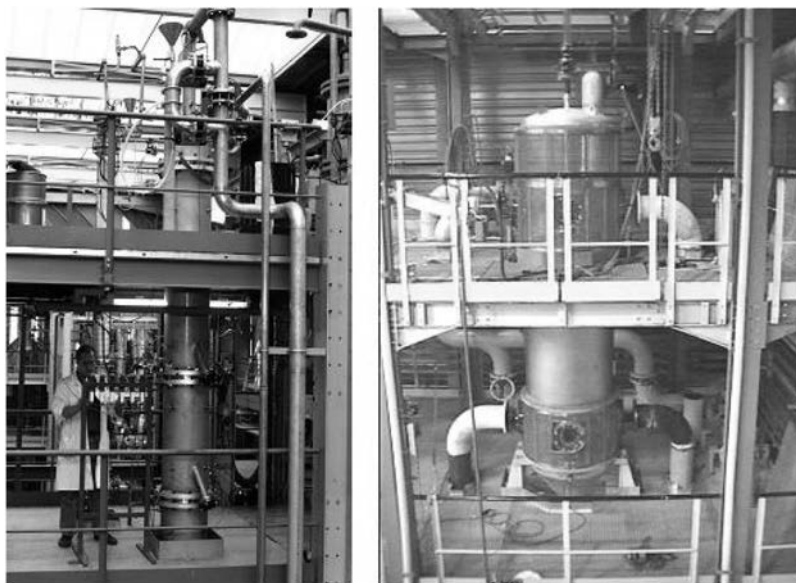


Figure 5.11. Examples of mock-ups used to study reactors using heterogeneous catalysts: fixed bed (left) and moving bed (right) © IFPEN, © P. Chevrolat

5.4.2.3.1. Modeling of hydrodynamic phenomena

Considering the phenomena at different scales is necessary to have a better understanding of the phenomena and to help ensure safety with scale-ups.

Figure 5.12 shows, in the case of a gas/liquid contactor which aimed to maximize the efficiency of mass transfer of gas to the liquid, the different scales to be considered [RAY 07].

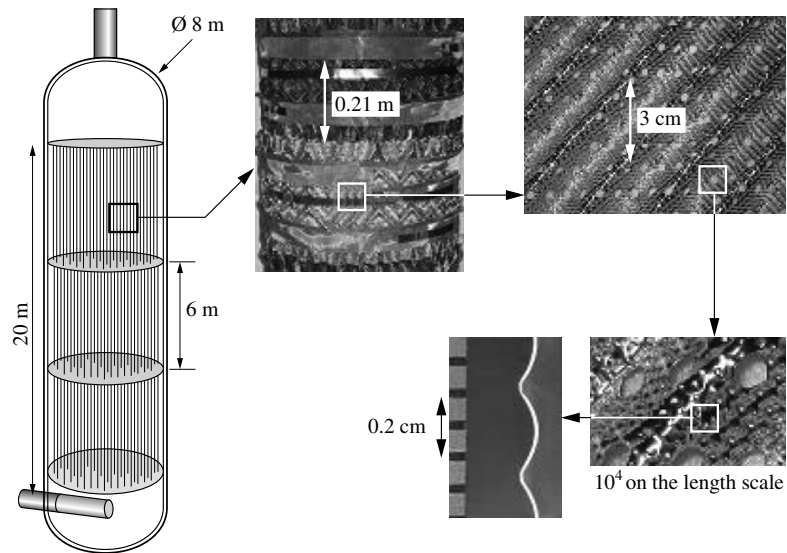


Figure 5.12. Study of a gas/liquid contactor, illustrating the different scales to be studied © IFPEN

Figure 5.13 illustrates in the case of a gas/liquid contactor, different types of reactor internals to be characterized in order to obtain the sizing criteria and selection of the best reactor internal geometry to maximize the performance.

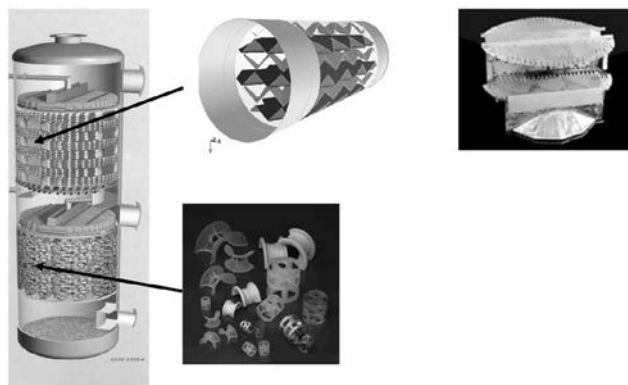


Figure 5.13. Different types of internals of gas/liquid contactor © IFPEN

Figure 5.14 illustrates some experimental tools that are used to determine the impact of different trays or distributors on the quality of fluid distribution in an adsorber.

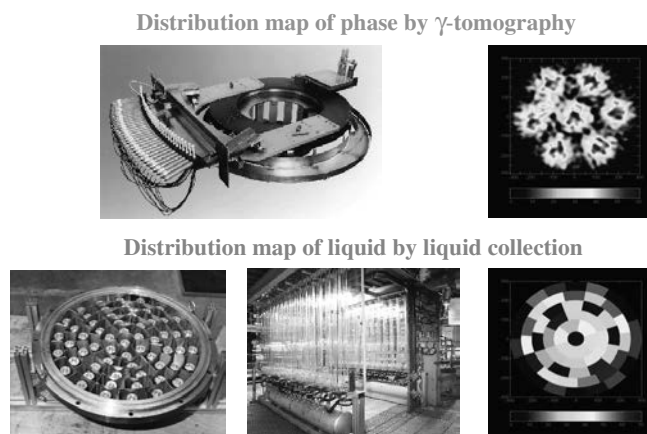


Figure 5.14. Tools used to describe the quality of a gas/liquid flow in a reactor © IFPEN

The CFD helps in better sizing of some critical technological equipment, such as the geometry of the gas distribution at the bottom of the absorption column in the case of gas/liquid contactors (Figure 5.15) [RAY 10].

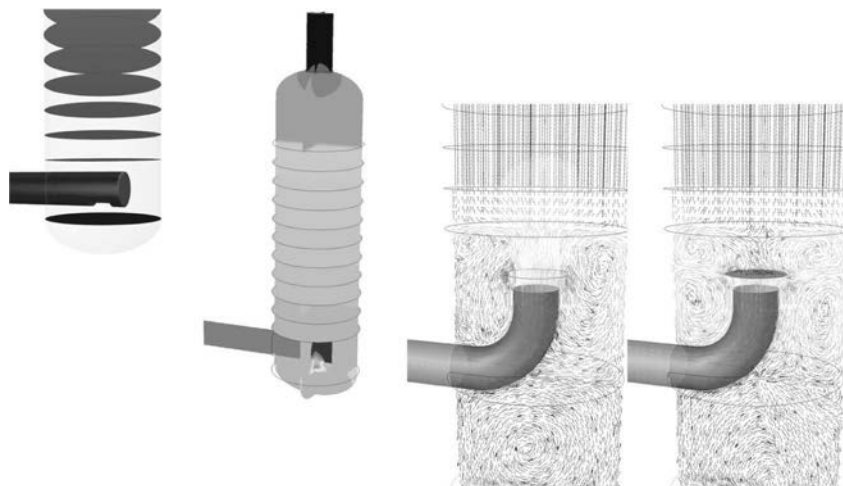


Figure 5.15. Usage of CFD to determine the geometry of the gas injection system at the bottom of an absorption column

The review of the use of CFD over recent years reveals some strong tendencies, related either to the availability of certain physical models in commercial codes (especially two-phase models), or to the improvement of computer calculations. These tendencies can also be projected on the future uses of CFD in the forthcoming years. We can cite the modeling of unsteady flows (local fluctuations of flow rates, fluid velocities, ratio of liquid and gas in case of gas/liquid system) and characterization of small-scale physical phenomena.

5.4.2.3.2. Unsteady flows

Many chemical reactors work with several phases: liquid/gas, gas/solid, for example. Modeling their behavior using simulation is a very complex domain, because these flows can show a highly unsteady nature at large scale (e.g. bubble columns, presence of low frequency oscillations). In recent years, the trend that has emerged is to resort to unsteady 3D models, which requires a lot of computing resources, but gives better results. This is particularly true in the case of dense flows of the gas/solid fluidized bed or dense bubble flow type, where the interactions between inclusions and with the flow of the continuous phase are very strong.

It is the same, but on a different scale, for the modeling of single-phase turbulent flows. The classical approach by RANS (Reynolds Averaged Navier Stokes) model is being progressively replaced by the models describing the unsteadiness caused by the turbulence, either by a direct approach (DNS *Direct Numerical Simulation*) and resolution of all scales of turbulence, or by a LES-type (Large-Eddy Simulation) approach, where only large scales are resolved. This type of tool is mainly used when the hydrodynamics and micro-mixture have a significant impact on reactive performance, that is to say, in the case of very fast kinetics.

The use of LES modeling is also relevant in the case of low or non-isotropic turbulence (e.g. modeling of flows in structured packings).

5.4.2.3.3. Characterization of small-scale physical phenomena

The CFD is increasingly used to characterize certain physical phenomena that are difficult to observe experimentally. Thus, some simulations on a very small scale (a few particles of catalyst, a periodic packing element, etc.) are made in order to quantify some local phenomena such as wetting of the catalyst or the gas/liquid transfer of structured packing in [AUG 10a, AUG 10b]. These results can then be applied to other models, multidimensional or not, thereby describing the overall functioning of the unitary operations. This is thus called the multiscale approach, an approach that tends to spread and shows that CFD can be used at several levels and with distinct purposes.

Figure 5.16 shows a typical example of the use of CFD as a tool to acquire local data. 3D simulations were conducted to calculate the coefficients of radial dispersion

in stacks of catalyst particles. The model solves the flow in the space between the grains and the transport of passive tracers in the flow. Post-processing of simulations, similar to that applied in the experimental data, helps us to trace the desired size.

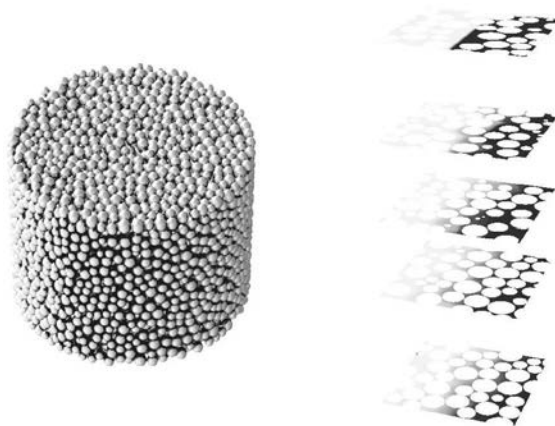


Figure 5.16. Example of simulation of the dispersion of chemical species in a fixed bed of catalyst. a) Computational domain, b) dispersion of the tracer (gray) in the transverse direction

5.4.2.4. Acquisition of thermodynamic data

Thermodynamics is a fundamental science. In most cases, it deals with the study of equilibria of liquid–vapor, liquid–solid, or liquid–liquid phases, and the properties of mixtures.

To deal with problems now considered to be relatively simple, such as equilibria of phases of hydrocarbons, for example, models of classical thermodynamics (cubic equation of state) coupled with a heavy experimentation but still achievable in a laboratory, helps to meet the demand.

The development and implementation of thermodynamic models require data on pure substances and their mixtures and then on real mixtures. These data should be somewhat similar to those seen in the process.

The experimental equipment used (Figure 5.17) helps to measure the equilibria and properties of phases in equilibrium, sampling systems also allow us to perform the analysis of phases. The pressure and temperature conditions signify that the technological challenges are significant and the implementations of these pieces of equipment are often long. In parallel with data acquisition, the databases are used.

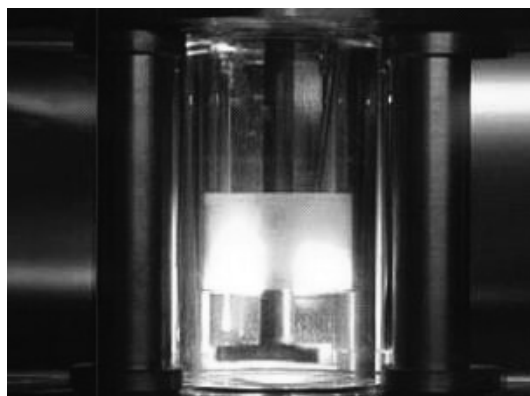


Figure 5.17. Cell allowing us to study the vapor–liquid equilibria © IFPEN

The domains currently being addressed require more accuracy. That means operating in high pressure and temperature domains, and with very different compositions. This is one of the reasons that led to the development of molecular simulation (prediction of physicochemical properties of fluids from the knowledge of intermolecular interactions), molecular dynamics, and quantum simulations.

The acquisition of fundamental thermodynamic data is therefore based on three tools: experiments, theoretical models (including equations of state), and molecular modeling.

The selection and development of the thermodynamic model are essential. This model will be chosen according to the characteristics of the process (aqueous phase, hydrocarbon phase, and the presence of ionic species). Once selected, the model should be adjusted for the process, according to the products used and their concentration, temperature, and pressure.

For example, in the case of the development of the CO₂ capture process, we use an aqueous solvent containing ionic species. A possible choice for the equilibrium model of phase, enthalpy and entropy, is a NRTL (Non-Random Two-Liquid) type model. Measurements of equilibria isotherms at high concentrations have been made to make up for the lack of data available in this area of the process. Then the data acquired in the laboratory and from the literature were compiled to obtain the coefficients of interaction between the components of the process. This model enables us to know the exact composition of liquid and gaseous phases based on the components present and the temperature and pressure conditions.

Another part of the model with regard to what is commonly called transport properties, are properties such as viscosity (gas and liquid), density (gas and liquid), and surface tension. They vary depending on the composition of the phases and the temperature and pressure conditions. They are the subject of studies to achieve either the parameters of a model or a correlation representing the domain of operation of the process. They will be required to precisely calculate equipment such as pumps or heat exchangers.

5.4.2.5. *Modeling of reactors*

The reactor model is used for scaling up; it helps us to define the type of industrial reactor best suited, and to specify the sizes for a target quantity of finished products to be produced.

Models of reactors, integrate kinetic model (s), hydrodynamic models and thermodynamic models.

The reactor models will predict the performance of a reactor for a given reactor technology, and they can also be integrated into a model of advanced control methods.

5.4.2.5.1. Establishment of the equations of reactor model

This section briefly explains the outline which led to the writing of equations.

The writing of equations must involve the following steps:

- defining a control volume;
- list of hypotheses expressed to write the model;
- list of variables used to describe the system;
- writing the equations relating the variables to each other;
- analysis of degrees of freedom.

Writing equations of a model usually starts from the writing of conservation balances of three values:

- material balance;
- energy balance;
- balance of momentum.

5.4.2.5.2. Definition of control volume

The control volume is the basic volume in which the equations are valid. In general, we choose the largest volume in which the variables are uniform. This

volume may be macroscopic (whole reactor if the variables are independent of the position in the reactor) or microscopic (if the variables depend on the position in the reactor). The control volume is characterized not only by its own volume but also by the surface that defines it which will be called as surface control.

Do not confuse control volume and reactor volume. These only fit in a very small number of cases.

5.4.2.5.3. Model hypotheses

Writing the equations involves a number of simplifying hypotheses that enable us to approach the reality through a mathematical description. Failure to comply with these hypotheses can lead to very large errors on the values predicted by the model.

5.4.2.5.4. Set of variables used

The set of variables used includes:

- the symbolic description used in writing equations (e.g. C, m, etc.);
- the definition of the value associated with the variable (e.g. concentration, mass, etc.);
- the unit of measure (e.g. kmole/m³, kg, etc.).

5.4.2.5.5. Writing of equations

The writing of equations is done by establishing the conservation balance on the control volume and surface by using the hypotheses of the model and variables listed.

The units of each term involved in the balances should be checked routinely.

5.4.2.5.6. Analysis of degrees of liberty

The analysis of degrees of liberty amounts to verifying whether the knowledge of the inputs of the system allows us to reconstruct the entire state of the system as well as its outputs.

This analysis is based on:

- the number of variables that are used to describe the system;
- the number of independent equations that describe the system.

To be able to predict the state and the outputs of the system, it is necessary to have at least as many independent equations as variables.

5.4.2.5.7. Conservation equations

Whatever it is, to describe the mass conservation, energy, or momentum balance, the conservation equations describe a summary of input/output and production in the control volume per unit of time.

The following three sections describe the balance applied to the simple control volumes on which the variable values are uniform and the inputs and outputs are clearly identified. A more mathematical formulation, which enables us to describe the macroscopic balances through a divergence theorem (Gauss/Ostrogradski), is better known as the theorem of flows. The use of these theorems is more difficult but enables us to write simply the same equations for any geometry of control volume.

5.4.2.5.8. Mass balances

The mass balance is written as:

$$\left[\begin{array}{c} \text{Accumulation} \\ \text{rate of the species } i \\ \text{in the system} \end{array} \right] = \left[\begin{array}{c} \text{Input stream} \\ \text{of the species } i \\ \text{in the system} \end{array} \right] - \left[\begin{array}{c} \text{Output stream} \\ \text{of the species } i \\ \text{in the system} \end{array} \right] + \left[\begin{array}{c} \text{Net rate of formation} \\ \text{of the species } i \\ \text{in the system} \end{array} \right]$$

where the net rate of formation takes into account the rates of formation (transformation of species j into species i) and rate of disappearance (transformation of species i into species k).

5.4.2.5.9. Heat balances

The expression of the first law of thermodynamics applied to an open system is written as:

$$\left[\begin{array}{c} \text{Rate of accumulation} \\ \text{of energy} \\ \text{in the system} \end{array} \right] = \left[\begin{array}{c} \text{Input stream} \\ \text{of energy from/to the} \\ \text{stream of matter} \\ \text{in the system} \end{array} \right] - \left[\begin{array}{c} \text{Output stream} \\ \text{of energy from/to the} \\ \text{stream of matter} \\ \text{in the system} \end{array} \right] + \dots$$

$$\dots + \left[\begin{array}{c} \text{Thermal balance} \\ \text{by addition} \\ \text{of heat} \end{array} \right] + \left[\begin{array}{c} \text{Thermal balance} \\ \text{brought in by the} \\ \text{environment} \end{array} \right]$$

5.4.2.5.10. Momentum balances

By applying the fundamental principle of dynamics:

$$\begin{bmatrix} \text{Rate of accumulation} \\ \text{of momentum} \\ \text{in the system} \end{bmatrix} = \begin{bmatrix} \text{Input stream} \\ \text{of momentum} \\ \text{in the system} \end{bmatrix} - \begin{bmatrix} \text{Output stream} \\ \text{of momentum} \\ \text{in the system} \end{bmatrix} + \dots \\ \dots + \begin{bmatrix} \text{Balance of forces} \\ \text{applied} \\ \text{to the system} \end{bmatrix}$$

5.4.2.5.11. Analysis of thermal stability in chemical reactors

Safety is a priority for the chemical industry as it is necessary to minimize the frequency and severity of accidents, while maintaining the productivity and quality of products obtained. The processes that implement the reactions that may undergo a thermal runaway are at high risk of an accident.

The detailed study of highly reactive reaction systems is imperative to ensure optimal and safe operation of existing processes and to develop new processes that are inherently safe.

In the domain of refining, petrochemistry, and chemistry, the risk of thermal runaway is a real phenomenon that has been observed on an industrial scale. Examples of processes that are affected by the risks of runaway include: selective hydrogenation, Fischer-Tropsch synthesis, hydroconversion of the residue in an ebullated bed, and hydrocracking. The consequences of thermal runaway may be premature coking of the catalyst the loss of operability of the plant and very rarely explosion of the compound. Obviously, there are security measures to avoid reaching the conditions of danger of explosion. These measures are as follows: the introduction of advanced control in the plant, setting alarm thresholds, installing exhaust valves and rupture discs, among others.

However, in the refining, petrochemical, and chemical industries, the alarm thresholds are set rather on experience and not on a scientific basis. Therefore, it is necessary to establish a rigorous field of safe operating conditions for processes.

The methodology for the study of stability of the reactors allows us to determine the operating conditions of the unit operation. This methodology must be valid for the reactors at the laboratory, pilot, and industrial scale, implementing simple and complex reaction systems.

The methodology consists of two main steps:

- study of the thermal stability in steady state: according to the Van Heerden criterion [VAN 53] and parametric sensitivity studies;
- study of the thermal stability in dynamic state: perturbation theory.

These studies are conducted based on a dynamic model of the reactive system to be developed, fitted, and validated upstream of stability studies.

This approach is one of the factors that led to the design of safer and more environmentally friendly processes.

5.4.3. *Process schemes, simulation, and optimization of the process as a whole*

This last phase of development is based on the set of data acquired (in the laboratory and development phase). It concerns the development of the complete process scheme with its list of necessary equipment to perform the optimization and heat integration and to quantify the investment and operating cost for the given production capacity.

As we progress in the research on the critical points of the process, the teams responsible for the processing update the technical and economic studies and possibly redirect the study of acquisition of basic data. These teams play the role of an integrator through the collection of basic data (kinetic data, thermodynamic data, hydrodynamic and transfer data, corrosion, aging of the catalysts, and separation agents) and, from these data, define the best process flow diagrams on technical, economic, and industrial development criteria.

The development phase is also an opportunity to protect the concepts being developed through the patent of innovative process schemes and to define the process guidelines.

The technical and economic evaluation of a process requires us to determine the mass and energy balances from which the main equipment will be designed and valued as well as consumption of utilities (cooling water, electricity, cold, low pressure steam, medium pressure and high pressure coolant) and estimated chemicals (catalysts, adsorbents, solvents, etc.).

The evaluation aims to determine the investment and operating costs of the process. The investment costs include fixed capital (material investment, cost of studies, and licenses), the depreciable capital (fixed capital and initial charges), as well as working capital. The operating cost includes expenses (i.e. expenses for the operation of the plant: labor, utilities, raw materials, labor, etc.), and fixed costs (costs related to the unit itself: depreciation investments, maintenance, interest, taxes, etc.). On the basis of these cost components, we can determine the cost of the finished product, the time of return on investment, and the internal rate of profitability. These elements can be used to compare the process economically studied with variants or other existing processes.

As for the simulation and optimization of process flow diagrams, various commercial tools are available. An example of a process flow diagram is shown in Figure 5.18.

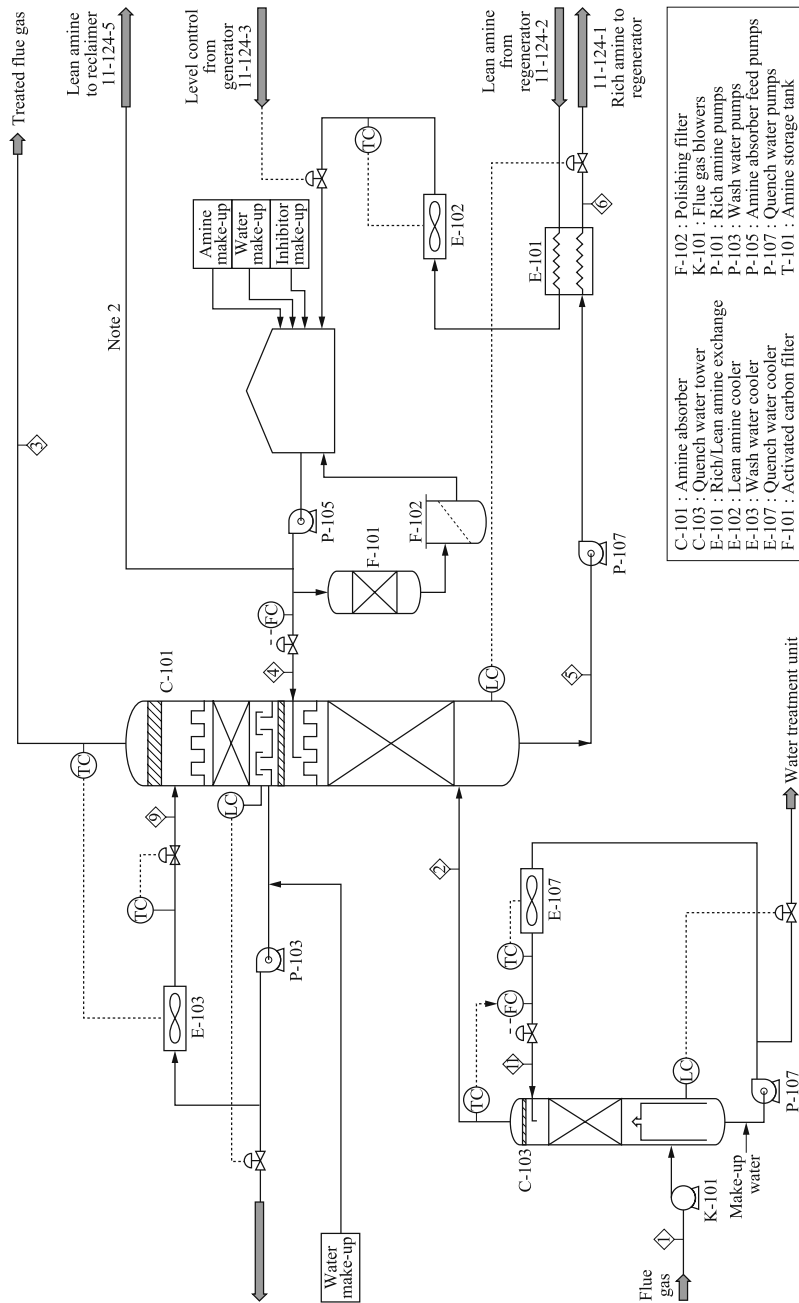


Figure 5.18. Example of a process flow diagram of gas treatment (only part of the diagram is shown in the figure)

The sizing of the equipment is established not only from the software developed by the teams which are responsible for the process but also through commercial software. For specific equipment, consultation with equipment manufacturers is carried out (e.g. gas turbine).

5.4.4. End of the development process, the foundations of industrialization

At the end of the development process, the project team is able to develop an executive summary “process guidelines for industrialization”; this document contains all the elements that are necessary to elaborate a process book and then engineering studies; the most important are listed below.

Specific considerations to the chemistry of the process:

- raw materials and their specifications (origin, impurities, etc.), and chemicals required (solvents, neutralizing agents of the catalyst, etc.);
- the products obtained at the output of the plant: specification of the desired product, by-products, waste and their management;
- the catalyst(s) required for processing;
- description of the chemical reactions involved (reaction mechanisms) and the corresponding kinetic models;
- models of chemical reactor and the optimum operating conditions, life of the catalyst, regeneration conditions;
- set of thermodynamic data (reactive and separating sections).

Considerations specific to the equipment of the process:

- sizing rules of the main technological equipment (reactor and its internals and other equipment such as: decanter, separation zones of liquid/gas, liquid/solid, etc.);
- recommendations on the choice of materials (corrosion, refractory, insulation, etc.).

Process flow and simulation diagrams as a whole:

- process flow diagram;
- list of major equipment needed.

Environmental balances:

- balance of greenhouse gas emissions.

Process control:

- recommendations for control;
- recommendations for instrumentation;
- recommendations for analysis.

Operating instructions:

- recommendations for the operation of the process;
- recommendations for starting and stopping of the process.

Industrial property:

- patents;
- freedom of use.

Once the process guidelines have been developed, the last step is the validation of the choices made. In this step, depending on the nature of the process developed, specific studies will be launched, aiming at developing prototypes:

- the development of industrial production methods of the catalysts necessary to process and validation of the performance of prototypes representing future industrial production;

- a complete simulation of the process allowing an extrapolation on paper, and obtaining a prototype process book;

- in some cases, for processes involving breakthrough technologies, an experimental prototype may be necessary.

5.5. General conclusion

The development process aims to transform an idea resulting from research conducted most often at a laboratory into an industrial innovation made up of a new reliable process, that is cost-effective with the smallest ecological footprint possible.

This chapter has served to illustrate the major stages of process development, until obtaining the foundations of industrialization, and to highlight the benefits of an “integrated” approach to the development process as well as the predominant place of modeling, at different stages of the development process. This methodological approach enables faster developments of processes, that are safer in terms of scale-up, the costs of the development phase being reduced. Figure 5.19 illustrates the process that was detailed in this chapter.

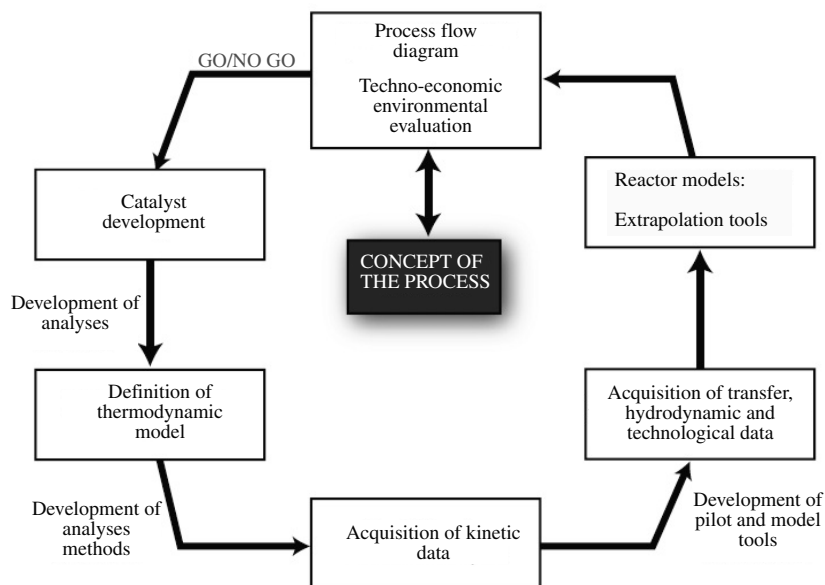


Figure 5.19. *Process of developing a process until obtaining the entire fundamental data for industrialization*

From the pre-development phase of a process, key points as well as any appropriate science and technological barriers that are to be removed in the further development of the process are identified. Pre-estimation of technical and economic performances of the process is also established from strong hypotheses, especially by assuming the removal of technological barriers identified in the initial design of the process scheme. From this first phase, the elements of decision which enable us to validate or not the viability of the concept and, if necessary, switch to the development phase of the existing process, were obtained through a rigorous scientific approach.

During the development phase, the acquisition of the set of data essential for the development of the process is the longest phase. The basic data to be acquired are defined at the end of the pre-development phase: reaction kinetics, product quality, stability over time of performances, thermodynamic data, mass and heat transfer, and so on.

The basic data are usually acquired using experimental facilities dedicated to the data that we wish to acquire with as much accuracy as possible. The systematic use of models (kinetic, mass transfer, etc.) helps to limit the experimentation necessary and to use experimental equipment of small size, and thereby reduces the cost and

development time. Modeling enables the development of simulators of the process so that it can be scaled-up in a rigorous and flexible manner.

Modeling at different scales (Figure 5.20) is a tool essential for today's development processes, from the development of the active phase to the optimization of the complete process flow diagram [CHA 10].

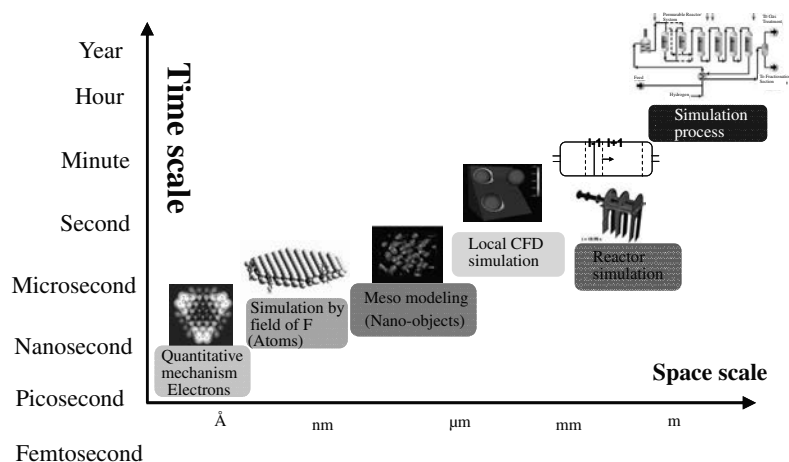


Figure 5.20. *The different scales of modeling*

From the complete set of experimental data available, the reactor models are developed as well as the design criteria of technological equipment, the process flow diagram is optimized on technical, economic and environmental criteria. Therefore, we have the necessary foundations for the future industrialization of the process.

Teams in charge of engineering begin to work, through the development of a process book and basic engineering studies. Once the decision on investment is made, detailed engineering will be conducted and the industrial production unit will be built and commissioned.

5.6. Bibliography

[AUG 10a] AUGIER F., IDOUX F., DELENNE J.-Y., "Numerical simulations of transfer and transport properties inside packed beds of spherical particles", *Chemical Engineering Science*, vol. 65, p. 1055-1064, 2010.

- [AUG 10b] AUGIER F., KOUDIL A., ROYON-LEBEAUD A., MUSZYNSKI L., YANOURI Q., “Numerical approach to predict wetting and catalyst efficiencies inside trickle bed reactors”, *Chemical Engineering Science*, vol. 65, p. 255-260, 2010.
- [CHA 01] CHAUVEL A., FOURNIER G., RAIMBAULT C., *Manuel d'évaluation économique des procédés*, Editions Technip, Paris, 2001.
- [CHA 10] CHARPENTIER J.C., “Among the trends for a modern chemical engineering, the third paradigm: the time and length multiscale approach as an efficient tool for process identification and product design and engineering”, *Chemical Engineering Research and Design*, vol. 88, p. 248-254, 2010.
- [CON 10] CONSTALES D., VAN KEER R., MARIN G.B., HEYNDERICKX G.J., “Mathematics in chemical kinetics and engineering: preface to the Mackie-2009 special issue”, *Chemical Engineering Science*, vol. 65, p. 2265-2266, 2010.
- [HUD 04] HUDEBINE D., VERSTRAETE J.J., “Molecular reconstruction of LCO gasoils from overall petroleum analyses”, *Chemical Engineering Science*, vol. 59, no. 22-23, p. 4755-4763, 2004.
- [JAV 08] JAVAD R.S., GUILLAUME D., ROUCHON P., DA COSTA P., “Stochastic simulation and single events kinetic modelling: application to olefin oligomerisation”, *Industrial & Engineering Chemistry Research*, vol. 47, no. 13, p. 4308-4316, 2008.
- [KLE 91] KLEIN M., *et al.*, “Monte Carlo modeling of complex reaction systems: and asphaltene example”, in SAPRE A.M., KRAMBECK F.J. (eds), *Chemical Reactions in Complex Mixtures: The Mobil Workshop*, Van Nostrand Reinhold, New York, p. 126-142, 1991.
- [KOR 94] KORRE S.C., *et al.*, “Hydrogenation of polynuclear aromatic hydrocarbons. 2. Quantitative structure/reactivity correlations”, *Chemical Engineering Science*, vol. 49, no. 24A, p. 4191-4210, 1994.
- [LIE 98] LIETO J., *Le génie chimique à l'usage des chimistes*, Lavoisier Tec & Doc, Paris, 1998.
- [POR 10] PORTHA J.-F., LOURET S., PONS M.-N., JAUBERT J.-N., “Estimation of the environmental impact of a petrochemical process using coupled LCA and exergy analysis”, *Resources, Conservation and Recycling*, vol. 54, p. 291-298, 2010.
- [PYL 09] PYL S.P., VAN GEEM K.M., REYNIERS M.-F., MARIN G.B., “Molecular reconstruction of complex hydrocarbon mixtures: an application of principal component analysis”, *Aiche Journal*, vol. 56, no. 12, p. 3174-3188, 2009.
- [RAY 07] RAYNAL L., ROYON-LEBEAUD A., “A multi-scale approach for CFD calculations of gas-liquid flow within large size column equipped with structured packing”, *Chemical Engineering Science*, vol. 62, p. 7196-7204, 2007.
- [RAY 10] RAYNAL L., FONT P., JANEIRO T., HAROUN Y., BOUILLON P.-A., “Use of multiscale simulations for lowering the cost of carbon dioxide capture”, *Distillation Absorption*, p. 121-126, 2010.
- [SCH 01] SCHWEICH D., *Génie de la réaction chimique - Traité de génie des procédés*, Tec & Doc, Paris, 2001.

- [SIE 98] SIE S.T., KRISHNA R., “Process development and scale up: III scale-up and scaledown of trickle bed processes”, *Reviews in Chemical Engineering*, vol. 14, no. 3, p. 203-248, 1998.
- [TOC 10] TOCK L., GASSNER M., MARÉCHAL F., “Thermochemical production of liquid fuels from biomass: thermo-economic modeling, process design and process integration analysis”, *Biomass and Bioenergy*, vol. 34, no. 12, p. 1838-1854, 2010.
- [TRA 02] TRAMBOUZE P., EUZEN J.-P., *Les réacteurs chimiques. De la conception à la mise en oeuvre*, Edition Technip, Paris, 2002.
- [VAN 53] VAN HEERDEN C., “Autothermic processes”, *Industrial and Engineering Chemistry*, vol. 45, no. 6, p. 1242-1247, 1953.
- [VAN 07] VAN GEEM K.M., *et al.*, “Molecular reconstruction of naphtha steam cracking feedstocks based on commercial indices”, *Computers & Chemical Engineering*, vol. 31, no. 9, p. 1020-1034, 2007.
- [VIL 93] VILLERMAUX J., *Génie de la réaction chimique. Conception et fonctionnement des réacteurs*, second edition, Tec & Doc, Paris, 1993.
- [VER 10] VERSTRAETE J.J., *et al.*, “Molecular reconstruction of heavy petroleum residue fractions”, *Chemical Engineering Science*, vol. 65, no. 1, p. 304-312, 2010.
- [VYN 91] VYNCKIER E., FROMENT G.F., *Kinetic and Thermodynamic Lumping of Multicomponent Mixtures*, Elsevier, Amsterdam, p. 131-161, 1991.
- [WAL 94] WALTER E., PRONZATO L., *Identification de modèles paramétriques à partir de données expérimentales*, Masson, Paris, 1994.
- [WIL 05] WILKES J.O., *Fluid mechanics for chemical engineers: with microfluidic and CFD*, second edition, Prentice Hall, New Jersey, 2005.

5.7. List of acronyms

FEED: Front-End Engineering Design (basic engineering).

CFD: Computational Fluid Dynamics (CFD).

HSV: Hourly Space Velocity volume flow rate of reagent (m^3/h) per reactor volume (m^3) per unit time (h).

LFER: Linear Free Energy Relationships.

MRI: Magnetic Resonance Imaging.

RANS: Reynolds-Averaged Navier-Stokes equations.

DNS: Direct Numerical Simulation.

LES: Large-Eddy Simulation.

NRTL: Non-Random Two-Liquid.