Latest Advances in Computational Chemistry for Petroleum and Petrochemical Processing

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1.Theme Description

The use of software for the solution of complex problems is dating in 1960s. Since then, computational chemistry grew up quickly by means of increasingly powerful computers:[1]

- in 1966 Simulation Science launched PROCESS a program for simulating distillation columns;
- in 1969 DESIGN, a flow-sheeting program for oil and gas processes, was commercialized;
- in the 1970s FORTRAN became the programming language of engineers;
- in 1976 the US Department of Energy of Massachusetts commercialized the simulation program ASPEN;
- In 1982 was launched the first Personal Computer, IBM 5150;

Since 1990s PC programs have played a key role and nowadays are widespread in petroleum and petrochemical processing. In the following section the basis of computational chemistry and the principles of the main commercial software are described.

2.Computational Chemistry

Computational Chemistry is part of the chemistry that uses mathematical models to be simulated on the computers:

- determining the physical properties of streams;
- improving the efficiency of the processes by means of sensitivity analysis;
- describing new compounds and materials.

The methods on which models are based can be divided in: Classical Computational Methods and Computational Quantum Chemistry.

2.1 Classical Computational Method

These methods are based on the law of classical mechanics and include:

- **Molecular Mechanism (MM)**[2] describes the molecules as a collection of balls held together by springs. The balls represent the atoms while the springs the chemical bonds. The model minimizes the molecular potential energy to find bond lengths, angles and dihedrals. Often is called force field method and allows to describe molecules with thousands of atoms.

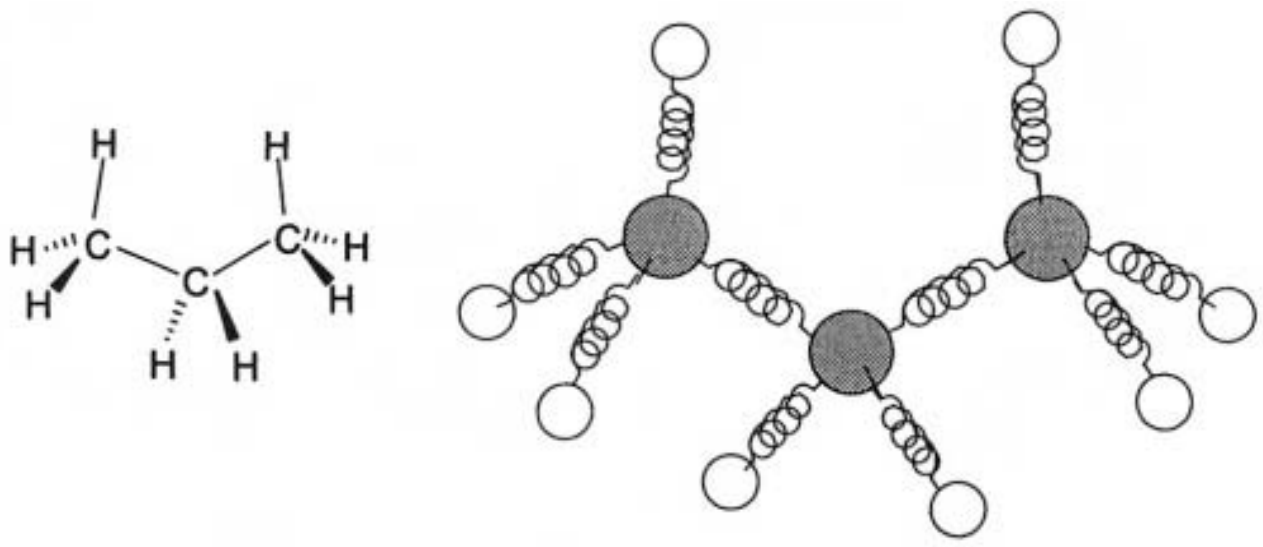

Figure 1 – Schematic Representation of a Molecule (2)

- **Molecular Dynamics (MD)**[3] describe vibrational/Brownian motion of a molecule. The momentums and forces of each atom are obtained by choosing the initial position and velocity of them. Then, new positions and velocity of molecules are processed by the information obtain in the previous step. The trajectory, the energy levels and conformation of substances are computed by iterating the algorithm. This method is suitable for protein application.
- **Monte Carlo Simulation (MC)**[3] unlike molecular dynamics, this method is not deterministic, but is based on statistical distribution. Indeed, after choosing the initial position of the atoms and computing the energy of the system, the movement of itis selected randomly. The new configuration is accepted if the system reproduces a Boltzmann distribution. Otherwise another trajectory or the previous position are used until the system is balanced.

2.2 Computational Quantum Chemistry

These methods are based on the law of quantum mechanics and include:

- **Ab Initio**[4], solves the Schrödinger equation giving the position of atoms, the electronic energy and density. It is based on the method of Hartree–Fockthat doesn't take into account the electron correlation. Therefore, it can be used only in few cases. Several methods have been introduced to overcome this restriction (Moller-Plesset perturbation theory, Coupled Cluster, Multireference perturbation method sand etc.)
- **Semi-empirical Quantum Mechanism**[5] treats only the valence electrons by ignoring some integrals. The errors due to the approximation are reduced by empirically parameters.
- **Density Functional Theory (DFT)** is based on Hohenberg–Kohn theorem. It represents the total energy of the system as a function of the electron energy. In this way is possible to solve the problem by knowing of three coordinates instead of 3N coordinates of the electrons.4

A combination of Quantum Mechanism and Molecular Mechanism is used to describe reaction in a condensate phase. A small part of the system is treated with Quantum Mechanism that takes into account the new configuration of electrons due to chemical reactions. The rest is treated with Molecular Mechanism that allows to describe the molecular geometry.[6]

2.3 Computational chemistry in Industrial Processes

Process simulation started in the 1966 when Simulation Science launched the program PROCESS (today PROII) for the simulation of distillation columns. Nowadays is widespread due to the possibility to simulate steady state and dynamic. Steady state is used for equipment design, debottlenecking of plants while dynamic simulations are used to reproduce start-up, shout-down, disturbances, operability etc.[7]

The main software use in Industrial Processes are based on two techniques [8]:

- **Sequential Modular Approach (SM)** divides the flowsheet in a series of block that need to be solved in series. In the presence of recycle streams a "tear stream approach" is used.8

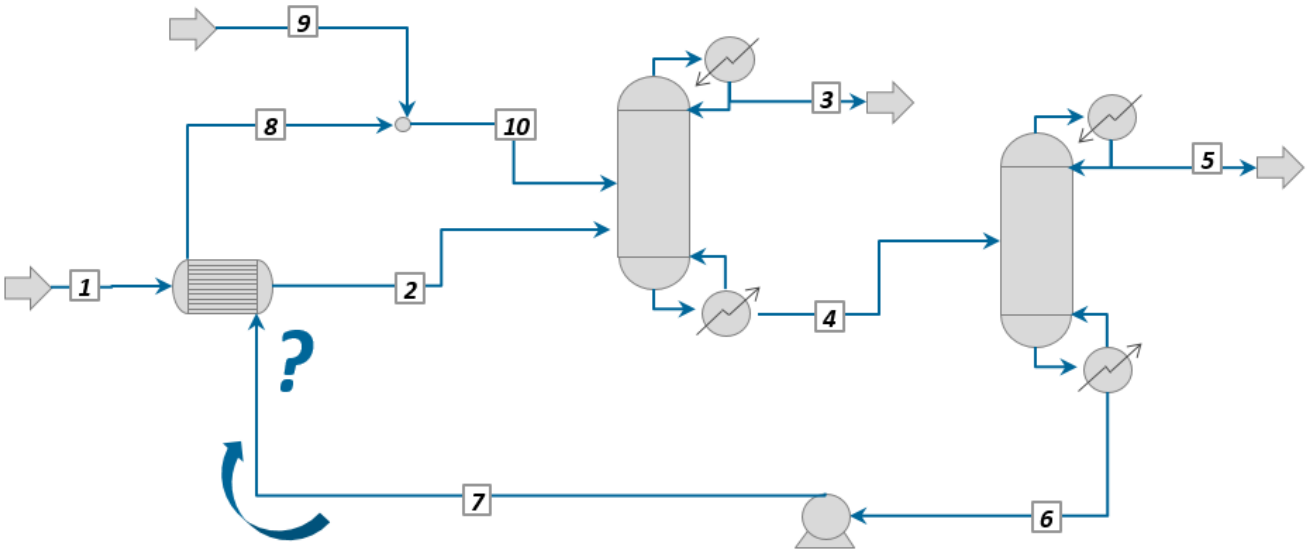

Figure 2 – Sequential Modular Approach [9]

The tear stream approach gives an initial value to the stream; in this way the blocks can be solved sequentially. Then the initial choice is checked by an algorithm, until converge is reached. The method is suitable for steady-state simulation, but it is time-consuming for very complex systems.

- **Equation-Oriented Approach (EO)** all the equations used in the software are solved simultaneously. It is suitable for object-oriented model approach and can simulate steady state (nonlinear, algebraic equation) and dynamics (differential equation).

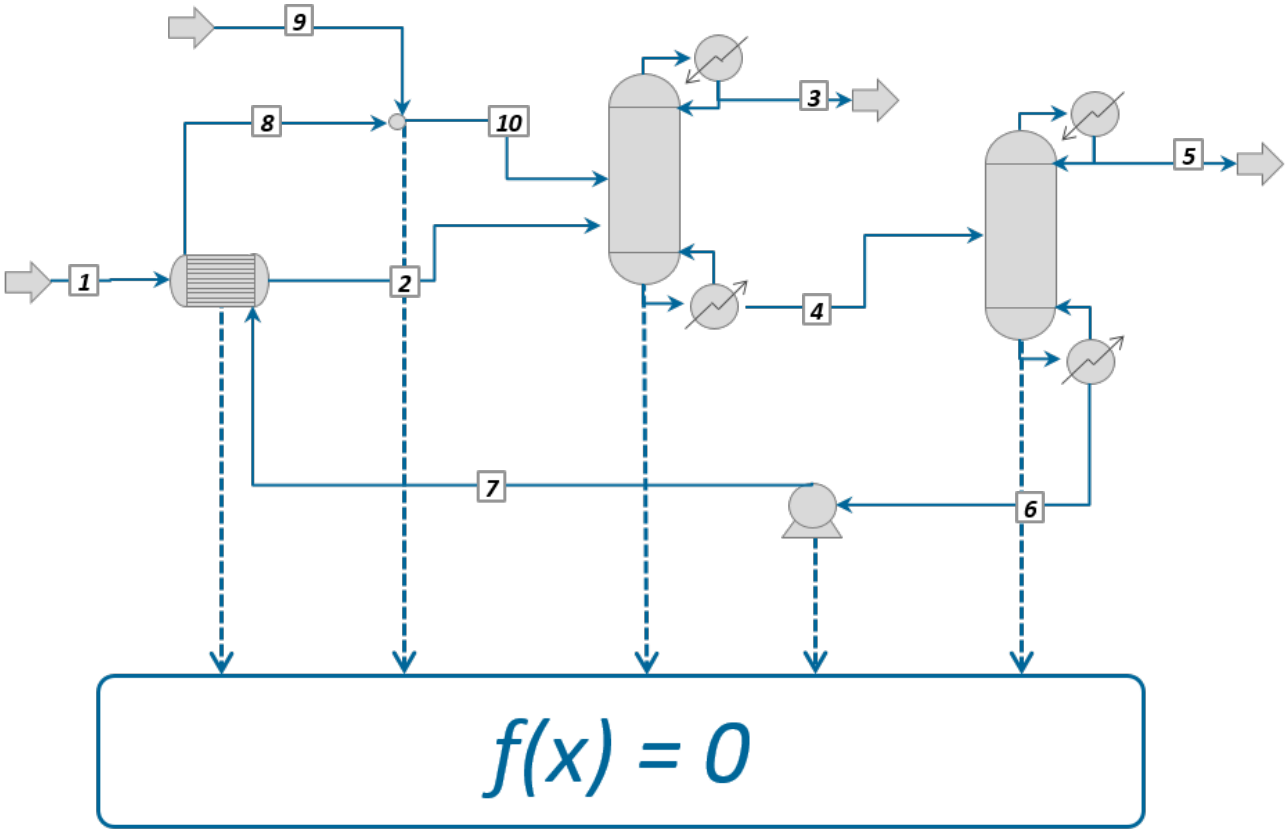

Figure 3 – Equation Oriented Approach (9)

The combination of the two models (SM & EO) is called Simultaneous Modular Approach.

2.4 Main Commercial Software

In this section, the main commercial software are listed:

- **AspenPlus** is one of the packages developed by AspenTech[10]. It's widespread in petrochemical and pharmaceutical processes. It has a database of about 5900 components from NIST. It can be integrated with cost analysis, heat exchanger design software and can be interfaced with Microsoft Excel by means of Visual Basic. It allows to make stead-state/dynamics simulation taking into account non-ideal and solid system.[11]
- **DESIGN II for Windows** produced by WinSim Inc.[12] is suitable for petrochemical processes. Indeed, it includes more than 60 thermodynamics methods, 1200 components and 38 worlds crude oils. Other compounds can be added with ChemTran that allows also to calculate non-ideal property of mixtures. It's automatic linked with Microsoft Excel, Visual Basic, Visual C++ interfaces and allows to use FORTRAN commands to define specific options.

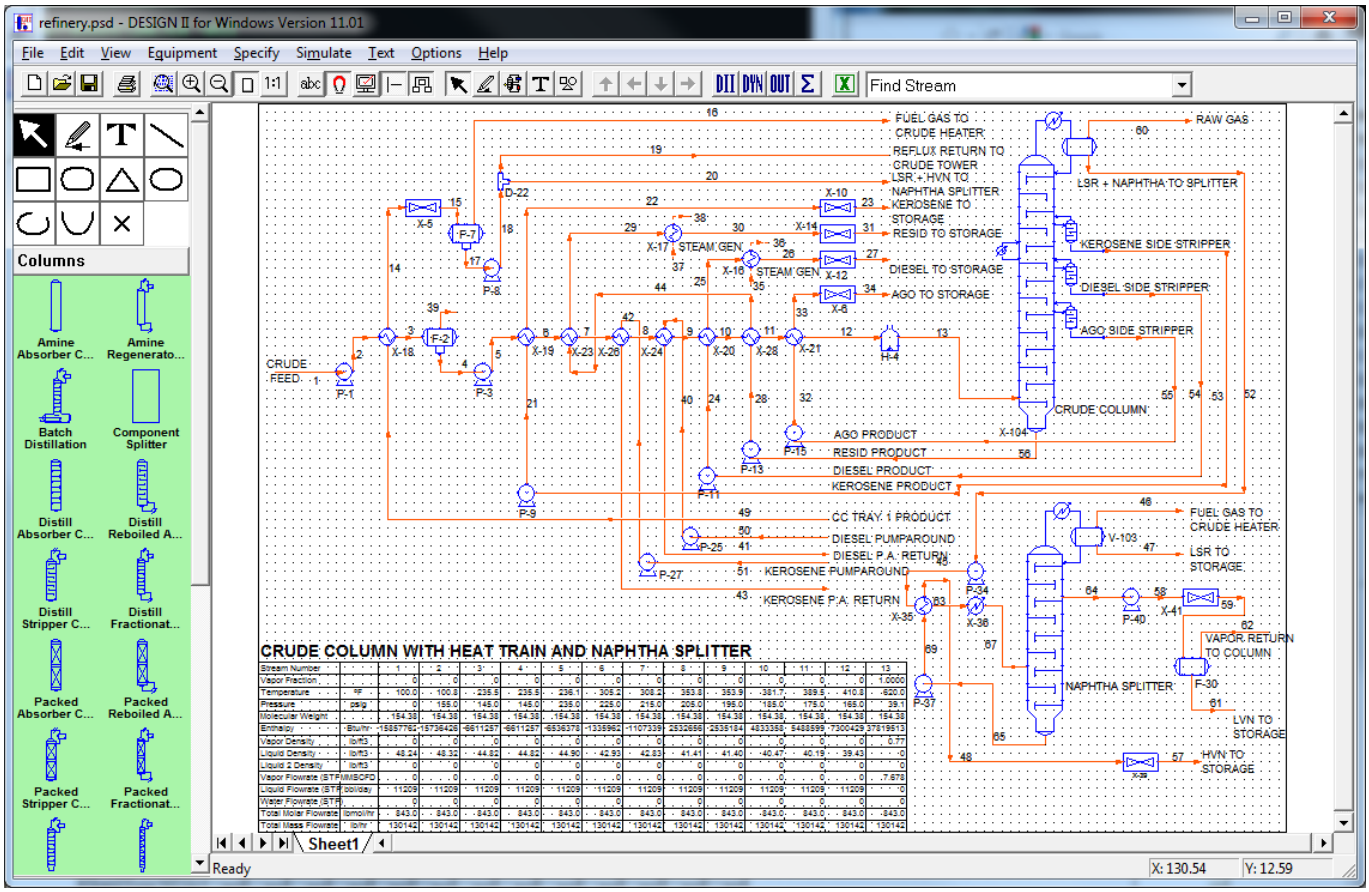

Figure 4 – Refinery flowsheet with Design II for Windows[13]

- **SimSci PRO/II** is owned by Invensys SimSci[14]. It allows to simulate steady-state processes in refining, polymerization and pharmaceutical applications. It performs rigorous mass and energy balance. Nowadays it includes also Spiral Crude Suite a package that features crude feedstock in detail. In this way more rigorous models are obtained.1
- **ChemCAD** commercialized by Chemstations Inc.[15] **includes several packages that allow to design new processes or improve existing ones. Indeed, wide thermodynamics data and unit operations cost are available. Furthermore, it's possible to simulate steady state and dynamics such as operability of the plants, loops control, operator training etc.**
- **gPROMS** developed by PS Enterprise[16] is based on

Equation Oriented approach. It allows to write differential equations, physical and chemical properties in the gProms model Builder. The resulting model is matched with experimental data to adjust the parameters. It can interface with Excel, Matlab and FLUENT environments. It is suitable to describe gas separation processes, crystallization, polymerization, fix bed reactors etc.[11]

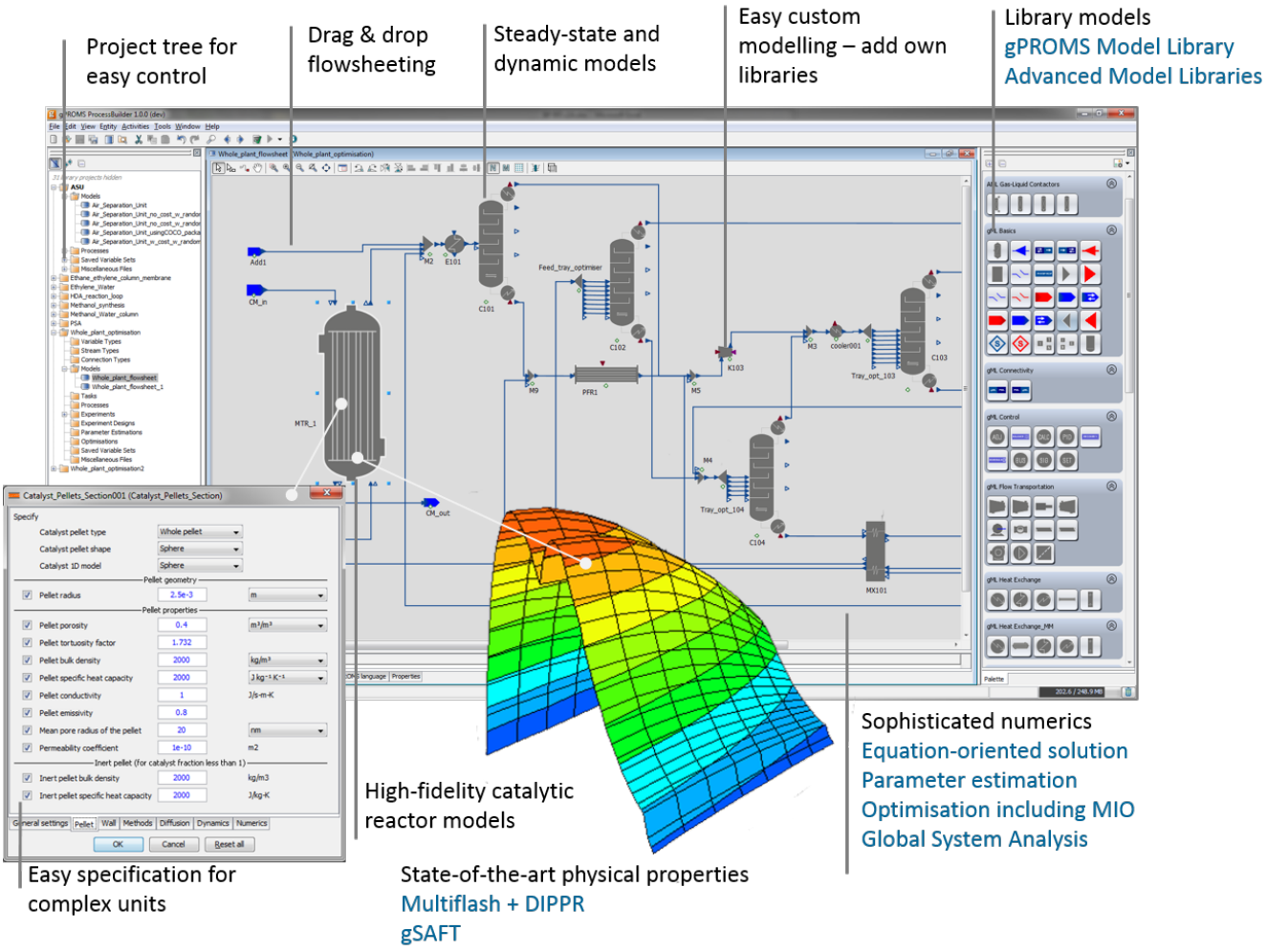

Figure 5 – gPromsprocess Builder (16)

3.Conclusions

Since 1960s computational chemistry (classical and quantum) has played a pivotal role in solving complex problems. Nowadays commercial programs are based on two mathematical models: Sequential Modular Approach (SM) and Equation Oriented Approach (EO). The SM is suitable for steady state solution, while the EO for dynamics processes and real-time optimization. There are several software (Aspen Plus, PRO/II, gProms etc.) that can reproduce the main petroleum and petrochemical processes; but despite there are more powerful PC, some simulations are time consuming. Therefore the future challenge is to reduce this time ever more and integrate different modelling components and environments through a standard interface (i.e. CAPEN-OPEN project[17]).

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[1]A.Dimian et al., Integrated Design and Simulation of Chemical Processes, Volume 13 2nd Edition, Elsevier Science 2014.

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[6] https://www.mpibpc.mpg.de/9638776/Groenhof_2013_Meth_Mol_Biol.pdf

[7]https://www.ncbi.nlm.nih.gov/books/NBK207665/

[8] D.C.Y.Foo, RafilElyas, Introduction to Process Simulation, Chapter1, Chemical Engineering Process Simulation

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[13] https://www.winsim.com/media/refinery.png

[14] http://software.schneider-electric.com/products/simsci/design/pro-ii/

[15] http://www.chemstations.com/Why_CHEMCAD/

[16] https://www.psenterprise.com/products/gproms

[17] http://www.colan.org/general-information-on-co-lan/