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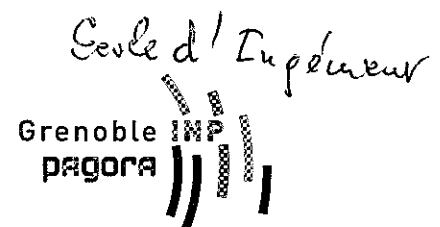
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Conception des procédés : un exemple de modélisation aux différentes échelles

Process design: an example of modeling at different scales

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Abstract:

For higher performance, increased selectivity and faster development of new processes, accurate models with a wide range of applicability are required. An adequate kinetic description of the reaction chemistry in combination with a sufficiently detailed reactor model is essential but not sufficient for that purpose.

This requires on the one hand that the chemistry involved is modeled accurately at the molecular scale. On the other hand, the proposed reactor model should be of sufficient complexity to allow a proper description of the studied system. This methodology has been applied to steam cracking of hydrocarbons. Design and optimization of industrial steam cracking reactors is focused on maximization of the product yields and the energy efficiency. Only a fundamental simulation model with a reaction network based on elementary reaction steps, a so called single event microkinetic (SEMK) model, enables accurate and efficient modeling of the numerous reactions taking place in a steam cracking reactor. The SEMK model contains two parts: 1. the single event reaction network and 2. the reactor model equations and solver of the resulting set of differential algebraic equations. The SEMK model for steam cracking is called COILSIM1D and allows simulation of the effluent composition obtained from cracking both gas and/or liquid feedstocks.¹

The detailed modeling of the cracking mechanisms of large hydrocarbons results in extensive number of reactions, the so-called reaction network. Even for cracking of light hydrocarbons, the networks describing the radical chemistry of the cracking process can contain up to thousands of reactions and hundreds of species. Reaction networks can be generated based on a limited number of rules corresponding to elementary reaction families defining the chemistry of the process. For steam cracking three elementary reaction families need to be considered:

- 1- radical addition to an unsaturated bond and the reverse β -scission
- 2- hydrogen abstraction
- 3- C-C and C-H bond scission and radical recombination reactions

This allows to generate a full reaction network in a systematic way².

It is one of the most challenging tasks in reaction engineering to provide these networks with accurate kinetic and thermodynamic data. For steam cracking, the lack of thermodynamic and kinetic parameters for all elementary steps is commonly circumvented by using a combination of parameters originating from various sources such as kinetic databases (e.g. the NIST database), model predictions (e.g. Evans-Polanyi relation, group additivity schemes) and fitting to experimentally observed product yields. However, there is frequently a rather large scatter on the reported kinetic data for a given reaction. Also, the use of rate coefficients that are fitted to the observed product yields can obscure deficiencies in the reaction network. A method is required that can yield accurate kinetic and thermodynamic data very fast for every possible reaction within a family. In this contribution the use of a consistent set of ab initio based kinetic and thermodynamic data will be demonstrated. The thermodynamic data are calculated using accurate quantum chemical CBS-QB3 calculations including corrections for hindered internal rotation, and the kinetics using CBS-QB3 based group additive models. Reactor simulations for steam cracking of ethane/propane/butane mixtures in pilot and industrial reactors over a wide range of process conditions show that, without adjusting any parameters, the main product yields can be predicted within 15% rel. of the experimentally observed cracking yields.

Another issue when one would like to apply the SEMK methodology in an industrial environment is that SEMK models requires the characterization of a feedstock in terms of types of molecules. In industry the available information is limited to commercial indices corresponding to macroscopic properties such as density and boiling point trajectory. So-called molecular reconstruction methods use this information to obtain a characterization of the feedstock in the terms required by e.g. a SEMK model. Three methods have been developed for these purpose: maximization of the Shannon entropy (MSE), artificial neural networks (ANN) and multiple linear regression (MLR)³. The last two methods are both able to reconstruct the composition of naphtha fractions with great accuracy, provided the considered naphtha has similar characteristics compared to the large number of training naphthas used to develop these reconstruction methods. A principal component analysis of the training set allowed to represent the training samples in a three dimensional space and to identify unambiguously the application range of the ANN and MLR methods. Within the application range defined by the training set, the ANN method is generally more accurate than the MSE method. However, outside this range the performance of the ANN decreases drastically, while the performance of the MSE is not influenced by the characteristics of the considered naphtha. The performance of the latter strongly depends on the number of available commercial indices and, in particular on the level of detail of the available distillation data.

Finally, to simulate an industrial cracker also the furnace needs to be simulated in full detail. The energy required for the steam cracking of the feed is provided by burners which can either be located in the side walls or the floor of the furnace. The heat flux profile at the reactor walls can be obtained by performing a coupled simulation of the furnace and the reactor tubes. COILSIM1D can be combined with Fluent⁴, where Fluent provides the heat flux profile from simulating the fire box. Another possibility is to obtain the heat flux profile from one of the in house developed software codes FURNACE⁵ or FLOWSIM⁶. Using these approaches makes it possible to obtain excellent agreement with the measured industrial products yields in combination with detailed insight on the fire-gas side.

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Short Curriculum Vitae

Guy B. Marin (1954) est professeur ordinaire en Génie Chimique à l'Université de Gand. Il a reçu son diplôme d'ingénieur civil chimiste en 1976 et a obtenu le titre de docteur en 1980. Après une année postdoctorale à Catalytica Associates à Stanford il fut nommé à l'Université de Gand en 1986. Il devient professeur ordinaire en 1988 à l'Université d'Eindhoven (Pays-Bas) où il a enseigné les réacteurs chimiques. Il est retourné à Gand en 1997 où il est directeur du "Laboratorium voor Chemische Technologie". Le génie des réactions chimiques, la catalyse en général et la cinétique des réactions chimiques en particulier font l'objet de son programme de recherche. Il est co-auteur de plus de 250 publications dans des journaux scientifiques internationaux. Il est rédacteur en chef de "Advances in Chemical Engineering" et co-rédacteur du Chemical Engineering Journal. Il dirige le programme « Multiscale Modeling and design of chemical Reactions and Reactors » (M2dcR2) et coordonne le Projet de Recherche Intégré Européen « Oxidative Coupling of Methane followed by Oligomerization » (OCMOL). Il est membre de plusieurs Commissions Scientifiques et conseils d'administration.

