# Process Simulation and Modeling for Sustainable Industrial Development

by Maurizio Fermeglia, Stanislav Miertus and Francesco Pizzio

*This paper illustrates the concept of sustainability and investigates how sustainable development can be related to industrial development with particular attention to the situation in developing countries. The role of chemistry and specifically that of chemical engineering is focused. Two main areas of interest for the development of sustainable processes are then investigated, namely process simulation and molecular modeling.*

As the Third Millennium draws near, sustainability is increasingly becoming a key social, political, scientific and engineering issue. Indeed, there are increasing signs that sustainability will become a major new paradigm influencing the society of tomorrow and the engineering it requires. With their knowledge of chemistry and physics, mass and energy flows, and process technology, chemical engineers are in a pre-eminent position to play a major role in implementing sustainable development. In this paper, a particular attention is given to the role of chemical engineering and industrial chemistry. This role is wide. Traditionally it concerns the design and operation of chemical process plants. Nowadays it also concerns ethical and rational public policy involving science and technology.

The sustainable development, that can very simply be defined as a process in which one tries not to take more from nature than nature can replenish, can be obtained without sacrificing the many benefits that modern technology has brought [1]. To reach the objective of sustainable development reconciling dynamic industrial growth with low environmental impact, highly advanced and sophisticated technologies must be made accessible to developing countries. This not only implies the transfer of advanced and new technologies, but also indicates the necessity to stimulate innovation and sound research applicable to industrial development. Sustainable development depends on harmonization of economic growth and environmental conservation and protection. The only problem is that technology respects the imposed constraints. Engineers are asked to do this by designing new processes and/or by modifying existing processes aiming at using renewable resources and producing by products that can be returned to the earth and biologically degraded [2].

Chemical Engineers have been dealing with areas such as safety, health and environment for years. These areas are actually comprised in the definition of sustainability. By extending the concept of scale, sustainability can easily be related to safety, health and environmental questions, which already receive a great deal of attention in (chemical) engineering and industry. Sustainable development is logically related to traditional well-developed areas in chemical engineering, like those relating to environment, safety and Loss Prevention. Existing techniques, such as used for hazard and risk analysis (e.g. QRA) and Environmental Impact Assessment, can be combined with newer techniques, like Life Cycle Analysis, to create powerful new tools for the design of chemical processes and products [3].

Molecular modeling on the other hand can provide useful and unique information to process engineers developing sustainable processes when thermo-physical data are missing or are scanty. In fact, one of the most important parts of any process simulation is the data bank of physical properties or the predictive methods (such as group contribution methods) included in the package. Recently it has been shown how it is possible to combine the molecular simulation techniques with process simulation for an integrated view of modeling in chemistry and engineering. In this way a very powerful set of tools will be available to process engineers for developing safe, clean and sustainable processes.

But sustainability can also be viewed quantitatively. Interesting is to observe quantitative trends in very long historical perspective. Examining the numbers in this way leads to startling results. Interesting is to compare these trends with more recent data, like numerical indicator data concerning social sustainability [4]. There is no doubt that sustainable industrial development requires a balance between the

Maurizio Fermeglia, DICAMP - Università di Trieste - Piazzale Europa, 1 - 34127 Trieste; Stanislav Miertus, Francesco Pizzio, ICS-UNIDO International Centre for Science and High Technology, Padriciano, 99 - 34012 Trieste.

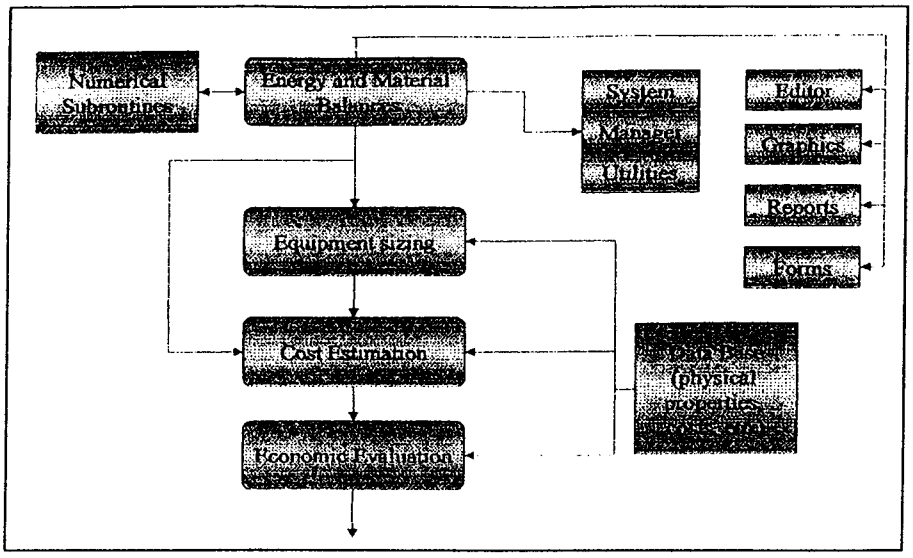


*Figure 1 - General scheme representing a steady state process simulator*

economic and the environmental aspect. Thus the necessity of cleaner technologies is becoming an imperative simply because the efficiency of the processes (especially those using new efficient catalytic systems) leads to the reduction of environmental impact and, at the same time, they should imply economic advantages. This is particularly important for developing countries and countries in transition, where "turn-key" solutions are not feasible due to prohibitive economic requirements.

In this context, modern tools like modeling and process simulation are of increasing importance, because they are able to evaluate possible technological solutions with much lower costs and time involved. On the other hand, one must be aware of the limits of this approach because of approximate nature and models imposed.

**Process simulation goals and definitions**

A process simulator solves material and energy balances by means of a computer code. A description of a typical process simulation code is reported in Figure 1 in which all the most important elements of a simulator and their connections are evidenced. Figure 1 shows clearly that a process simulator include cost estimation routines as well as economic evaluation. The importance of the database is shown in the figure as a necessary source of information for different objects in the structure [5].

The following different approaches are available in the process simulation:

- Steady state simulation which considers a snapshot in time of the process
- Dynamic simulation which considers the evolution in the time domain of the equations describing the process
- Integrated steady state - dynamic simulation, which combines the two previously, described approaches.

The approaches listed above may be used in three different philosophies when dealing with process simulation. One possibility is to perform a process analysis, in which an existing process is studied and alternative conditions as well as dynamic behavior is investigated for the appraisal of effectiveness of design. The second approach is the process synthesis, in which different process configurations are compared aiming to the identification of the optimal choice of units and the connections between them. The third possible stage in design a process is the process design and simulation, aiming at the establishment of the optimal operating conditions of a given process. In all the possible philosophies of application, process simulation impact on industry is pervasive rather than restricted to a single moment in the development of the process. Process simulation has effected strongly the way engineering knowledge is used in processes. The traditional way of using process simulation was mainly focused on flow sheet design and on equipment critical parameters definition, such as distillation column stages, column diameter, and so on. Today engineers are oriented to a more comprehensive use of process simulation in the entire 'life' of the plant such as the control strategies design, the process parameters optimization, the time evolution of the process for understanding start up and shut down processes and performing risk analysis, the operator training and the definition of procedure to reduce the unsteady state operations. The main benefits one can gain from such a comprehensive use of the process simulation are the partial or total replacement of Pilot Plant operations (reduction of the number of runs and runs planning), the reduction of time to market for the development of new processes, the fast screening of process alternatives to select the best solution in terms of economic aspects, environmental aspects, energy consumption aspects and flexibility of the proposed process.

Due to the high complexity of chemical processes, to get those benefits one must critically simplify the process and apply process simulation techniques in the entire life cycle of a process. Figure 2 shows how process simulation methods can help engineers in different periods of the life cycle of a process, from the process synthesis to the control strategies design.

The solutions of the material and energy balance equations can be performed by an equation-oriented strategy, namely the simultaneous solution of all the model equations or the sequential modular approach. In the first case, one must write down the entire set of equation, identify the constraints and solve the non-liner system. In the Sequential Modular approach each subsystem is solved independently, starting from the first one: the output streams for the solved subsystems are input streams for the next subsystem. In the sequential modular approach the main problem is to deal with recycle streams (recycle of material, energy and information).

There is another possible approach, which is a mixture of the two fundamental approaches in which equations can be lumped into modules that can be represented by polynomials that fit input-output information. The main advantages of the sequential modular approach are the following:

- The flow-sheet architecture is easily understood because it closely follow the process;
- Individual modules can easily be added and removed;

- Modules of different levels of accuracy can be substituted.

The drawbacks of this approach are:

- The input of a module is the output of a module: you cannot arbitrarily introduce an output or input;
- The modules need extra time to generate derivatives (perturbation of the input);
- The modules may require a fixed procedure for the order of solution: slow convergence;
- Parameter specification is done with control loops: possibility of introducing nested loops;
- Phase equilibrium instability during the convergence of the process.

Steady state simulators are considered the core products of process simulation and are used for process design, evaluating process changes and analyzing what-if scenarios.

All the other kind of simulations are normally performed after a steady state simulation: dynamic simulation, process synthesis with Pinch technology, detailed equipment design, off-line and on-line equation-based optimization, application technologies for vertical markets, e.g. polymers.

The problems involved in a process simulation run are the definition of an accurate thermodynamic model [6] (Equations of state or Excess Gibbs Energy model), the necessity of defining dummy operations, not always easy to identify and the tear streams identification to achieve rapid convergence.

As far as the Dynamic Simulation is concerned, applications can be found in continuous processes, concurrent process and control design, evaluation of alternative control strategies, troubleshooting process operability, verification of process safety. The most important benefits of Dynamic Modeling is the capital avoidance and lower operating costs through better engineering decisions, the throughput, product quality, safety and environmental improvements through improved process understanding, the increased productivity through enhanced integration of engineering work processes.

An important feature of modern process simulators is related to its usability and interoperability with other applications. A user familiar graphical interface and easy and standard interprocess communication techniques are key elements to obtain the Workflow integration in the process design.

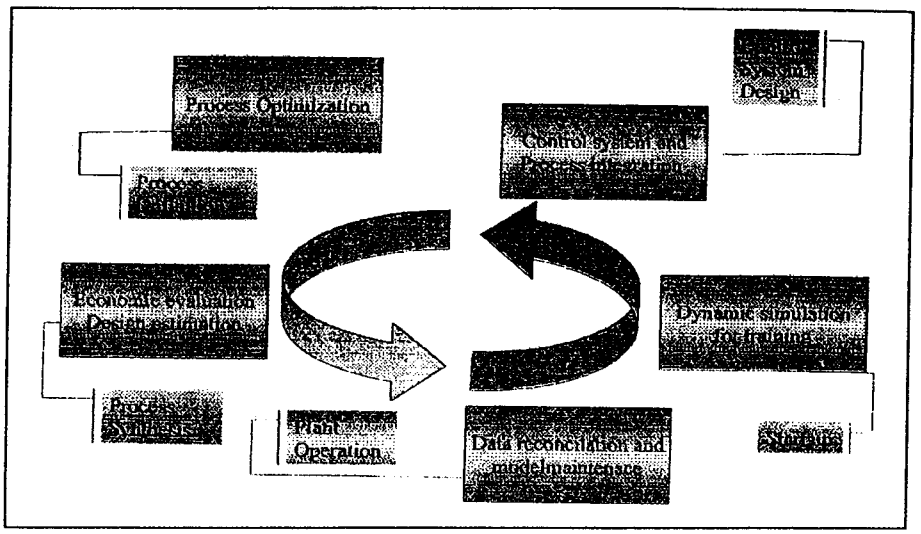


*Figure 2 - Process simulation and the life cycle of a process*

To obtain the engineering Workflow Integration it is necessary that the software can exchange information with other applications. This is done through the basic Windows interoperability by using the Microsoft COM/OLE Automation technology.

A two-way data transfer between the software and other Windows applications via copy, paste, paste link should be performed, Windows should give access to all inputs & results and give access to plots and flow sheet graphics. It should be possible to copy data tables and spreadsheets into the simulator for Data Regression, Data-Fit, etc. Another important point in the workflow Integration is the support to interfaces to specific 3rd-party engineering applications such as equipment design (B-JAC, HTRI, HTFS), engineering databases (Aspen Zyqad, PASCE), costing packages (ICARUS) and in-house technologies. In summary, the benefits of the workflow integration are the following:

- Support for engineering infrastructures that integrate engineering work processes
- Error-free data transfer into 3rd party Windows engineering programs
- Quick and consistent use of simulation results throughout the engineering lifecycle
- Improved engineering quality
- Work Flow Integration.

**A bridge between molecular modeling and process simulation**

More than seventy five per cent of the code in process simulators is dedicated to physical properties estimation, calculation and predictions. Data banks storing pure component parameters and binary interaction parameters for phase equilibrium calculation are extensively used and continuously implemented in modern process simulators. This gives an idea of the important role that physical property availability plays in process simulation. This role become of paramount importance when dealing with new products, with new processes and/or with the revamping, in terms of more sustainability, of existing processes. In most cases substances are used or produced whose physical properties are not known and in some cases are not even measurable.

Molecular modeling can be seen as a very useful tool to process engineers, by providing the results of virtual experiments, pure components physical properties in a wide range of process conditions, phase equilibrium and kinetic data as well as an interesting tool for screening new and interesting products and reaction schemes.

There are several possibilities for coupling molecular modeling and process simulation. Among them a very interesting one has been recently proposed for combining molecular modeling and chemical engineering oriented semi-empirical models such as equations of state and excess Gibbs energy models [7, 8]. The general idea here is to use molecular dynamics and Monte Carlo methods for generating the parameters of an equation of state that will subsequently be used in process simulation. In this way one can still perform process simulation with a reasonable

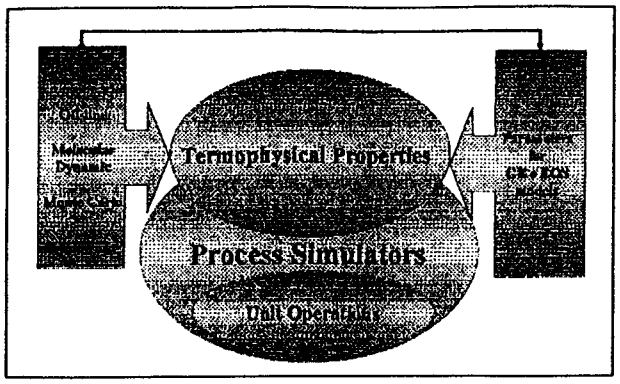


*Figure 3 - Process simulation and molecular modeling*

hardware (a PC, as well as a workstation) and with a reasonable CPU consumption. In fact, the present computer technology do not allow us to perform a process simulation with integrated molecular modeling tools. The general scheme is reported in Figure 3 in which two possibilities are shown:

- Generation of thermo-physical data by means of virtual experiments,
- Generation of parameters to be used in semi - empirical model built in process simulators.

Traditionally experimental work has been and is still carried out to provide information to process engineers. The cost of collecting one vapor-liquid equilibria (VLE) data point (i.e., one temperature and composition for just one binary mixture) has been estimated to be around $ 2,600 and to take 2 days [9]. Thus, we can reasonable hope to perform an experimental characterization of VLE for a minute fraction of the total possible mixtures, temperatures and compositions.

With the computing power and technology available nowadays, computer molecular simulations can be considered cheaper and faster than true experiments, especially for simple molecular fluids. Therefore, provided we properly account for the two major problems encountered in any virtual experiment (i.e., the size of the configurational space that is accessible to the molecular system and the accuracy of the molecular model or atomic interaction function or force field that is used to model the molecular system), we can think of computer simulation at least as a first way of screening among the plethora of possible system candidates.

Indeed, during the last decades virtual experiments based on quantum/molecular mechanics (QM/MM) calculations and molecular dynamics (MD) simulation techniques have opened avenues in the estimation and prevision of thermophysical properties (both under equilibrium and non-equilibrium conditions) of simple molecular fluids [10, 11]. The treatment of molecular systems in the vapor/gas phase by quantum mechanics is quite simple, due to the possibility of reducing the many-particle problem to a few-particle one based on the low density of a system in the gas phase. If the classical statistical mechanics approximation is permitted, the problem becomes even simpler. Nevertheless, for both amorphous solid states and liquid systems such as solutions and polymers we remain faced with an essentially many-particle systems, for which no simple reduction to a few degrees of freedom is possible, and a full treatment of many degrees of freedom is necessary to adequately describe the properties of molecular systems in the fluid-like state. In such cases, to obtain reliable estimations of dynamic and non-equilibrium properties dynamic simulation methods that produce trajectories in the phase space are to be used. The method of MD solves Newton's equation of motion for a given molecular system, which results in space trajectories for all atoms in the system. From these atomic trajectories, a plethora of thermophysical properties can then be calculated as time averages from the relevant microscopic relationships expressed in terms of molecular positions and momenta.

As mentioned above, the aim of computer simulations of molecular systems is to compute macroscopic behavior from microscopic interactions. The major contributions a microscopic consideration can afford are (a) the understanding and (b) interpretation of experimental results; (c) semiquantitative estimates of experimental results and, last but not least, (d) the possibility to interpolate or extrapolate experimental data into regions that are only difficultly realizable, if at all, in the laboratory.

Figure 4 shows the general connection scheme and the possible interactions between molecular modeling and process simulation. The fundamental starting point of the scheme is the quantum chemistry and the quantum mechanics ab initio calculation. Fundamental studies in this field are of paramount importance for defining a theoretical framework within which to develop expressions and parameters for the interaction potential and force fields. Structure and properties of simple materials are used both for developing methods and for the validation of the obtained force fields. Structure and properties may directly be used for defining reaction mechanism and kinetics, which are one of the key input to any process simulation run involving reactions and chemical transformation. Force fields, on the other hand, have a direct application to molecular dynamics and Monte Carlo calculations which are the key techniques for determining pure component and phase equilibrium properties for simple and complex substances. These calculations may be directly applied to the design of new materials and new chemicals (drugs, agrochemicals, ...) to the calculation of parameters of semi empirical models such as equations of state and excess Gibbs energy models or the model development and model validation.

Parameters obtained by this procedure are then stored in data base and used by process simulation coupled with semi empirical models, which are by far computationally simpler than any molecular dynamic or Monte Carlo method and therefore affordable in a process simulation.

The boxes depicted in Figure 4 rely on the availability of data that are necessary in different parts of the scheme: force fields and model validation, reaction modeling, process simulation etc. A service database is provided for the entire process containing data on thermodynamic properties, phase equilibrium, kinetics, costs and profits, structure and geometry. Furthermore another general service to scheme should contain subroutines implementing all the numerical methods needed for parameter estimation and for solving differential and algebraic equation.

Another traditional method to obtain physico-chemical properties used for screening different possibilities in process synthesis is based on the approach belonging to the group of methods called Computer aided molecular design [12]. It provides a mean for de-

signing molecules (CAMD) or mixtures of molecules (CAMMD) having a desirable set of physico-chemical properties. As the physico-chemical properties are directly or indirectly related to the structure of the molecule(s), methodologies for CAMD and CAMMD are typically based on "exploiting" these relationships. Currently, CAMD/CAMMD has found useful industrial applications. However, the application range is restricted because of the limitations on the complexity of the generated molecular structures and on the availability of suitable models for property prediction. Recently, molecular-level information has been combined with the current group contribution based methods for opening new horizons of applicability and accuracy of CAMD. At the same time, CAMD approaches, including molecular mechanics, are extensively used for interpretation of molecular structure and properties and design of new molecules with the desired properties (drugs, agrochemicals, new materials etc.)

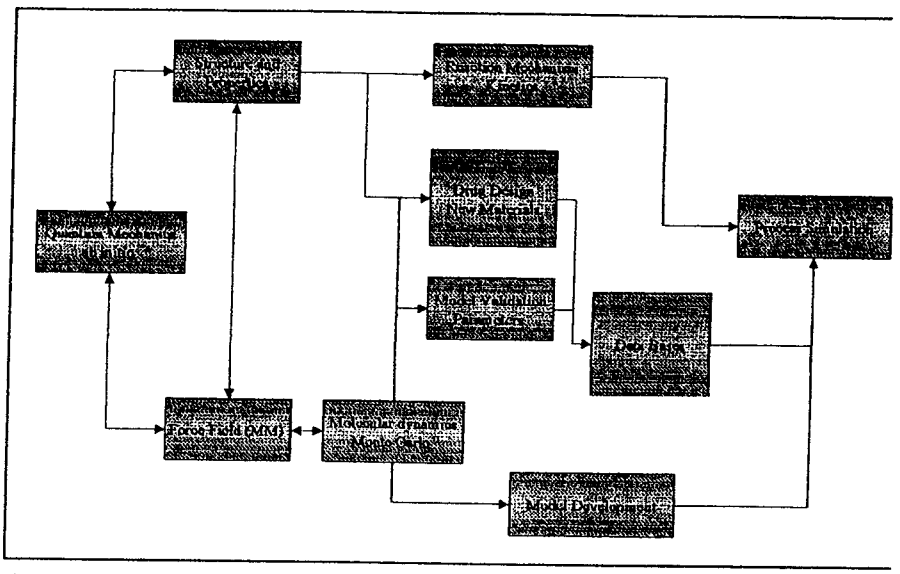

*Figure 4 - General scheme of bridging molecular modeling and process simulation*

**Importance for developing countries, ICS-UNIDO activity**

Developing and in transition countries are fully aware of their urgent need to become acquainted with modern technologies, so that local enterprises can remain competitive and economically viable in the coming decades and gain expertise in application practice.
Both molecular modeling and process simulation are unanimously considered to be powerful tools for the implementation of a country's capabilities in drug design, agrochemistry, new materials and upgrading of industrial processes. These are essential if a developing country wants to have the possibility to enter the market competition. The above considerations are reinforces considering that many developing countries have a large potential in terms of natural resources, that are at present definitely under-exploited.
Furthermore, molecular modeling and process simulation are approaches requiring low investment, and can thus easily be applied in R&D as well as in industries (even SMEs) in developing countries, working in pharma, agrochemistry and natural product exploitation. Evaluation of these approaches should indicate their applicability in R&D institutions and especially in industries (including SMEs) in developing and transition-economy countries. This should also facilitate optimization of production processes to reduce environmental impact, which is particularly important for obsolete processes often in use in these countries. The role and applicability of modeling have recently been evaluated in its overall sense during an Expert Group Meeting (with the focus on Central and Eastern European and Mediterranean countries) on "Modeling in Chemistry and Chemical Industries", which was held at and organized by ICS-UNIDO (International Centre for Science and High Technology of the United Nations Industrial Development Organization), in Trieste, Italy, on 14-16 October 1998. The subjects dealt with ranged from modeling of molecular structures and properties, modeling of molecular processes and complex molecular systems to process simulation at a macroscopic level complemented by preventive risk analysis of industrial pollution. It was concluded that although several highly qualified groups exist in these regions, the industrial applications are rare, probably because of the transforming economies characterizing these countries. The plan of networking Central and Eastern European and Mediterranean countries with the involvement of the Italian Institutions has been agreed upon. The networking activity will be coordinated by ICS-UNIDO in Trieste, Italy. ◆

**References**

[1] B. Lemmes, ORCA Technical publications, n. 1-7, Organic Reclamation and Composting Association, Brussels
[2] Pé.R. White, M. Franke, P. Hindle, Integrated Solid Waste Management: a Lifecycle Inventory, Blackie Academic & Professional, Chapman and Hall, 1995.
[3] H. Cabezas, J.C. Bare, Pollution Prevention with Chemical Process Simulators: The Generalized Waste Reduction (WAR) Algorithm, *Computers and Chemical Engineering*, 1997 21 (Supplement), S305-S310.
[4] S. Lemkowitz, G.J. Harmsen H.W. Nugteren, The Challenge of Sustainable Development to Chemical Engineering: A New Paradigm for the 21st Century?, AIChE Annual meeting, Miami, USA, 1998.
[5] System Engineering: Principle and Practice of Computer-Based System Engineering, B. Thome (Ed.), 1993, Wiley, New York.
[6] J.M. Prausnitz, R.N. Lichtenthaler, E. Gomes de Azevedo, Molecular Thermodynamics of Fluid Phase Equilibria, 3rd Ed., Prentice-Hall, 1998.
[7] M. Fermeglia, S. Pricl, *Fluid Phase Equilibria*, in press.
[8] A.K. Sum, S.I. Sandler, *Fluid Phase Equilibria*, in press.
[9] Molecular Simulations and Industrial Applications, K.E. Gubbins, N. Quirke (Eds.), 1996, Gordon & Breach, Amsterdam.
[10] P.T. Cummings, *Fluid Phase Equilibria*, 1996, **116**, 237, 248.
[11] A.Z., Panagiotopoulos, *Fluid Phase Equilibria*, 1996, **116**, 257.
[12] R. Gani, L. Constantinou, *Fluid Phase Equilibria*, 1996, **116**, 75.