Semi-mechanistic Model Applied to the Search for Economically Optimal Conditions and Blending of Gasoline Feedstock for Steam-cracking Process

Adam Karaba[1,a], Petr Zámostný[2,a], Tomáš Herink[3] and Vendula Kelbichova[3]

[1]*Unipetrol Centre of Research and Education (UniCRE), Areal Chempark, 436 70 Litvinov, Czech Republic*
[2]*University of Chemistry and Technology Prague, Department of Organic Technology, Technicka 5, 166 28 Prague 6 - Dejvice, Czech Republic*
[3]*Unipetrol RPA, Záluží 1, 436 70 Litvínov, Czech Republic*

Abstract. Steam-cracking is energetically intensive large-scaled process which transforms a wide range of hydrocarbons feedstock to petrochemical products. The dependence of products yields on feedstock composition and reaction conditions has been successfully described by mathematical models which are very useful tools for the optimization of cracker operation. Remaining problem is to formulate objective function for such an optimization. Quantitative criterion based on the process economy is proposed in this paper. Previously developed and verified industrial steam-cracking semi-mechanistic model is utilized as supporting tool for economic evaluation of selected gasoline feedstock. Economic criterion is established as the difference between value of products obtained by cracking of studied feedstock under given conditions and the value of products obtained by cracking of reference feedstock under reference conditions. As an example of method utilization, optimal reaction conditions were searched for each of selected feedstock. Potential benefit of individual cracking and cracking of grouped feedstocks in the contrast to cracking under the middle of optimums is evaluated and also compared to cracking under usual conditions.

1 Scope and Introduction

Steam-cracking is an important industrial process which transforms a wide range of hydrocarbons feedstock to valued petrochemical commodities, olefins and aromatics. Usual types of feedstock include ethane, liquefied petroleum gas and gasoline non-aromatic fractions. Product stream is a wide mixture with major content of light olefins (ethylene, propylene and butadiene), light aromatics (benzene, toluene, xylenes), certain portion of heavy hydrocarbons and many other side-products including hydrogen. The products distribution depends on the feedstock composition and on the cracking conditions as well. Since the process is large-scaled, there is no easy way for direct data transfer from lab-scale to process-scale, therefore mathematical models of cracking are very useful tools for cracking unit operation, control and optimization.

There are numerous papers aimed at modelling of steam-cracking, usually focused to the description of pure substances behaviour [1-3] or the behaviour of simple mixtures. There are also other groups of researches [4-6], mostly focused to experimental investigation of cracking kinetics in lab-scale intended to create mechanistic model. But mechanistic models of industrial steam-cracking of complex mixtures are much less frequent than models developed for lab-scale pyrolysis because the kinetic model is only one part of such a modelling tool. Complicated coil geometry, mixture fluid dynamics including pressure-drop, modelling of the heat transfer in radiant chamber and transfer line exchanger together with mathematical complications with differential-algebraic system and complexity of industrial feedstock makes the creation of end-point-application very extensive and tedious. Therefore, many industrial models are entirely or partially empirical [7-10].

One of the most intended research group, Dente et. al. [11, 12] used mechanistic principles to create a detailed model of steam-cracking using minimum of simplifying assumptions. Their work continued from a simple ethane cracking model and propane-butane mixtures to gasoline fraction cracking. By including more modelling tools (such as coke-formation description, etc.) they created SPYRO® model which is industrially usable.

Another group of researches [13] published their ethane cracking model which is based on detailed and fully mechanistic description of the cracking kinetics using theoretical tools for kinetic parameters estimation.

There are also several studies interested in cracking condition optimization, usually focused to extend the operational period of cracking coil by minimizing of the coke-formation rate [14, 15].

However, there are only several published studies using a mechanistic cracking model for industrial

[a] Corresponding author: adam.karaba@vscht.cz; petr.zamostny@vscht.cz

application. This study is aimed at the application of previously developed model PYROL to the optimization of cracking unit operation with gasoline feedstock and with respect to market values of cracking products.

2 Model Brief Description

Model PYROL development documentation and technical details including implementation and model parameters tuning has been reported in sufficient details in our previous papers [16-18]. This study is aimed at application only, therefore we offer brief description of the model in this paragraph. The model is based on the combination of semi-mechanistic approach to the description of heavy components decomposition and the semi-empirical model of light components behaviour. Primary reactions are described by radical model considering the steady-state of active radicals and thus pseudo-monomolecular hydrogen abstraction is assumed. Secondary reactions, especially mutual reactions of light species (H_2-C_4), are described by enhanced version of well-established system of formal molecular reactions firstly introduced by Van Damme et. al. [19] as it is also documented in our previous papers.

Reactor is modelled as a plug-flow reactor considering the pressure-drop and it is divided to three parts: cracking coil placed in radiant chamber, adiabatic zone and transfer line exchanger. For the heat transfer modelling, the coil is modelled by a system of surface zones. The radiant chamber is considered to be a system of volumetric zones modelling the flow of flue gas.

Table 1. Model prediction accuracy indicators (average of products composition deviations and average absolute values of ones) for the cracking of gasoline [20].

	Experiment	Balance
N	29	85
COT, °C	812-852	795-845
Component	AVG(Δw_i), wt. % AVG($\lvert\Delta w_i\rvert$), wt. %	
Hydrogen	-0.31 0.31	-
Methane	0.09 0.45	-
Ethane	0.69 0.69	-
Ethylene	0.53 0.64	-0.04 0.43
Propylene	-0.31 0.52	-0.06 0.60
C4	-0.45 0.81	-
C5	0.07 0.24	-
Benzene	-0.29 0.51	-
C6-C9	-4,57 4,57	-
Oil	1,52 1,52	-

The input of the model is formed by feedstock composition (per component basis) and operational parameters of cracking furnace. Output is the product stream composition, presumed fuel gas consumption and several other parameters.

Model PYROL has been tested in details in our recent paper where it was verified as balance tool [20]. From all reported data, determined deviation in the model prediction is relevant for current work. Table 1 demonstrates determined deviations between model predictions and experimental data (obtained by direct hot gas sampling, for method details see [21]) for the gasoline feedstock and also the comparison to process mass balance results but for all possible types of feedstock together.

3 Economic Criterion: Cracking Value

Cracking products distribution depends on the feedstock composition and reaction conditions. There are many theoretical and experimental studies published that are aimed at searching of ethylene (or other product) maximum yield for some selected feedstock. General rules, about trends in products yields are common knowledge. In this study, we propose relatively simple method for economic evaluation instead technical one.

From a large set of data, provided by our industrial partner, Unipetrol RPA, a very average gasoline, typical cracking feedstock, was chosen as a referential feedstock. A set of conditions typical for gasoline processing on GK6 reactor was chosen as referential. This feedstock provides a typical products distribution under these conditions and the distribution can be priced according to current prices. We propose this cost relativized on a tonne of feedstock as a reference zero point.

Value of any studied feedstock *A* with composition $\mathbf{w_A}$, cracked under a set of cracking conditions **p**, can be evaluated according to current prices of products **P** using products flow $\mathbf{F} = \mathbf{F}(\mathbf{p},\mathbf{w_A})$ predicted by simulation. This value in specific form (relativized to the feedstock mass) is referred to the specific value of products obtained by processing of referential feedstock (composition $\mathbf{w°}$) under referential conditions $\mathbf{p°}$.

$$CV_A\,(\mathbf{p},\mathbf{w_A}) = \mathbf{F}(\mathbf{p},\mathbf{w_A})\cdot\mathbf{P}/\mathrm{FR} - \mathbf{F}(\mathbf{p°},\mathbf{w°})\cdot\mathbf{P}/\mathrm{FR°} \quad (1)$$

It is interesting information for industrial producers about the relative profit/loss received from a tonne of studied feedstock cracked under selected conditions **p** in comparison to typical feedstock processed under typical conditions $\mathbf{p°}$, but this evaluation is valid only for current prices of products **P**.

Moreover, the cracking value is significantly depended on the reaction conditions and the construction parameters of reactor coil. Therefore, conditions can be optimized for the maximum of cracking value for given feedstock and given reactor coil but the planner must realize fact, this criterion does not take the heating cost into account. From all operational parameters the coil outlet temperature (COT) has the most significant impact to the products yield. Other parameters, such as feedstock rate (FR), temperature on the outlet of transfer line exchanger (TLXT), are usually determined by facility capacity or had been determined empirically and cannot

be easily changed. Dilution of feedstock by steam (SO) is typical for the type of feedstock and the pressure on the outlet of coil (COP) is depended on current state of coil and feedstock rate.

4 Data Needed for Evaluation

In this paragraph, a data needed for evaluation will be shown except product prices because we are not allowed to public wholesale trade prices. Those ones, which were considered for evaluation, were valid for the end of May 2012.

From all historically collected gasoline composition processed or considered to be processed by Unipetrol RPA, referential gasoline feedstock was chosen (see Table 2) and also reaction conditions, typical for the processing of such a feedstock.

Table 2. Reference gasoline feedstock simple characterization and reference conditions on GK6 and SRT III reactor.

Components	Content	Parameter	GK6	SRT III
Paraffins, wt. %	26.9	COT, °C	840.0	833.0
Isoparaffins, wt. %	34.0	COP, kPa	200	198.0
Olefins, wt. %	0.6	FR, kg/h	27.9	26.1
Naphthenes, wt. %	29.2	SO, kg/kg	0.5	0.5
Aromatics, wt. %	9.3	XOT, °C	584.5	600.0
Density, $kg \cdot m^{-3}$	812.0	TLXT, °C	512.7	583.0

Basic characteristics of currently investigated gasoline feedstock are provided in the Table 3. For the mechanistic model, a detailed (per component) composition is required which includes more than 100 individual components. It is not provided for its vastness. For the completeness, a source of each gasoline fraction is provided: A = Light gasoline from the gasoline redestillation, B = Light gasoline from primary distillation, C = Middle fraction from gasoline redestillation, D = Light gasoline separated from hydrocracked vacuum distillates, E = Heavy gasoline from primary distillation, F = Gasoline fraction from hydrocracked products (sharper hydrocracking conditions), G = Heavy gasoline from hydrocracked vacuum distillates, H = Gasoline isolated from the hydo-treating of the atmospheric gas oil and kerosene.

Table 3. Feedstocks PIONA (wt. %) and density ($g \cdot l^{-1}$).

Item	P	I	O	N	A	ρ
A	46,1	37,8	0,2	14,5	1,4	666,2
B	43,4	34,9	0,5	18,3	2,9	686,2
C	30,8	35,0	0,6	30,2	3,5	705,1
D	21,2	44,2	0,4	28,2	6,0	692,5
E	27,0	33,6	1,6	27,8	10,0	738,0
F	11,7	37,6	1,7	40,2	8,8	783,2
G	9,3	34,4	2,2	40,5	13,6	768,5
H	18,0	29,7	1,6	30,4	20,3	772,2

The most difficult on this approach is, to determine total prices of individual products, because many cracking products are often transformed to another one in the separation part of cracking unit (selective hydrogenation of acetylene, dealkylation of toluene, etc.).

5 Results and Discussion

In this paragraph, a discussion around the results of CV calculation for selected feedstock and its dependence on reaction conditions will be provided.

5.1 Reaction condition optimization

Current target is to optimize cracking conditions for feedstock which were selected by our industrial partner (see Table 3). Analysis of CV depending on coil outlet temperature with other parameters remaining constant for the reference feedstock is shown on the Figure 1.

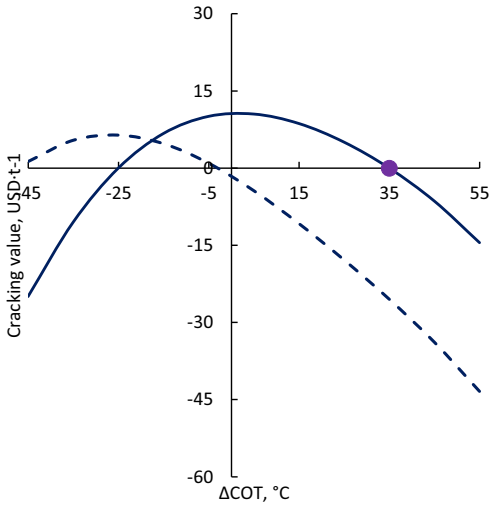

Figure 1. Dependence of cracking value for reference gasoline feedstock (see Table 2) under varying coil outlet temperature (COT) from optimal one, remaining parameters are constant (Table 2) for reactors GK6 (solid ─) and SRT III (dashed - - -). The reference conditions are depicted as point (●).

Now, it is obvious, GK6 reactor allows a little wider range of conditions that are profitable than the SRT III reactor for this reference feedstock. The maximum CV is placed at lower temperature for SRT III than for the GK6 but the maximal CV for GK6 is generally higher than the one for SRT III. It is also interesting, reference conditions (and mean of real conditions in the facility as well) are a little sharper than the optimal ones, especially for SRT III reactor, where mean of COT per long period was determined to ΔCOT = +28 °C gives CV = -20.1 $USD \cdot t^{-1}$.

The existence of optimum is logical, because under growing temperature, the most desired product yield (ethylene) grows. But the yields of other important products, such as propylene and C4 hydrocarbons, pass a maximum and fall down. Yield of other desired products also grows (e.g. benzene) but other products (not such desired) grow as well. The yields of important products obtained by cracking of reference gasoline on the GK6 reactor in dependence on coil outlet temperature is shown on the Figure 2.

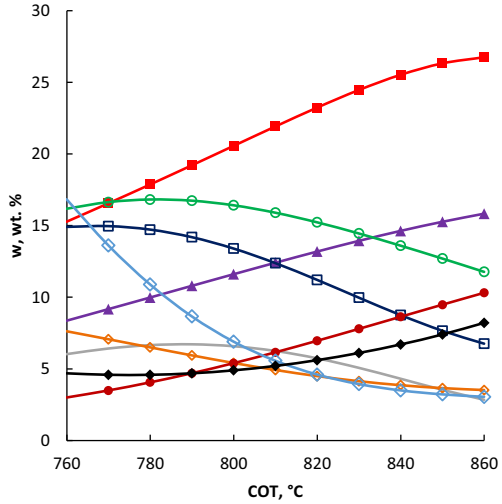

Figure 2. Dependence of products stream composition (simulated) obtained by cracking of reference gasoline feedstock (see Table 2) under varying coil outlet temperature (COT), other parameters remains constant (Table 2), reactor GK6: ethylene (red ■), propylene (green ○), methane (purple ▲), C_4 fraction (navy blue □), sum C_6-C_9 (sky blue ◊), benzene (brown ●), oil (black ♦), ethane (brown line).

The complexity of this dependence is the main reason why cracking value is a very good indicator for evaluation directly in the money per tonne of feedstock.

Similar analysis has been done for selected gasoline feedstock (Table 3) to find the optimal COT for both reactors, GK6 and SRT III. All these data are depicted in the Figure 3.

Figure 4 demonstrates expected difference of cracking value for selected gasoline feedstock separately cracked on individual reactors under the reference (usual) and optimized conditions. These optimized conditions were selected as a mean on previously searched optimal COT for individual feedstock (see Figure 3). As it is obvious, there is an increase of CV between reference (usual) and these optimal conditions for the same set of feedstock.

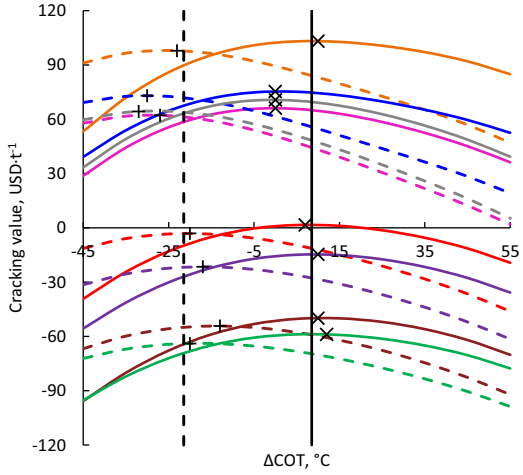

Figure 3. Dependence of cracking value on COT (coil outlet temperature), other parameters remain constant (see Table 2) on both studied reactors (GK6 solid, SRT III dashed) for selected gasoline feedstock: A (orange), B (blue), C (gray), D (pink), E (red), F(purple), G (brown) and H (light green). Optimal temperatures for GK6 (x) and SRT III (+) used for grouping for GK6 (solid black line) and for SRT III (dashed black line).

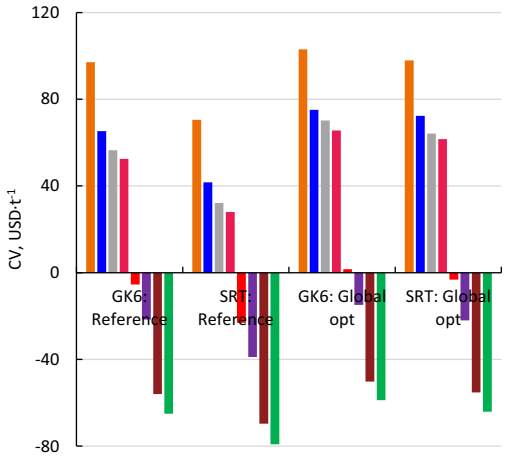

Figure 4. Cracking value of selected gasolines on reactors GK6 and SRT III under reference (usual) and optimal (global optimum for all feedstock) conditions: A (orange), B (blue), C (gray), D (pink), E (red), F(purple), G (brown) and H (light green).

5.2 Optimal feedstock blending

In this paragraph, another type of analysis is provided. If there is a possibility to blend all these gasoline feedstock to two separate tanks in the currently studied facility, it is possible to establish an optimal blending schema to maximize CV. Those two mixtures would be processed separately under conditions specific for resulting mixtures which could provide higher benefit than blending all feedstock together a cracking them at "common optimum" of conditions.

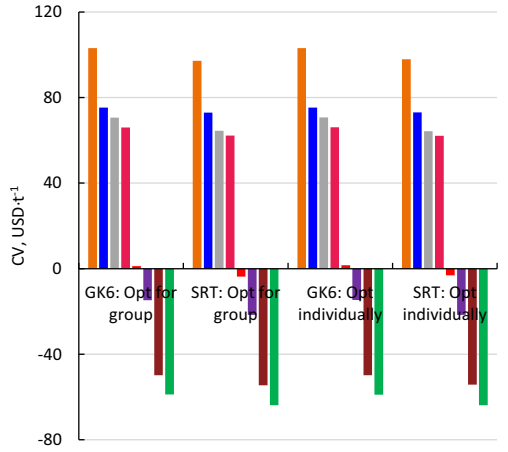

Figure 5. Cracking value of selected gasolines on reactors GK6 and SRT III under conditions optimized for groups and conditions optimized individually: A (orange), B (blue), C (gray), D (pink), E (red), F(purple), G (brown) and H (light green).

As it is shown on the Figure 3, optimal cracking conditions for individual feedstock can be grouped to two groups. These groups are divided by the vertical line (solid for GK6, dashed for SRT III). In this study, grouping of feedstock by the optimal COT on the GK6 reactor is demonstrated. On the Figure 5, cracking value of selected feedstock expected on individual reactors is shown for the case of conditions when these feedstock

were grouped by the optimal COT for GK6 rector. COT optimal for group was chosen as arithmetic average of individual optimums. For comparison, cracking values expected under individually optimized conditions for each feedstock on both reactors is shown.

Interesting point is, there is very little potential difference between cracking value obtained by grouped feedstock optimization and individually optimized mode of cracking for each one of feedstock. But it is necessary to remind, there are also another requirement which has to be satisfied in the real facility, such as capacity of cracking coils and non-equal flows of individual feedstocks. Then the optimal blending schema must be evaluated with respect to satisfy optimal capacity of cracking coil and the assignment of individual feedstock to groups can be conditioned right by the satisfying the capacity which has stronger economic impact then optimal products yields (and CV).

As the last comparison, cracking value obtained by processing of all selected feedstock (with assumption of equal flow of these feedstocks) for individual cracking reactors (GK6 and SRT III) is shown on the Figure 6 for individual modes: the individually optimized conditions for each one of feedstocks, those conditions optimized for grouped feedstocks, only one "commonly optimal" conditions as global optimum and reference (usual) conditions.

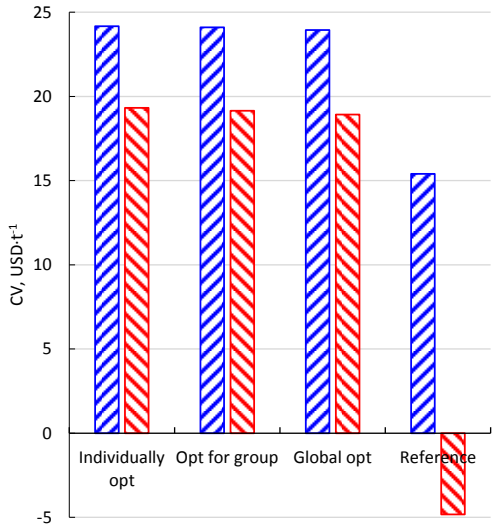

Figure 6. Cracking value expected from the cracking of all feedstocks (with assumption of equal flows) on reactors GK6 (blue, incr. hatched) and SRT III (red, decr. hatched) under individually optimized conditions, conditions optimized for groups, global optimum (for all feedstocks) and reference conditions.

6 Conclusions

An economic criterion CV (cracking value) was proposed in this paper. It is based on the evaluation of expected products yields (determined by previously verified semi-mechanistic model of steam cracking). Total price of products obtained by cracking of given feedstock under given reaction conditions relativized on the feedstock mass is referred (decreased by) the total prise of products obtained by the cracking of reference feedstock under reference conditions.

Using this method, different steam-cracking feedstock can be compared with respect to economic value of obtained products distribution. Optimal cracking conditions can be also determined using CV but these evaluations are valid only for given prices of products and therefore are not constant in time.

Optimal cracking conditions for several selected gasoline feedstocks were searched in this paper. A search for optimal blending scheme was also demonstrated using this criterion. Evaluation of selected 8 available feedstock showed, conditions usual for the processing of gasoline in our industrial partner facility are not the most optimal but a little sharper.

Analysis also reveal, there is a little potential benefit in the possibility to blend selected feedstocks into two separate streams and process them under reaction conditions optimal for resulting mixtures (in comparison with all-over blending). The benefit of individually optimized conditions for each feedstock is negligible.

Acknowledgement

This publication is a result of research project solved in a frame of UniCRE centre whose infrastructure was supported by European Regional Development Fund and the state budget of the Czech Republic. The publication was supported by institutional funds (Ministry of Industry and Trade of the Czech Republic).

References

[1] Van Geem K.M., Reyniers M.-F., Marin G.B., Song J., Green W.H., Matheu D.M.: *AIChE J.*, *52*, 718 (2006).
[2] Xu C., Al S.A.S., Wang C., Carstensen H.-H., Dean A.M.: *J. Phys. Chem. A*, *115*, 10470 (2011).
[3] Herbinet O., Marquaire P.M., Battin-Leclerc F., Fournet R.: *J. Anal. Appl. Pyrol.*, *78*, 419 (2007).
[4] Sabbe M.K., Van G.K.M., Reyniers M.-F., Marin G.B.: *AIChE J.*, *57*, 482 (2011).
[5] Bounaceur R., Burkle-Vitzthum V., Marquaire P.-M., Fusetti L.: *J. Anal. Appl. Pyrolysis*, *103*, 240 (2013).
[6] Raman S., Carstensen H.-H.: *Int. J. Chem. Kinet.*, *44*, 327 (2012).
[7] Villora Cano G., Bodalo Santoyo A., Lopez Cabanes A., Gomez Carrasco J.L.: *An. Quim., Ser. A*, *82*, 137 (1986).
[8] Nabavi R., Niaei A., Salari D., Towfighi J.: *J. Anal. Appl. Pyrol.*, *80*, 175 (2007).
[9] Abghari S.Z., Sadi M.: *J. Taiwan Inst. Chem. Eng.*, *44*, 365 (2013).
[10] Sedighi M., Keyvanloo K., Towfighi J.: *Iran. J. Chem. Chem. Eng. Vol*, *29*, (2010).
[11] Dente M., Ranzi E., Goossens A.G.: *Comput. Chem. Eng.*, *3*, 61 (1979).
[12] van Goethem M.W., Barendregt S., Grievink J., Verheijen P.J., Dente M., Ranzi E.: *Chem. Eng. Res. Des.*, *91*, 1106 (2013).

[13] Ranjan P., Kannan P., Al S.A., Srinivasakannan C.: *Chem. Eng. Technol.*, *35*, 1093 (2012).
[14] Edwin E.H., Balchen J.G.: *Chem. Eng. Sci.*, *56*, 989 (2001).
[15] Barazandeh K., Dehghani O., Hamidi M., Aryafard E., Rahimpour M.R.: *Chem. Eng. Res. Des.*, *94*, 307 (2015).
[16] Belohlav Z., Zamostny P., Herink T.: *Chem. Eng. Process.*, *42*, 461 (2003).
[17] Doskocil J., Belohlav Z., Herink T., Zamostny P.: *Chem. Listy*, *97*, 1176 (2003).
[18] Zamostny P., Belohlav Z.: *Pet. Coal*, *45*, 142 (2003).
[19] Van Damme P.S., Narayanan S., Froment G.F.: *AIChE J.*, *21*, 1065 (1975).
[20] Karaba A., Zamostny P., Belohlav Z., Lederer J., Herink T.: *Chem. Eng. Technol.*, *38*, 609 (2015).
[21] Herink T., Fulin P., Lederer J., Belohlav Z.: *Oil Gas J.*, *99*, 50 (2001).