A RIGOROUS MODEL OF ETHYLENE PYROLYSIS AND ITS APPLICATIONS

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Abstract. *A mathematical model of the cracking of ethane, liquefied petroleum gases, naphthas and alkenic mixtures based on the compilation of a semi-mechanistic model of radical decomposition and a semi-empirical model of formal molecular reactions has been developed. The kinetic parameters of the formal molecular reaction system were adjusted to achieve an agreement between model simulations and a set of large-scale experiments carried out in the Chemopetrol Company. Three case studies, including the operational comparison of SRT III and GK 6 coils, evaluation of different primary naphtha feedstocks cracking, and analysis of recycled C5 fraction with standard feeds co-cracking, were performed utilizing the results of mode simulations.*

Key words: *ethylene pyrolysis; mathematical modeling*

Introduction

A mathematical model of industrial hydrocarbon thermal cracking is an attractive tool for optimal feedstock selecting and mixing, production planning, optimal reactor control, and reactor design. In order to achieve reliable model response to various feedstocks and plant-operation settings, the model should be as much mechanistic as possible. However, several important aspects affect the possible complexity of the cracking furnace modeling. Pyrolysis reactions are reasonably well-understood and most final products are followed with satisfactory reliability. Still, the plant hydrocarbon cracking involves an extensive reaction system with many intermediates and minor species, the concentrations of which are very small and unmeasured. Therefore, all models of pyrolysis reactions are subject to simplifications unless the model is limited to simple feedstocks. Simplified and substitute characterization of pyrolysed hydrocarbon feedstocks is mainly enforced by the difficult analysis of high-boiling hydrocarbons and also by the necessity of reaction components reduction with respect to the rational potential of mathematical models. Therefore, all higher-boiling feeds are partly or fully described by a set of representative pseudo-components [1]. The limited amount of reliable experimental data and theoretical information do not prevent the development of fully phenomenological models of industrial reactors. However, thorough model tuning and verification must make up for the complex of simplifications in the kinetic models.

Model Development

The developed model of the thermal cracking reactor was aimed for practical application. It is intended to perform simulations of real feedstocks pyrolysis in real cracking reactors. The simulations are primarily used for the estimation of pyrolysis product yields of unknown feedstocks, the selection of the most suitable feedstock from a broader offer palette, and the testing of co-pyrolysis of recycled hydrocarbon fractions with primary feedstocks.

The cracking reactor model was compiled from three basic sections – radiant coil (the reactor), adiabatic zone (heat-insulated transfer line), and quench zone (transfer-line exchanger). The radiant coils are designed as one-dimensional stationary plug flow reactors, consisted of three building blocks - straight tubes, bends and junctions and their properties (inner and outer diameters, curvatures, lengths, tube spacing and construction steels). The adiabatic transfer line is described as a straight tube of given inner and outer diameters, length and construction steel. The zonal method was used for radiation chamber modeling. The radiation chamber geometry was simplified by assuming box shape. The space of the chamber is divided horizontally into 7 isothermal volume zones confined by 30 surface zones.

The kinetic model is a compilation of two different approaches – a semi-mechanistic model of radical decomposition based on the simplified theory of radical and pure molecular reactions and a semi-empirical model of formal molecular reactions. The description of radical reactions is based on the long propagation chains assumption (allowing to neglect initiation and termination reactions), immediate decomposition of heavier unstable radicals, and pseudo-stationary concentration of small reactive radicals in the reaction mixture. Other reactions of the propagation phase, mainly radical additions to unsaturated molecules, are modeled by the set of formal molecular reactions. The kinetic model involves rate controlling radical hydrogen abstractions and molecular reactions and fast radical transformations – intra-molecular isomerizations, bond scissions and H-absorptions. The radicals are gradually transformed to the molecular products and lower radicals in each differential segment of the reactor tube. The concentration of the radical or unsaturated molecular products in a link of a radical disintegration chain can be expressed as an analogy of Exodus method for a simulation of discrete Marcov chains. As the second order hydrogen absorption involves the concentration of hydrogen atoms, the pseudo-first order rate constant was introduced for the hydrogen absorption.

The description of pyrolysed feedstocks corresponds to the complexity of pyrolysed hydrocarbon blends. Ethane and liquefied petroleum gases are modeled in detail, because their compositions are simple and easily detectable. Contrariwise, primary naphthas contain over 180 hydrocarbon individuals, most of which are identifiable by the chromatographic analysis. Although the information on the ratio of some geometric isomers (e.g. cis and trans but-2-enes) was obtained from chromatographic analysis, it was discarded for the purpose of modeling and both geometric isomers were treated as a single compound. Additionally, around 80 compounds occurring in lower concentrations were split into 22 groups of compounds likely to behave similarly during pyrolysis. Each group was replaced by one pseudo-compound identical to the most frequent group member. Thus some methylalkanes, methylcycloalkanes, and methylbenzenes comprise the less frequently occurring isomers. Hence, the number of component concentrations used to characterize the feedstock composition was 89.

The model optimization was based on ten large-scale experiments carried out in the Chemopetrol Company, including experiments with ethane, LPG, and primary naphtha cracking and LPG with recycled alkenes co-cracking. The coke layers on inside coil and transfer lines walls were neglected, since all experiments were scheduled at the beginning of reactor operating periods. The other set of forty-two experiments enriched by several co-cracking of primary naphtha with recycled alkenes were utilized for model verification. All ten selected experiments were firstly used for molecular reaction system optimization simultaneously, but the process was tremendously slow and offered very limited possibilities to obtain some intermediate results applicable for the refinement of the reaction network itself. The changes and additions to the reaction system were necessary due to the semi-empirical character of the formal molecular reaction system. Therefore, a sequential approach was employed for the optimization process including rough, refinement and tuning phases with reaction scheme modification rather than the previous all-in-one approach. The verification of the kinetic scheme was performed on the basis of forty-two experiments involving ethane, LPG, primary naphtha cracking and recycled alkenes co-cracking in coils of different geometry [2].

Case Studies Overview

The model was used to solve a set of case studies aimed for the evaluation of different feedstocks processed in Chemopetrol Litvinov in cracking reactors before and after the pyrolysis unit revamping [3].

A. Operational comparison of SRT III and GK 6 coils

The replacement of old cracking reactors Lummus SRT III for new Gradient Kinetics GK 6 (see Figure 1) was an essential part of the Chemopetrol cracking unit revamping carried out in years 1999 – 2001.

This simulation study was performed to illustrate the basic technological parameters of these two reactors. The constant propylene/ethylene ratio was used as the base for comparison. Operation parameters used for the simulation are summarized in the Table I.

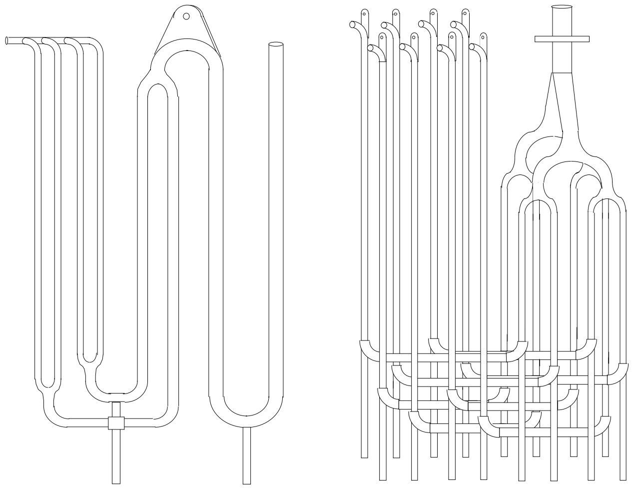

Figure 1. SRT III (left) and GK 6 (right) coils

Table 1. Operational parameters settings for cracking reactors distribution

Coil input temperature, °C	630
Coil output temperature , °C	850 (GK 6), 835 (SRT III)
Steam/oil ratio, $kg{\cdot}kg^{-1}$	0.5
Coil output pressure, kPa	180
Severity (Propylene/Ethylene), $kg{\cdot}kg^{-1}$	0.49
Feed rate, $t{\cdot}hr^{-1}$	26.1 (GK 6), 24.8 (SRT III)
Feedstock	Primary naphtha (700 $kg{\cdot}m^{-3}$)

Figure 2 shows the profiles of the reaction mixture temperature along the reactor and the adiabatic zone. Reactor GK 6 has much steeper temperature profile which makes up for the shorter overall residence time. The temperature maximum is given by the coil output temperature, set for each reactor and corresponds to the used for that reactor in Chemopetrol. Shorter GK 6 coil has substantially lower pressure drop (see Figure 3) than SRT III and therefore it allows lower pressure along the reactor if the coil output pressure is the same for both. It diminishes the effect of undesirable condensation reaction and thus it also slightly contributes to the ethylene yields.

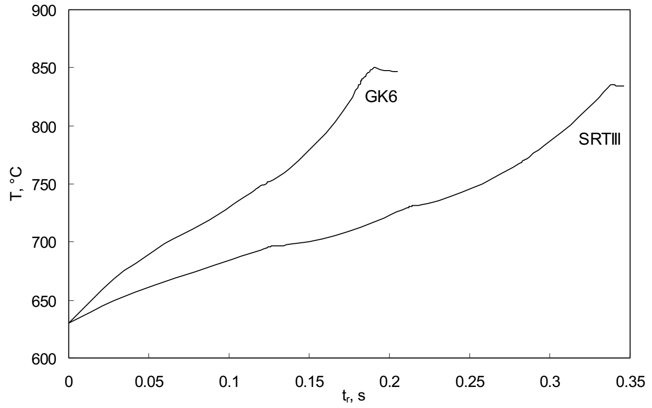

Figure 2. Profile of the reaction mixture temperature T along the GK6 and SRTIII reactors during primary naphtha cracking (t_r = residence time)

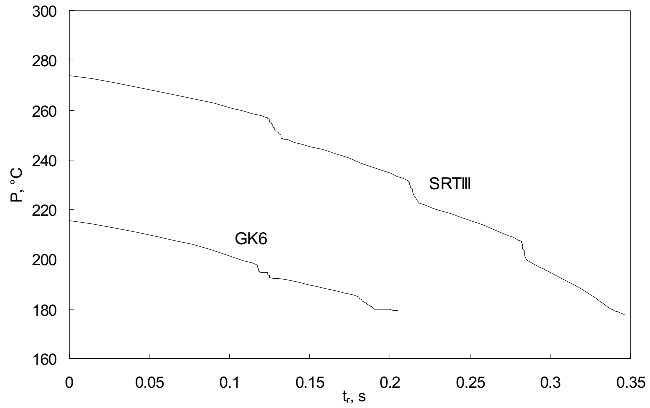

Figure 3. Profile of the reaction mixture pressure P along the GK6 and SRTIII reactors during primary naphtha cracking (t_r = residence time)

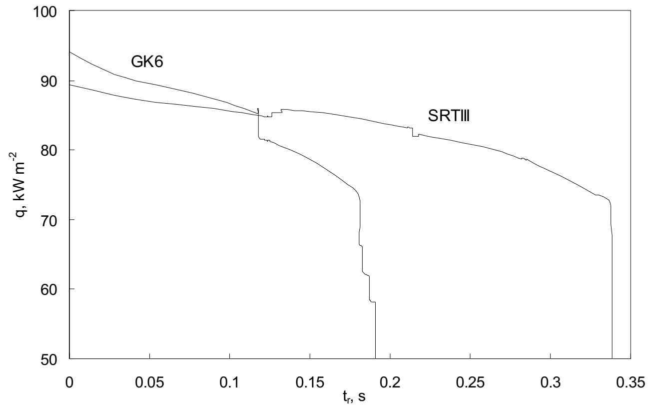

Figure 4. Profile of the heat flux density q trough the reactor wall along the GK6 and SRTIII reactors during primary naphtha cracking (t_r = residence time)

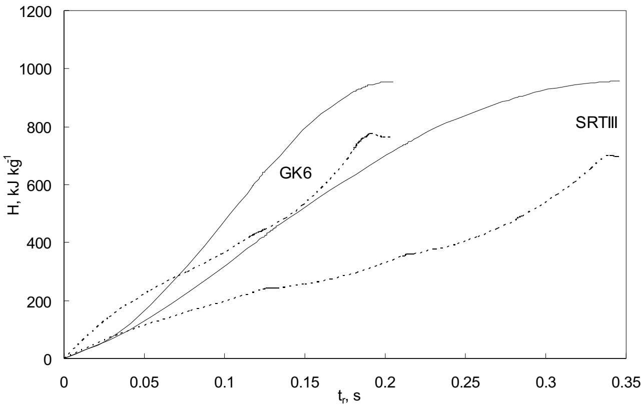

Figure 5. Integral specific heat H consumed for reaction mixture heating (---) and for endothermic reactions (—) along the GK6 and SRTIII reactors during primary naphtha cracking (t_r = residence time)

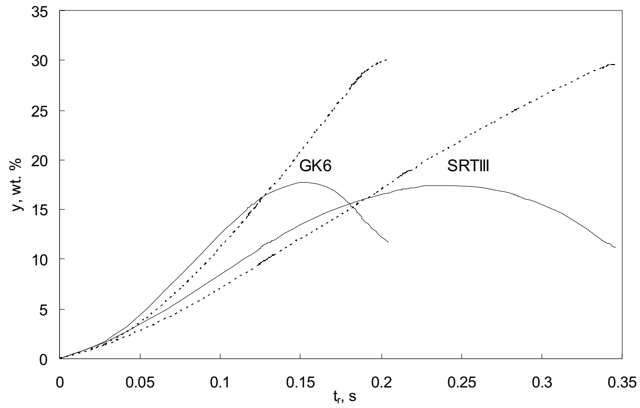

Figure 6. Profiles of ethylene (---) and propylene (—) yields in the reaction mixture along the GK6 and SRTIII reactors during primary naphtha cracking (t_r = residence time)

GK 6 coil achieves higher heat flux density through the reactor wall (see Figure 4) which together with its larger surface/feed rate ratio allows faster heat transport to the reaction mixture. Simulated profiles of integral heat consumption are shown in Figure 5 for both reactors. Since the GK 6 coil has a shorter residence time while the cracking severity is the same for both reactors, the heat consumption for endothermic cracking reactions is higher for that reactor. The heat is consumed preferably by the heating of the reaction mixture at the start of the reactors. After its temperature reach approximately 700 °C, the endothermic cracking reactions start to proceed extensively consuming most of the heat. At the end of the reactor the exothermic condensation reactions compensate the endothermic cracking and therefore again majority of the incoming heat is consumed by heating the reaction mixture.

Figure 6 shows the simulated profiles of concentrations of two main products – ethylene and propylene – along the reactor. Both products concentrations rise from the start of the reactor. While the propylene concentration has a maximum, that of ethylene increases until the end of the coil. This is caused by significant decomposition of propylene to ethylene and methane at high temperatures at the end of the coil. The yield of ethylene (and due to the constant severity propylene as well) is higher by approx. 0.5 wt. % in GK 6 reactor. It is allowed by the higher outlet temperature at the end of that reactor, lower pressure drop, and shorter residence time in that reactor.

B. Cracking of different primary naphtha feedstocks

The most general way of evaluating a naphtha feedstock quality is to check its aromatics content and its ratio of n-/iso-alkanes. In this simulations study, the effect of those two qualities was examined. The primary naphtha used in the previous section was taken as the standard for further computations. Since the naphtha sample was analyzed and its significant components were identified, it was possible to assign each component into one of the four groups – n-alkanes, isoalkanes, cycloalkanes, and aromatics.

Several modified feedstocks were derived from the standard primary naphtha to evaluate the influence of aromatics by increasing or decreasing the aromatics concentrations and conversely changing the concentrations of non-aromatic compounds. Applying this approach, the series of feedstocks with increasing aromatics content and constant relative representation of all other compounds was acquired. The simulated ethylene yields for all modified feedstocks were obtained for identical operation parameters as described in the previous section and are shown in the Figure 7. The yields decrease linearly with increasing aromatics content in the feedstock regardless the reactor type. This behavior corresponds to the fact that lighter aromatics present in primary naphtha do not undergo many changes during the pyrolysis process and act much like inert in the reaction mixture.

The second part of this study used another set of hypothetical feedstock derived again from the standard naphtha feedstock, so as the aromatics and cycloalkanes concentrations were the same and only the ratio of n-/iso alkanes changed. The simulated yields of ethylene are shown in Figure 8. The effect of this feedstock quality is significantly smaller than that of aromatics content. Obviously the feedstocks with higher content of n-alkanes are better in the sense of ethylene yields.

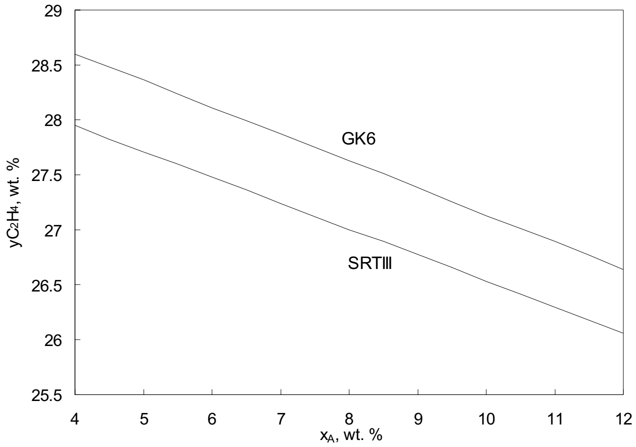

Figure 7. Ethylene yields y_{C2H4} of primary naphthas with varying aromatics content x_A in the GK6 and SRTIII reactors

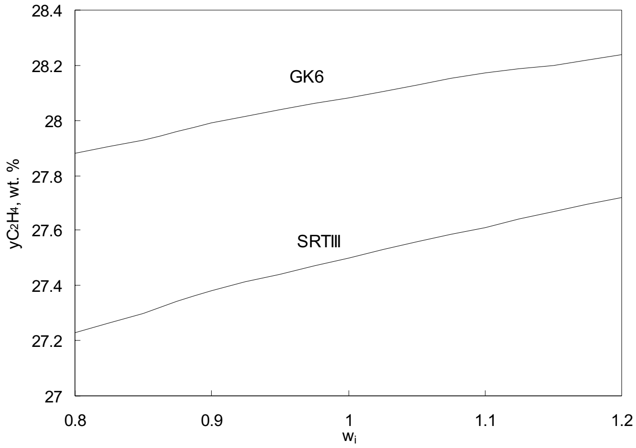

Figure 8. Ethylene yields y_{C2H4} of primary naphthas with varying n-/iso- alkanes ratio w_i in the GK6 and SRTIII reactors

C. Co-cracking of recycled C5 fraction with standard feeds

The last field of the model application is the simulation of co-pyrolysis of minor feedstock with either LPG or primary naphtha. Typical example of such a feedstock is partially hydrogenated C5 fraction - recycled pyrolysis product (see Table 2).

Table 2. Composition of co-pyrolysed C5 fraction

Component	Concentration, wt. %
2-methyl-2-butene	24.0
cyclopentene	18.0
2-pentene	18.0
cyclopentane	17.0
n-pentane	9.0
2-methyl-1-butene	6.0
2-methylbutane	5.5
1-hexene	1.0
rest	0.5

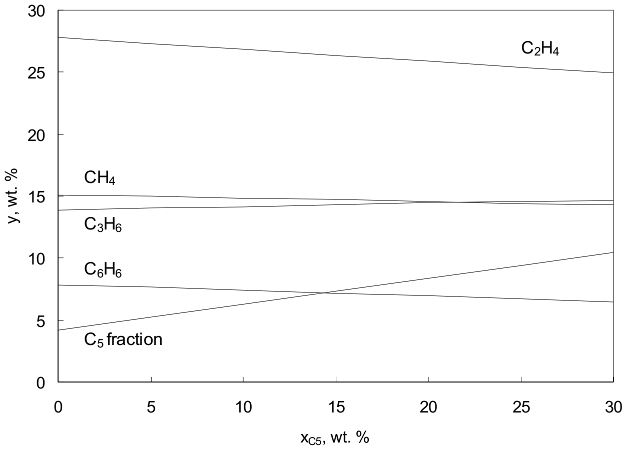

Figure 9. Selected products yields y for primary naphtha and recycled C5 fraction co-pyrolysis in GK6 reactor (x_{C5} – mass fraction of C5 hydrocarbons)

Simulation of C5 fraction co-pyrolysis with typical primary naphtha and LPG was performed for constant operating parameters for C5 fraction taking up to 30 wt. % of total feed rate. The simulated yields of most important products for pyrolysis carried out under constant operating parameters (F = 25

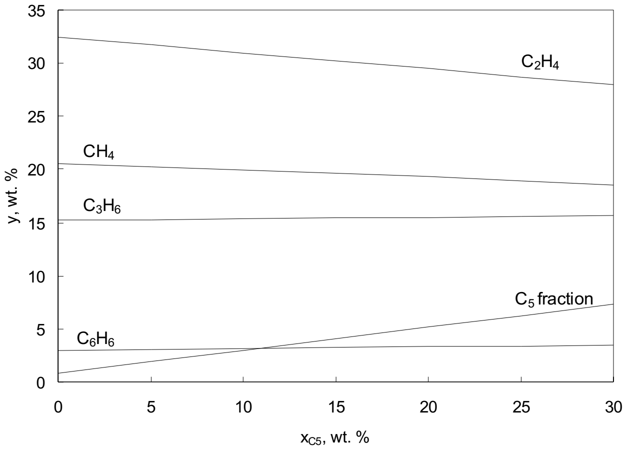

Figure 10. Selected products yields y for LPG and recycled C5 fraction co-pyrolysis in GK6 reactor (x_{C5} – mass fraction of C5 hydrocarbons)

t·hr^{-1}, T_{out} = 845 °C) are shown on figures 9 and 10. The most significant trends are the decreasing yield of ethylene and increasing yield of C5-products.

All trends are approximately linear which means that the yields of the co-pyrolysis are not much different from the yields of separate pyrolysis of both feedstocks weighted average. It seems that the C5 co-pyrolysis has no potential to bring any good in the sense of higher yields compared to the separate pyrolysis, although there is still advantage of avoiding excessive coking and other associated technological problems. However, closer inspection reveals that the severity (propylene/ethylene) ratio drops significantly as the C5 content in feedstock rises. Therefore another set of simulations was performed not using constant operating parameters but constant severity of the process.

Constant severity 0.45 was achieved by changing the coil outlet temperature. Results of the simulations are provided in Figure 11. It is apparent from the figure that the addition of C5 fraction into the feedstock has an augmenting effect, provided the operating parameters are adapted to maintain constant severity of the process. The profile of the ethylene yield in Figure 11 is concave and thus the co-pyrolysis of up to 25 wt. % of C5 fraction with primary naphtha can bring better ethylene yield than the weighted average of separate pyrolysis yields. Similar study of co-pyrolysis of C5 fraction with LPG was also attempted, but achieving desired severity for any C5 fraction addition larger than 10 % was impossible within the valid range of operating parameters.

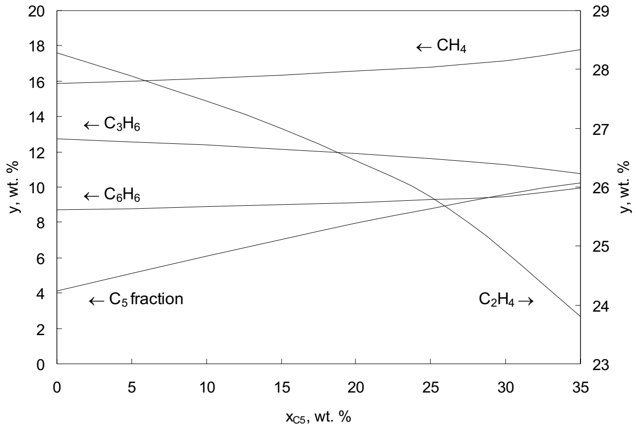

Figure 11. Selected products yields y for primary naphtha and recycled C5 fraction co-pyrolysis in GK6 reactor (x_{C5} – mass fraction of C5 hydrocarbons)

Conclusions

The developed semi-empirical model was successfully used to compare different radiant coils, feedstocks, and evaluate co-pyrolysis possibilities. It was found that the aromatics content in naphtha feedstocks is the main factor of influence on the ethylene yields. Although it was shown that the reactor type has a significant impact on the product yields from a particular feedstock, the reactor type was not affecting the yields difference between various feedstocks. The possible benefits of hydrogenated recycled C5 fraction with LPG and primary naphthas were evaluated. It was found that C5 fraction addition up to 15 – 25 wt. % to the primary naphtha pyrolysis is probably the optimal way of its pyrolysis treatment.

Acknowledgements

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References

[1] Dente, M., Pierucci, S., Ranzi, F., New improvements in modeling kinetic schemes for hydrocarbon pyrolysis reactors, Chem. Eng. Sci. 47, 2629-2634 (1992).

[2] Bělohlav, Z., Zámostný, P., Herink, T., The kinetic model of thermal cracking for olefins production, Chem. Eng. Proc., 42, 461-473 (2003).

[3] Doskocil, J., Belohlav, Z., Herink, T., Zamostny, P., Intenzifikace pyrolyznich peci v Chemopetrolu Litvinov, Chem. Listy 97, 1176-1180 (2003).