

Olefin production: opportunities and challenges for chemical reaction engineering

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Highlights

- Complex reaction networks can be generated with little user input
- Ab initio kinetics can describe accurately steam cracker yields
- 3D reactor technology allows to mitigate fouling
- Autothermal adiabatic oxidative coupling of methane is possible

This lecture will give an overview of recent advances in the field of olefin production with focus on steam cracking. Both the present industrial production process as well as emerging technologies will be discussed. The latter relate to the use of alternative feed stocks either methane or renewables on hand and to new reactor technologies on the other hand. The role of the increasing power of computational and experimental techniques will be highlighted.

The implementation of comprehensive GCxGC analytical techniques has allowed to quantify the composition of feed stocks way beyond the naphtha cut of crude oil. This includes hydrotreated mixtures of triglycerides and fatty acids, as well as shale oil [1]. These detailed analytical results provide a training set for reconstruction methods, including Principal Component Analysis, Artificial Neural Networks, Multiple Linear Regression and Shannon entropy maximization [2]. They correlate available macroscopic properties such as density and boiling point trajectory of feed stocks with molecular composition to a level of detail required for the application of fundamental so-called Single-Event MicroKinetic (SEMK) models.

The latter are based on the identification of the elementary reaction families involved in the conversion of feed stock to products. Very often, if not always, their number is limited. Hence, only a limited number of kinetic parameters corresponding to well-defined changes in the electronic configuration of the reactants has to be known. An automatic reaction network generation tool Genesys (<https://github.ugent.be/LCT/Genesys>) transforms the identification of the relevant elementary reaction families into algorithms using the open source chemo informatics toolkit Chemistry Development Kit (CDK). CDK requires among other things the input of reactant molecules in InChI or SMILES format. The latter is then converted by Genesys into a graph representation. The identification of sub-molecular patterns required for a particular transformation is of key importance and based on graph iso- and automorphism [3-6].

High level ab initio calculations are within reach of even non-specialists and can be performed on a laptop for molecules containing as many as 20 atoms. Group contribution methods, originally developed by Benson to calculate thermodynamic properties, can also be applied to calculate the kinetic parameters corresponding to transformations of larger molecules. For homogeneous gas phase reactions a thermodynamic and kinetic data base of group contributions obtained by high level ab initio calculations involving small but representative molecules and reactions has been constructed [7-10].

The SEMK model has been implemented in reactor models which allow to investigate the effect of a so-called 3D [11,12] geometry on the heat transfer from the furnace to the process gas. The latter determines the rate at which coke is deposited on the internal walls [13]. By simulating the influence of the reactor geometry on product yields and coking rates, existing designs can be evaluated and new reactor designs can be put forward. See e.g. Kubota's patented 'Mixing Element Radiant Tube' (MERT), Technip's Swirl Coil design and a recent patent application filed by BASF. Finally, accounting for the interaction between the furnace and the reactor coils an accurate and fast estimation of the run length of steam cracking furnaces can be performed [14].

In contrast to steam cracking heterogeneously catalyzed reactions play a crucial role in oxidative coupling of methane (OCM) next to homogeneous free radical reactions. For the former chemisorption and reaction

enthalpies, initial sticking probabilities and active site density are used as catalyst descriptors [15]. The high exothermicity of OCM makes heat management quite challenging, but provides also opportunities e.g. autothermal operation [16]. The developed detailed kinetics allow to understand the ignition and extinction phenomena as well as oscillations of the reactor temperature when operating OCM adiabatically. Conditions for which a steady state operation with inlet temperatures close to ambient can be expected provided there is sufficient thermal back mixing could be delineated. A novel reactor type for which this can be implemented will be discussed.

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Keywords

steam cracking; oxidative coupling; chemo informatics; kinetics