

MODELING AND SIMULATION OF STEAM CRACKERS

T. Gál¹ and B. G. Lakatos²

¹Tisza Chemical Works Co. Ltd., Tiszaújváros, Hungary, e-mail: galt@tvk.hu,
Department of Process Engineering, University of Veszprém, Veszprém, Hungary, e-mail: lakatos@fmt.vein.hu

Abstract. Steam cracking of hydrocarbons (pyrolysis) is the main source of principal feedstocks in petrochemical industry. Because of the relatively high price of the so called „traditional” European cracker feeds (mainly naphtha and gas oil), as well as the demand-increment could be realized in last decade for monomers, made it necessary to search for new feedstocks. The economics associated with different feeds and effluents of the crackers are very large and continuously changing, which need a careful choice of feeds and operating conditions. The mathematical models and simulation can help in choosing the feeds and optimize operations. One of the existing furnaces at TVK Co. Ltd. /Tiszai Vegyi Kombinát RT., Hungary/ processes the recycled and hydrogenated C4/C5-cut. The aim of this work was to investigate kinetics and product distribution in cracking of a C4/C5-mixture under conditions representative for industrial scale. The results show a good coincidence with the laboratory analysis.

Key words: hydrocarbons, pyrolysis, C4/C5 – cut, modeling, simulation

Introduction

The main objective of a mathematical model is to accurately simulate the system. Namely, to predict the process behavior both inside and outside the range of experimental data.

Reliable mathematical models for the steam cracking /pyrolysis/ of hydrocarbons are generally accepted as very useful tools for several purposes. Increasing flexibilities of the reactors are claimed both for the effluent distribution and for the feedstock utilization.

Mathematical models and simulation can help in solving these problems and optimize operations. Costly and time-consuming experimental programs can often be minimized or even avoided. Completeness and complexity of the models proposed recently is related to the evolution of computation facilities that permit handling of much larger numerical problems. On basis of these models, new types of cracking reactors /furnaces/, as well as highly developed process control systems were developed in last decade, which make possible a reliable prediction of effluent distribution.

Modeling on Industrial Scale

Mathematical modeling of a process is, in general, based on at least three considerations:

- 1) phenomenological description of the process system, which has to be as accurate and complete as possible
- 2) translation into mathematical terms of the chemical and physical steps
- 3) numerical methods to solve the set of equations and conditions

Because of the large number of chemical species involved, the number and type of reactions and uncertainties of the mech-

anisms, the first two aspects of the modeling activity are critical in establishing the degree of simplifications that can be accepted. To be suitably flexible, an overall model for the simulation of pyrolysis reactors should include the heat-, momentum- and mass-balance differential equations, physicochemical properties, firing-box patterns and sometimes fluid dynamic characterizations. A convenient classification of model types can be based on degree of sophistication. With some arbitrariness, at least three major types can be considered: empirical-, molecular- and mechanistic models.

In our examined case three streams of C4 and C5 cuts are collected, mixed and hydrogenated then re-pyrolysed in the Olefin Unit of TVK. Mixing of purchased n-butane and C5-condensates into the furnace feed is also a practice. In conclusion, the feedstock composition may vary with time significantly, so it is very important to study the operating conditions in order that the process can be controlled successfully. Furthermore, an overall kinetic equation is not sufficient for the purpose since the prediction of product distribution may be carried out merely based on a detailed set of kinetic equations of reactions, yielding the products of interest.

This furnace has been selected for the following reasons:

- the number of hydrocarbons can be found in the feed is relatively small
- the number of species and elementary reactions can relatively easily be identified
- co-cracking of purchased n-butane and/or C5-condensates is a practice
- to examine the possibilities of propane and/or ethane co-cracking

A typical composition of the C4/C5-cut up-and downstream hydrogenation as well as one of cracked gas can be seen in Table 1.

Table 1. A typical composition of C4/C5 – feed and cracked gas – wt%

Component/Stream	Hydrogenation down	Hydrogenation up	Cracked gas
Hydrogen			1.04
CO			0.05
Methane			20.40
Ethane			3.90
Ethylene			35.87
Propane	0.05	0.04	0.50
Propylene	0.68	0.36	20.08
Acetylene			0.59
i-butane	1.77	4.81	0.50
MAPD			0.25
n-butane	17.25	63.43	7.80
Buthenes	42.50	6.95	3.92
C5	19.75	19.95	1.08
Butadienes	14.12		4.39

The elementary reaction schemes have been derived from the observed input and output compositions, radical mechanisms and thermodynamic principles. A number of parameters were taken from the published literature data whilst those remaining were estimated by using a non-linear regression procedure based on the steady-state equations of the model. The form of the model was based on the material- and energy-balances formulated in terms of the plug flow reactor model [1,2]:

$$\frac{\partial c_i(x,t)}{\partial t} = \sum_{k=1}^{N_r} \alpha_{ik} r_k(c,T) - v \frac{\partial c_i(x,t)}{\partial x}, \quad i = 1 \rightarrow N_c, k = 1 \rightarrow N_r \quad (1)$$

$$\left(\sum_{i=1}^{N_c} C_{pi} c_i \right) \frac{\partial T(x,t)}{\partial t} = \sum_{k=1}^{N_r} (-\Delta H_k) r_k(c,T) - v \left(\sum_{i=1}^{N_c} C_{pi} c_i \right) \frac{\partial T(x,t)}{\partial x} + Q(x,t) \quad (2)$$

subject to the following initial

$$c_i(x,0) = c_{i0}(x) \quad i = 1 \rightarrow N_c, \quad T(x,0) = T_0(0) \quad (3)$$

and boundary conditions:

$$c_i(0,t) = c_{iin}(t) \quad i = 1 \rightarrow N_c, \quad T(0,t) = T_{in}(t) \quad (4)$$

(c_i – concentration; r_k – reaction rate; v – velocity; C_p – heat capacity; T – temperature; ΔH_k – reaction heat; Q – heat supply)

A fragment of elementary reaction scheme is presented in Table 2.

Most reactions involve radicals, but some purely molecular reactions play a significant role. It was observed [2] that the exclusion of molecular reactions that occur simultaneously with radical reactions has been responsible for some misleading conclusions of rate parameters, particularly for olefins and diolefins. Decompositions of radicals are performed according to the so-called β -rule, namely, the second C-C bond is broken counted from the end of hydrocarbon chain. [6] In fact, once the values for the frequency factor and the activation energy for the reference reaction have been obtained experimentally and found to be in accordance with the theoretical predictions of thermo-chemical kinetics, analogous reactions can be predicted with little or no experimental investigations. It was stated [4] that the yields of propylene and higher olefins show a maximum at certain conversion values. The supposed reason is that propylene and higher olefins slow down the further reactions because the chain-forwarder radicals react with them by

Table 2. A part of elementary reaction scheme with their kinetic data

Nr.	Reaction	Ao (1/sec)	E (kcal/mol)	Source
1.	$C_2H_6 > 2CH_3^*$	4.0×10^{16}	87.5	2
2.	$C_3H_8 > 2C_2H_5^* + CH_3^*$	2.0×10^{16}	84.5	2
3.	$n-C_4H_{10} > 1-C_3H_7^* + CH_3^*$	1.5×10^{16}	82.1	2
...				
12.	$C_2H_4 + H^* > C_2H_3^* + H_2$	8.0×10^8	4.0	2
...				
101.	$n-C_5H_{12} > C_3H_7^* + C_2H_5^*$	1.1×10^{16}	80	estimated
...				
142.	$2-C_6H_{12} > 2-C_5H_9^* + CH_3^*$	9.0×10^{14}	62	estimated
...				

addition. [5] This phenomenon is also named auto-inhibition. The other reason is that primary olefin products get into different secondary reactions such as decomposition of primary olefins, dehydrogenation and condensation.

The compositions of feeds and cracked gases were measured by laboratory- and process chromatographs. The furnace outlet temperatures were ranged between 835-840 °C, while the dilution steam ratios were between 0.39-0.41 kg steam/kg hydrocarbon. The furnace outlet pressures were of 0.5-0.7 bar, while the pressure drop along the radiant coil was ranged between 0.8-1.1 bar.

The basic parameters of the examined furnace can be seen in Table 3.

Table 3. Operating parameters of the simulated furnace /SOR: start of run; EOR: end of run/

Parameter	SOR	EOR	Unit
Hydrocarbon feed	19400	19400	kg/h
Inlet pressure	3.98	4.02	bar(g)
Dilution steam	7800	7800	kg/h
Inlet temperature	106	106	degC
COT	835	840	degC
Cracked gas temperature after TLE	354	450	degC
BFW quantity	20800	20600	kg/h
Flue gas cross-over temperature	1160	1250	degC
HP steam temperature	487	502	degC

Simulation with ChemCAD – Comparison of Simulated Results with Lab Analysis

During theoretical examinations 224 elementary reactions and 54 species were identified. As the aim of the steady-state and dynamic simulation tests it was to be presented which parameters can the desired optimum yields be reached by, from the feedstocks available. On basis of its sufficiently large thermochemical and kinetic database, the ChemCAD software was selected for the computer-aided simulation. Applicability of the ChemCAD simulator was also checked by re-simulating the pyrolysis of n-butane, a model published by Sundaram and Froment [3]. The result of comparison is shown in Figure 1.

As it can be seen in the figure, the ethylene yields, for example, are practically identical at each conversion for both the

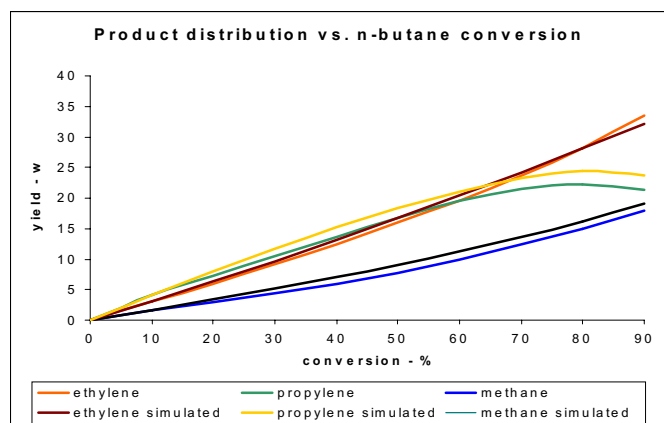


Figure 1. Comparison of published and simulated results for n-butane cracking

published and ChemCAD-simulated models. Though there are minor differences in the yields of other products, the simulator was considered to be suitable for the purpose.

For simulation of the existing pyrolysis furnace, it was divided into zones. A different zone started when there was a modification in cross-sectional area of the reactor. Since the temperatures entering and leaving the radiant section are well known, a temperature profile was to be built up along the radiant coil. Though this profile can also be created by the simulator itself, it was verified by the thermal-balance equations as well. Using the standard kinetics, the published [3] and estimated kinetic parameters, the temperature profile and coil geometry were dedicated as input data for simulation. The results are shown in Fig.2 in comparison with the laboratory analysis.

Although the simulated yields of basic products /ethylene and propylene/ show a good coincidence with the experimental data /cracked gas analysis by the lab/ the sensitivity analysis of the model is still in progress.

Since a large number of kinetic data were to have been estimated /namely, for 67 elementary reactions/, a system of 134 parameters are to be mathematically determined in order that their values can be specified as accurately as possible. Of course, many simplifications are also possible due to the similarities existing between the reactions. On basis of these ideas, the values of those parameters /activation energies and pre-exponential factors, respectively/, which could not be found in published literature, were estimated by a "try-and-error" procedure.

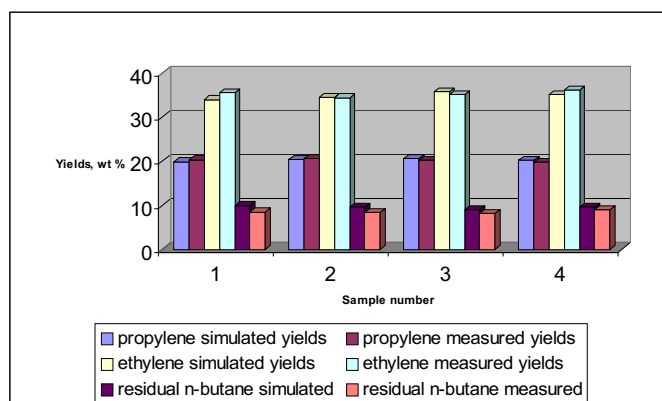


Figure 2. Comparison of simulated and measured yields

Summary

The good match between the experimental and simulated results indicates large opportunities of applying the simulation program in cracking of gaseous feeds and their mixtures. After a longer control period the model will also be applied for online simulation as a tool for parameter optimization. In order that the furnace in question and its feed-stock system can be treated as a whole, building up the model of hydrogenation reactor is also intended.

As far as the further examinations are concerned, the different co-cracking possibilities, opportunities for parameter-optimization, as well as the integration of the model into the existing APC /Advanced Process Control System/ are still to be investigated.

References

- [1] G.F. Froment, K.B. Bischoff: Chemical Reactor Analysis and Design; Wiley & Sons, **1990**.
- [2] M.E. Dente, E.M. Ranzi: Mathematical Modeling of Hydrocarbon Pyrolysis Reactions. Academic Press, **1983**.
- [3] K.M. Sundaram, G.F. Froment, *Ind. Eng. Chem.* **1978**.
- [4] F.O. Rice, O.L. Polly: *Chem. Phys.* 6, 273 **1938**.
- [5] S.B. Zdonik, E.J. Green, L.P. Hallee: *Oil and Gas Journal*, 26,96 **1967**.
- [6] F.O. Rice, K.F. Herzfeld: *J. Am.Chem. Soc.* 74, 324 **1954**.