Using the semi-mechanistic steam-cracking model to improve steam-cracker operation

A. Karaba\textsuperscript{a} \textsuperscript{a}, P. Zamostny\textsuperscript{a}, T. Herink\textsuperscript{b}, J. Lederer\textsuperscript{c}

\textsuperscript{a}Department of Organic Technology, Institute of Chemical Technology Prague, Technicka 5, Prague 166 28, Czech Republic
\textsuperscript{b}Unipetrol RPA s.r.o. Litvinov, 436 70 Litvinov – Zaluzi, Czech Republic
\textsuperscript{c}Vyzkumn\’y Ustav Anorganickie Chemie, a. s., Revolucni 1521/84, 400 01 Usti nad Labem, Czech Republic

Abstract

This work is aimed at development of complex tool using semi-mechanistic mathematical model of steam-cracking process for industrial daily balancing utilization. Models of different types of feedstock were compiled together into universal simulation tool. Models for steam cracking of ethane, LPG, and naphtha used real composition, the model for gas-oil and the hydrocracking product used substitutive composition derived by unique procedure. The model was used to simulate industrial steam cracking unit of ten crackers over a several months period. Simulation results were compared to measured product balance and used for evaluate the model performance.

© 2012 Published by Elsevier Ltd. Selection under responsibility of the Congress Scientific Committee (Petr Kluson) Open access under CC BY-NC-ND license.

Keywords: Steam-cracking; mathematical modeling; process control; process monitoring

1. Introduction

Steam-cracking of hydrocarbons is very important industrial process that produces basic chemical commodities: olefins such as ethylene, propylene, butadiene and other important products such as benzene, toluene and xylenes. This process forms a core of chemical industry in many countries. Since the process is energy-intensive and large-scale it is very important for the process to be as efficient as possible in terms of process parameters and/or the feedstocks processed. As it is usual in cases of similar processes,
direct transfer of data obtained in lab-scale to industrial scale is not possible. Therefore, mathematical models of steam-cracking process are frequently used for process optimization. Steam-cracking is a feedstock-flexible process and thus the mathematical model is a very attractive tool for industrial companies. It allows to respond quickly and precisely to actual prices and available quantities of feedstocks, products and energies on the market and its fluctuations. Of course, mechanistic models have special position among models of steam cracking.

Historically, the first models [1-4] were developed usually for one particular feedstock compound like ethane or other light paraffin. Recommended methods and procedures of steam-cracking kinetics research were established and also most of simplifying assumptions were examined in this period, such as the influence of quasi-steady state approach for describing radicals concentration [5] and match of 1D and 2D model of reactor [6]. Later, also models of heavy feedstocks steam cracking [7, 8] were developed as well.

The common drawback of all models given above consists in their dependence on a particular feedstock. In recent years, development continues by systematic efforts to generate radical decomposition model automatically [9-15]. It continues by careful investigations such as checking of possible pathways in mechanism [16-19], pressure dependence of kinetic parameters [18], effect of radial temperature profile to products yield [20], etc. Conclusions of these investigations are very important, e.g. confidence of using quasi-steady state approach. Effect of this presumption to products yields is very small in steam-cracking conditions and becoming to be negligible when it is applied only to heavy species of reactions network (>C5). Simplifying the reactor model to one-dimensional is fully justified in cases of industrial coils. While most developed models were designed only to describe data obtained on laboratory apparatus, typically tailored to one component or simple mixture as feedstock, several models were developed that describe industrial steam-cracking process [14, 21-24].

Our former work included the development of mathematical model of steam-cracking unit aimed specifically at the industrial utilization [25]. The model is flexible enough to simulate steam-cracking of most industrial feedstocks ranging from gases to heavy gasoils and employs the component based coil simulation that enables to accommodate for different coil geometries. The reaction kinetics model is based on published data, basically adjusted according to the results of laboratory [26] and plant-scale [27, 28] experiments.

Our recent effort was aimed at extending the model over whole steam-cracking facility in Litvinov plant (Unipetrol, Czech Republic) to enable this model for routine balancing of ethylene production unit consisting of ten crackers. This service would provide not only previously listed possibilities but also the opportunity to find causes of unexpected outages in production for the industrial partner, but also valuable feedback data for process monitoring, bringing us the possibility of further improving the reliability of the model.

In order to accomplish the task, the model was required to be able to describe behavior of different types of feedstock during steam cracking on different coils. In Litvinov, common types of feedstock such as ethane, C4 (even non-saturated), and gasoline are processed, Also more specific atmospheric gas oil and hydrocracked vacuum residue distillate are also processed in substantial quantities. Model of the last named feedstock had also to be developed.

2. Model description

Reactor model was described in details in previous publication [25] including heat transfer and pressure drop modeling, so only basic information will be summarized in this paper.
2.1. Reactor arrangement

Calculation begins at the point of preheating the feedstock; its temperature and feed rate are required inputs. Following dilution by steam is given by the ratio of flow hydrocarbon feedstock to flow of steam. Mixture enters to the coil which is located in radiant chamber. Coil is described as a series of one-dimensional segments of different shapes (plug flow, pressure drop is considered). Entire coil can be specified segment by segment. Ten crackers located in Litvinov facility were implemented into the model:

- 1x SRT I (Lummus): Non-branched tube reactor usually occupied by the ethane feedstock
- 5x SRT III (Lummus): Two times branched reactor.
- 4x GK 6 (Technip): Tree times branched reactor.

Radiant chamber is described using zonal method. The space of chamber is divided horizontally to isothermal volumetric zones and coil to surface zones. The effect of furnace geometry is captured by an integration process performing Monte Carlo method. Flue gas, the flow of which between zones is balanced, is considered not to be fully transparent medium.

The transfer line exchanger (TLX) is actually system of tube-in-tube exchangers. An adiabatic zone is placed between radiant chamber and TLX.

2.2. Numerical solver

Non-linear equations are solved by the Newton-Raphson method and differential equations system by the Runge-Kutta-Merson method. It is possible because the pseudo-steady state assumption eliminates the system’s STIFF character which would enforce us to use someone of special stiff-resistant methods.

Missing parameters (inlet feedstock pressure and inlet flue gas rate) are iteratively estimated by the Newton method comparing reaction mixture temperature and pressure on the outlet of radiant chamber (computed against entered).

2.3. Kinetics

Description of chemical kinetics was also reported in details [25]. Chemical reactions are considered along one-dimensional system from dilution of feedstock by steam cross radiant chamber and adiabatic zone to TLX (included).

Kinetics of hydrogen transfer is the second order [1] but only several radicals has important role as attackers in this reaction. Moreover, level of these radicals concentration is established very quickly and is stable along length coordinate [5, 15]. If radical activity is constant, hydrogen transfer can be considered to be a pseudo-monomolecular reaction and the value of radical activity can be included to kinetic constant of this reaction. Model recognizes unified frequency factor for all hydrogen transfer reactions. Activating energies are divided for hydrogen transfer on primary, secondary and tertiary carbon.

Decomposition of generated radicals is modeled on the basis of steady-state, so all radicals are transformed in each integration step. The most important beta-scission reactions are modeled using temperature dependent selectivities. Beta-scission is divided to scission of C-H and C-C bonds. C-H scission recognizes primary, secondary and tertiary carbon atoms and C-C bonds scissions are divided according to the count of substituents (substituents of the bond).

Radical isomerizations are also considered, specifically 1-4 and 1-5 position isomerization reactions. All non-fissile radicals such as hydrogen, methyl and allyl are terminated by hydrogen radicals. Radical decomposition model is supplemented by a system of reactions:
Secondary reactions such as Diels-Alder reactions, (de)hydrogenations
Several formal reactions replacing radical additions, isomerizations and scission of light components whose mechanism is very complex and its kinetic parameters are very hardly to obtain.

Each one of feedstocks was characterized by its own set of kinetic parameters. Original models were able to describe behavior of ethane, C4, gasoline [25] and AGO [29], but model of hydrocracate steam-cracking was needed to be created using an approach similar to AGO.

Kinetic parameters of each one of models were initially estimated using data about similar reactions known from literature and using bonds energies or similar characteristic values. The results of such model exhibited systematic deviations from the experimental data. Therefore, it was necessary to optimize the parameters of the model to fit data that were obtained during plant-scale processing experiments using so called “hot-gas sampling” method [30]. This method allowed us to obtain samples of reaction mixture on the outlet of TLE exchanger. These experiments were carried out together with feedstock sampling and careful conditions monitoring. It was possible to recreate experimental conditions on the mathematical model and optimize its parameters using this data. It is necessary to understand that data are obtained in a very costly manner using the hot-gas sampling; it can be utilized for limited number of process experiments, but not for routine monitoring.

2.4. HCVD feedstock model and its optimization

HCVD feedstock is different from light feedstock types. An exact component composition of feedstock is required input of mechanistic model but it can not be obtained in the case of HCVD feedstock. The first step of model building was selection of substitute composition based on real compounds. We have chosen different components having molecular weight in the range of HCVD molecular weight distribution.

Fig. 1. Structure of substitute components utilized for HCVD feedstock characterization
Table 1. Data obtained using hot-gas sampling method utilized for optimization of model parameters

| Experiment | A          | B          | C          | D          | E          | F          | G          | H          |
|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Coil       | SRT III    | SRT III    | SRT III    | SRT III    | SRT III    | SRT III    | SRT III    | SRT III    |
| COT, °C    | 793.0      | 793.2      | 795.0      | 789.8      | 794.5      | 795.1      | 797.6      | 4797.2     |
| XOT, °C    | 545.5      | 541.8      | 526.9      | 520.8      | 535.7      | 520.8      | 609.7      | 587.1      |
| TLE, °C    | 603.6      | 593.9      | 594.4      | 612.5      | 593.2      | 549.1      | 602.8      | 558.5      |
| COP, kPa   | 191.3      | 239.9      | 205.0      | 248.9      | 215.1      | 192.8      | 270.9      | 201.7      |
| Feed, t/h  | 25.4       | 25.7       | 23.5       | 24.5       | 23.8       | 23.7       | 26.2       | 26.7       |
| Dilution   | 0.77       | 0.77       | 0.75       | 0.75       | 0.80       | 0.80       | 0.75       | 0.75       |
| BMCI       | 20.8       | 19.8       | 21.6       | 21.5       | 18.0       | 17.9       | 19.6       | 19.6       |

Index BMCI is the only one routinely measured characteristic of HCVD feedstock in Litvinov facility, so the first attempt of feedstock characterization was built on this information. Recalculation of BMCI to composition compiled from substitute components uses empirical approach because the BMCI itself is empirical. Mass-fractions of substitute components are linear function of BMCI. Calculated composition is then normalized. In order to find the best parameters of this relationship, we found theoretical products yields of pure substantial components by mathematical model that was optimized to the steam-cracking of gasoline. Then we adapted the formula for calculating composition from BMCI, so as to fit the experimental data as well as possible.
After this step, model was prepared for optimization of kinetic parameters. This optimization procedure using modified “simulated annealing” method [31] was carefully described in cases of other types of feedstock [25]. Optimization process continued similarly in the case of HCVD model.
3. Results

Developed model was used for a series of simulations representing the Litvinov steam-cracking unit during the period of 4th April to 23rd December 2011, including total of 134 days of measurement. 45 points were excluded due to days when feedstock composition not being available, days when process was out of steady-state. Data on figure 4 clearly indicates model ability to fit trends of main products yields.

![Fig. 4. Comparison of products flow on the outlet of production unit (mixed from ten crackers) – prediction against data obtained from process balance](image)

Residues in products flow on the outlet of ethylene production unit (between predicted values and values extracted form process balance, fig. 4) are good indicators exploitable for validation of the model.

There are slight systematic deviations between simulation results and obtained real numbers. Good indicator of systematic deviation is average of deviations or its relative form. Indicators created form residues absolute values provide simple information about model accuracy.

Table 2. Residues between measured and predicted main products flow on the outlet of production unit

|                          | Ethylene flow | Propylene flow |
|--------------------------|---------------|----------------|
|                          | Median        | Average        | Median  | Average |
| Residues, t/h            | 0.03          | -0.06          | -0.58   | -0.58   |
| Relative residues, %     | < 0.1         | -0.1           | -2.1    | -2.1    |
| Residues abs. val., t/h  | 0.65          | 0.81           | 1.09    | 1.28    |
| Relative res. abs. val., %| 1.2           | 1.5            | 3.9     | 4.6     |
4. Conclusions

A model usable for processing operation was created. Steam-cracking unit balancing, which is possible only on the level of whole unit, are now possible being analyzed at the level of individual cracker. It allows for more detailed analysis of the process efficiency. Additionally a feedback between industrial process balance and the model exists and there is an opportunity for statistical evaluation of differences between the model and process monitoring needed for further improvement of the model reliability.

Acknowledgements

The publication was supported by the UniCRE project, funded by the EU Structural Funds and the state budget of the Czech Republic.

References

[1] Allara DL, Shaw R. A compilation of kinetic parameters for the thermal degradation of n-alkane molecules. *J Phys Chem Ref Data* 1980;9:523-559.
[2] Sundaram KM, Froment GF. Modeling of thermal cracking kinetics. I. Thermal cracking of ethane, propane and their mixtures. *Chem Eng Sci* 1977;32:601-608.
[3] Ranzi E, Dente M, Pierucci S, Biardi G. Initial product distributions from pyrolysis of normal and branched paraffins. *Ind Eng Chem Fundam* 1983;22:132-139.
[4] Sundaram KM, Froment GF. Modeling of thermal cracking kinetics II. Cracking of iso-butane, of n-butane and of mixtures ethane-propane-n-butane. *Chem Eng Sci* 1977;32:609-617.
[5] Sundaram KM, Froment GF. The accuracy of the pseudo-steady-state approximation for radicals in thermal cracking. *Int J Chem Kinet* 1978;10:1189-1193.
[6] Sundaram KM, Froment GF. Two dimensional model for the simulation of tubular reactors for thermal cracking. *Chem Eng Sci* 1980;35:364-371.
[7] Depeyre D, Flicoteaux C, Arbabzadeh F, Zabaniotou A. Modeling of thermal steam cracking of an atmospheric gas oil. *Ind Eng Chem Res* 1989;28:967-976.
[8] Depeyre D, Flicoteaux C. Modeling of thermal steam cracking of n-hexadecane. *Ind Eng Chem Res* 1991;30:1116-1130.
[9] Di MFP, Lignola PG. KING, a Kinetic Network Generator. *Chem Eng Sci* 1992;47:2713-2718.
[10] Broadbelt LJ, Stark SM, Klein MT. Computer Generated Pyrolysis Modeling: On-the-Fly Generation of Species, Reactions, and Rates. *Ind Eng Chem Res* 1994;33:790-799.
[11] Green WH, Barton PI, Bhattacharjee B, Matheu DM, Schwer DA, Song J, et al. Computer Construction of Detailed Chemical Kinetic Models for Gas-Phase Reactors. *Ind Eng Chem Res* 2001;40:5362-5370.
[12] Matheu DM, Green WH, Jr., Grenda JM. Automated chemical mechanism generation: Including pressure-dependent rates, in, American Chemical Society, 2002, pp. PHYS-181.
[13] Van Geem KM, Reyniers MF, Marin GB. First principles based reaction network for petroleum thermal cracking, in, American Institute of Chemical Engineers, 2004, pp. 560D/1-D/7.
[14] Sabbe MK, Van Geem KM, Reyniers M-F, Marin GB. First principle-based simulation of ethane steam cracking. *AIChE J* 2011;57:482-496.
[15] Van Geem KM, Reyniers M-F, Marin GB, Song J, Green WH, Matheu DM. Automatic reaction network generation using RMG for steam cracking of n-hexane. *AIChE J* 2006;52:718-730.
[16] Matheu D, Grenda JM, Saey S, Green WH, Jr., New, computer-discovered pathways for methane and ethane pyrolysis, in, American Chemical Society, 2003, pp. FUEL-083.
[17] Matheu D, Grenda JM, Saey S, Green WH, Jr. Automated construction of pressure-dependent gas-phase kinetic models: New pathways for old problems, in, American Chemical Society, 2003, pp. IEC-107.
[18] Van Geem KM, Heynderickx GJ, Marin GB. Effect of radial temperature profiles on yields in steam cracking. *AIChE J* 2004;50:173-183.
[21] Dente M, Ranzi E, Goossens AG. Detailed prediction of olefin yields from hydrocarbon pyrolysis through a fundamental simulation model (SPYRO). Comput Chem Eng 1979;3:61-75.

[22] van GMWM, Barendregt S, Grieves J, Moulijn JA, Verheijen PJ. Model-based, thermo-physical optimisation for high olefin yield in steam cracking reactors. Chem Eng Res Des 2010;88:1305-19.

[23] Hayasaka T, Akamatsu T, Fujisawa Y. Development of combined LP model for petroleum refinery and petrochemical industrial complex. Idemitsu Giho 2007;50:113-20.

[24] Schietekat CM, Van Geem KM, Pyl SP, Dijkmans T, Reyniers M-F, Marin GB, Steam cracking of heavy oil fractions revisited, in: American Institute of Chemical Engineers, 2011, pp. schie1/-schie/17.

[25] Belohlav Z, Zamostny P, Herink T. The kinetic model of thermal cracking for olefins production. Chem Eng Process 2003;42:461-73.

[26] Zamostny P, Belohlav Z, Starkbaumova L, Patera J. Experimental study of hydrocarbon structure effects on the composition of its pyrolysis products. J Anal Appl Pyrolysis 2010;87:207-16.

[27] Herink T, Belohlav Z, Zamostny P, Doskocil J. Application of hydrocarbon cracking experiments to ethylene unit control and optimization. Pet Chem 2006;46:237-45.

[28] Herink T, Belohlav Z, Zamostny P, Doskocil J, Lederer J, Svoboda P. Complex research of hydrocarbon pyrolysis in the chempetrol Litvinov plant. Chemické Listy 2005;99:443-6.

[29] Belohlav Z, Zamostny P, Herink T, Eckert E, Vanek T. A novel approach for the prediction of hydrocarbon thermal cracking product yields from the substitute feedstock composition. Chem Eng Technol 2005;28:1166-76.

[30] Herink T, Fulin P, Lederer J, Belohlav Z. Improved hot gas sampler allows for more-precise analysis. Oil Gas J 2001;99:50-3.

[31] Metropolis N, Rosenbluth AW, Rosenbluth MN, Teller AH, Teller E. Equation-of-state calculations by fast computing machines. J Chem Phys 1953;21:1087-92.