

4-LUMP Kinetic Model for Hydrotreated Gas Oil Catalytic Cracking

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This study has monitored the influence of one of the hydrodesulphurisation process parameters H_2/CH amount ratio on the properties of three catalytic cracking products (gas, petrol, light cyclic oil, and heavy cyclic oil).

The microactivity test (MAT) was applied to all kinetic measurements. A 4-lump, non-isothermal, and non-stationary kinetic model for the fixed, plug-flow MAT reactor was developed to model catalytic cracking of hydrotreated gas oil. Kinetic coefficients were estimated by the Nelder Mead method. The product yields, predicted by the model, showed good conformity with experimental data.

Key words:

Microactivity test, gas oil catalytic cracking, lump kinetic model

Introduction

The fluid catalytic cracking process (FCC) is one of the most important refinery unit operations. Its design and operation are primarily aimed at the production of petrol and diesel from vacuum gas oil, atmospheric gas oils, and hydrocracker bottoms. The catalytic cracking products, primarily the FCC petrol and light cyclic oil, represent the main sources of sulphur in petrol and diesel fuels.^{1–3}

Even more rigorous requirements for the quality of motor fuels are additionally directed towards the reduction of sulphur, aromatic, and olefine content.^{4,5}

The hydrotreatment of the FCC feeds is considered to be the most efficient method of sulphur, nitrogen, and aromatic removal from, both, cracking products and flue gases. The advantage of this technology lies in the fact that conversion and petrol yield increase, while sulphur and aromatic contents are reduced. Increased conversion in the FCC process leads to a higher refinery profit, while at the same time it reduces the yields of coke, light cyclic oil, and heavy cyclic oil. Removal of metals in hydrotreatment reduces hydrogen production and increases the catalyst activity.^{6–10}

The hydrodesulphurisation process has led to the increase in the share of paraffinic hydrocarbons from naphthenic hydrocarbons in the feed, considerably enhance its tendency to cracking. The basic process quantities are reactor temperature, pressure, flow rate, and hydrogen/feed amount ratio (H_2/CH). The H_2/CH ratio is a very complex parameter in hydrodesulphurisation process and it has the key

impact on the deactivation of catalysts. The H_2/CH ratio at other constant quantities (temperature, pressure and flow rate) affects the evaporation of hydrocarbon blend, partial hydrogen pressure, and time of stay.^{11,12}

Many complex reactions occur during the FCC process and the product consists of a mixture of many compounds. The catalytic cracking kinetics is difficult to study because of a mutual interaction of feed, process quantities, and heat factor. Predicting and improving the FCC process require understanding and modelling chemical kinetics of the main reactions.

The complex mixtures were described by many researchers by means of lumping a large number of chemical compounds into smaller groups of pseudo-components. *Weekman*¹³ developed the first 3-lump model. *Lee et al.*¹⁴ and *Yen et al.*¹⁵ gave a 4-lump model. *John and Wojciechoeski*¹⁶ designed a detailed model of the cracking oil. *Frences and Corrella*¹⁷ and *Ancheyta-Juarez et al.*¹⁸ gave a 5-lump model. *Delattre et al.*¹⁹ and *Takatsuka et al.*²⁰ developed a 6-lump model of catalytic cracking. Some authors presented very complex models, such as a 10-lump model^{21,22} and a 12-lump model by *Cerqueira*.²³ The complex models are mathematically more complicated and need more experimental parameters which are difficult to estimate.

Wallenstein,²⁴ *Lappas et al.*²⁵ and *Spare*²⁶ were modelling kinetic data obtained from the microactivity testing of FCC catalysts and FCC feed.

In this work we applied a 4-lump kinetic model based on the assumption of three main cracking

products – gasoline, gas, and coke. (Gas is considered to be a sum of dry gas and LPG). Rather complex reactor model was used in the modeling taking into account the non stationary reaction period and near adiabatic regime during this period. This work presents the results of kinetic analysis followed by the modeling and simulation of nonisothermal and nonstationary fixed – bed plug reactor using data obtained from MAT apparatus.

Experimental

Materials

The authors used the feed they submitted to the hydrodesulphurisation process at various H_2/CH ratios, and they obtained three gas oils of similar physical and chemical characteristics (Table 2). These three gas oils were submitted to catalytic cracking by the microactivity test at different reaction temperatures (Table 3). Due to that, catalytic cracking products obtained from the hydrodesulphurised gas oils at the same temperature of catalytic cracking reaction may be compared only on the basis of a different H_2/CH ratio.

The experimental conditions of hydrodesulphurisation process are given in Table 1. Physical and chemical characteristics of the feeds are given in Table 2.

Table 1 – The experimental conditions applied in the hydrodesulphurisation process

Feedstock	Feedstock 1	Feedstock 2	Feedstock 3
T, K	593.15	593.15	593.15
p, Pa	$4 \cdot 10^6$	$4 \cdot 10^6$	$4 \cdot 10^6$
H_2/CH	100	200	300
HSW, h^{-1}	1	1	1

Methods

Gas oil hydrodesulphurisation process was performed on a high-pressure pilot plant unit A. Hofer, using a commercial HDS catalyst. Gas oil dosage was carried out by a pump from a dosage vessel and gas oil was mixed with hydrogen at different ratios of 100, 200, and 300, and heated to 593.15 K under the pressure of $4 \times 10^6 Pa$ and constant HSV of $1 h^{-1}$ during the reaction time of 75 s. The feed and hydrogen mixture passed through a catalyst bed where hydrodesulphurisation reaction occurred. After cooling, the condensed product went to a high-pressure separator. Upon stripping in a low-pressure

Table 2 – Physical and chemical characteristics of the feeds

Properties	Feed 1	Feed2	Feed 3
Density, 15 °C, $kg\ dm^{-3}$	0.8784	0.8771	0.8767
°API	29.58	29.83	29.90
Distillation, ASTM D 2887			
IBP, °C	192.3	198.4	198.8
$\varphi = 10\ %$	284.3	290.4	290.3
$\varphi = 50\ %$	379.7	382.6	381.4
$\varphi = 90\ %$	466.2	466.4	466.9
$\varphi = 95\ %$	484.6	484.2	485.4
Sulphur, m/m %	0.43	0.36	0.34
Viscosity $mm^2\ s^{-1}$, 40 °C	14.76	14.32	14.62
	100 °C	3.38	3.33
Pour point, °C	30	30	30
Refractive index, 70 °C	1.4887	1.4890	1.4883
Average molecular mass	350	348	360
n-d-M analysis, % C_A	17.17	17.91	17.35
% C_N	13.27	11.71	11.27
% C_p	69.56	70.38	71.38

separator, liquid products of hydrodesulphurisation were discharged into a reception vessel, their physical and chemical characteristics were determined, and they were used as feeds for catalytic cracking.

The hydrodesulphurised gas oil testing was performed by a modified ASTM D 3907 method of the microactivity test (MAT). It is a completely automated unit, equipped with a control system enabling the process monitoring and regulation, as well as test data recording by means of a software. The unit also comprises of two gas chromatographs: one linked to the MAT apparatus and used for on-line analysis of the FCC gas, the other used for liquid product analysis, whereby the petrol and cyclic-oil fraction yields are determined by the simulated distillation method.

Catalyst testing by the ASTM procedure is conducted in a tubular reactor with a fixed bed of catalyst under nitrogen purge. When the standard working temperature of 755.15 K is achieved, cracking begins with the introduction of 1.33 g of gas oil with constant rate during a period of 75 s.

The resulting gas and liquid products are gathered and analysed by gas chromatography. The gas analysis reveals the mass fraction (%) of hydrocarbons up to C₅₊ (methane, ethane, ethene, propane, propene, isobutane, *n*-butane, *trans*-butene, butene-1, isobutene, *cis*-butene, isopentane, *n*-pentane, 1,3-butadien, C₅₊ fraction). The next step after nitrogen stripping is a catalyst regeneration by air. The main products of coke combustion are CO and CO₂. CO is converted into CO₂ in the catalytic converter with copper oxide, followed by the determination of CO₂ in the air mixture, using an IR analyser.

In catalyst testing, the most frequent changes occur in reactor temperature and catalyst mass, while other test parameters remain constant. MAT unit catalyst testing conditions are shown in Table 3. The catalyst used in this study was an equilibrium catalyst taken from a FCC unit.

Table 3 – Experimental conditions applied in the MAT unit

Mass of catalyst, m / kg	4.000×10^{-3}
Mass ratio, $\zeta_{\text{cat/oil}}$	3.01
Mass feed flow rate per unit catalyst mass, WHSV h^{-1}	15.96
Mass of injection feedstock, m_f / kg	1.330×10^{-3}
Reaction temperature, T / K	755.15–793.15

On the basis of experimental data, obtained by the chromatographic method of simulated distillation (ASTM D 2887) of liquid sample, yields of the liquid product particular components were calculated (petrol yield, C₅–216 °C boiling temperature, LCO 216–343 °C yield, HCO yield above 343 °C). By fractionating the liquid product on a micro-fractionator, the FCC petrol fraction, as well as light and heavy cyclic oil fractions, were obtained.

The aromatic group type content was observed in the FCC petrol, according to the EN 12916 standard by normal phase – high-performance liquid chromatography (NP-HPLC). Separation was performed on –NH₂ modified silica column which showed a little affinity to non-aromatic hydrocarbon, but a pronounced selectivity for aromatic hydrocarbon. The RI detector was applied to samples of higher polyaromatic content. Due to the column selectivity, aromatic hydrocarbons were separated, according to the number of aromatic rings in the structure, into mono-, di-, tri+aromatics.

Results and discussion

The dependence of conversion and cracking yields (gas, petrol, LCO, HCO and coke) on the cracking temperature was tested. Figure 1. shows dependence of conversion on the cracking temperature. Temperature increase has caused the conversion increase. The highest conversion values were achieved by Feed 3 with the highest H₂/CH ratio. All the feeds used were of paraffinic type, extremely prone to cracking, as may be seen from their physical and chemical proprieties (Table 1).

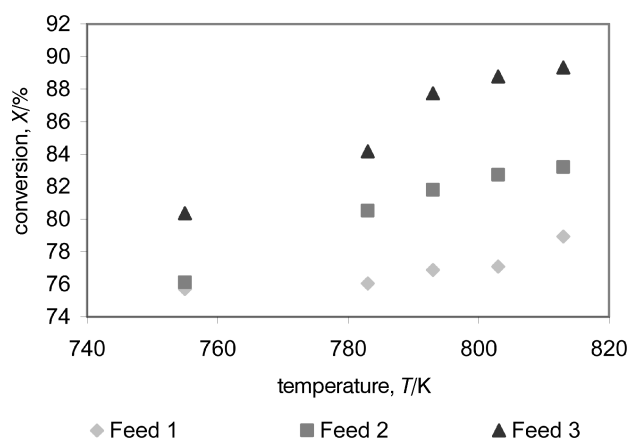


Fig. 1 – Dependence of conversions on the cracking temperature

The dependence of gas yields on the cracking temperature was shown in Figure 2. By increasing the temperature, i.e. conversion, the gas yield increased. The highest gas yield and petrol yield were achieved with Feed 3 (Figure 3). The data of n-d-M analysis reveal that Feed 3 is the most easily cracked, because it contains majority of the long-chained paraffinic hydrocarbons and minimum naphthenic hydrocarbons ($\% C_p = 71.38$, $\% C_n = 11.27$).

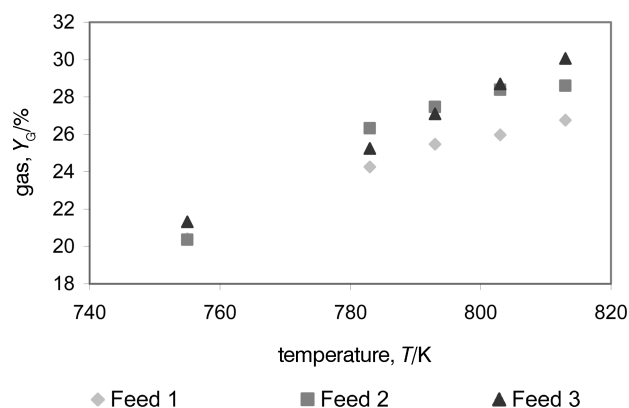


Fig. 2 – Dependence of gas yield on the cracking temperature

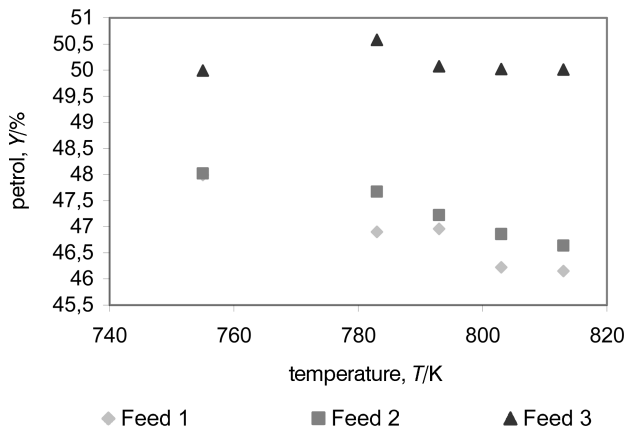


Fig. 3 – Dependence of petrol yield on the cracking temperature

Overcracking is noticed at conversion above 75 %, and it is characterised by a decrease in the yield of petrol, which undergoes secondary reactions to give C₃ and C₄ olefines and isobutene.²⁷

Figures 4 and 5 show the dependence of LCO and HCO yields on the cracking temperature. LCO and HCO yields are reduced by the temperature, en-

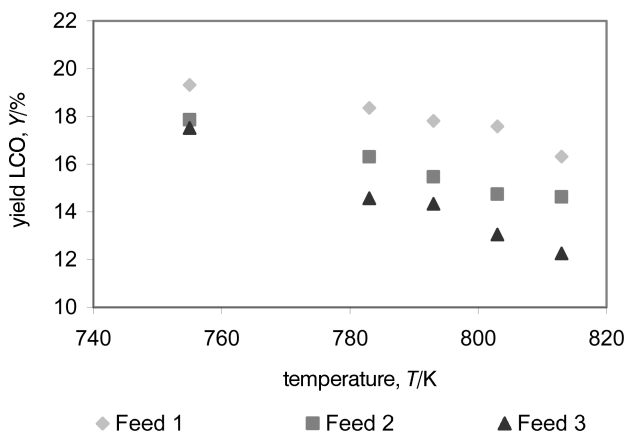


Fig. 4 – Dependence of LCO yield on the cracking temperature

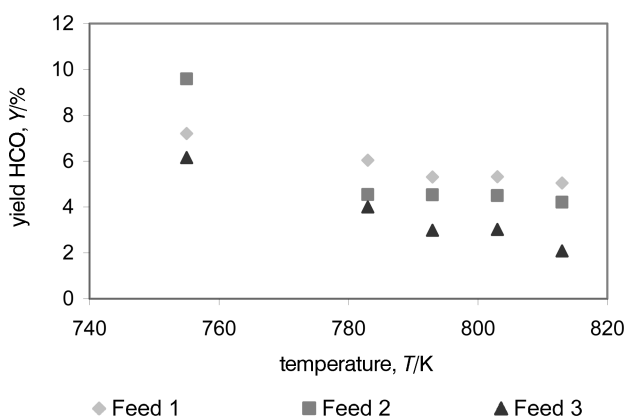


Fig. 5 – Dependence of HCO yield on the cracking temperature

hanced by all the three used feeds. Feed 3 with the highest H₂/CH ratio achieved the minimum LCO and HCO yields. This is desirable, because petrol and LPG today are the most desired products from the FCC process. In the yields of gas, LCO and TCO, the exact yield difference is noticed as the sharpness of hydrodesulphurisation parameters rises.

Table 4 shows content of aromatic hydrocarbon in FCC petrol from the three used feeds. The aromatic hydrocarbons have the highest octane number value among pure hydrocarbons. At a higher temperature, increased amount of aromatics was formed from saturates for all three types of feeds used. The cracking reactions and dehydrogenation reactions in which aromatics arise are endothermic and are favourable at high temperature.^{1,2,28} The results in Table 4 reveal that increased H₂/CH ratio increased the content of total aromatics. In this manner Petrol 3 from Feed 3, with the highest H₂/CH amount ratio, was obtained with the highest fraction of aromatics.

Table 4 – Fraction of aromatic hydrocarbons in FCC petrol (HPLC method with RI detector)

FCC petrol	1			2			3		
<i>T</i> / K	755	793	813	755	793	813	755	793	813
total aromatics, w / %	24.2	28.6	29.0	24.5	29.4	29.8	25.1	31.6	35.3

Evidently, the origin and type of the feed will have an effect on the FCC petrol aromatics. Aromatics in the FCC petrol are mainly formed via dealkylation of mono-aromatics in the feed, cycling of olefins, and conversion of cycles compounds to aromatics by hydrogen transfer. Yield of FCC petrol, as well as of aromatics, is similar to that in Feeds 1 and 2. The assumption is, that more aromatics have been created in Feed 3, due to a larger quantity of paraffin, transferred to naphthenes by cyclisation, i.e. by dehydrogenation and hydrogen transfer into aromatics.

Kinetic modelling

The basis for conforming the experimental data is a four-lump model.^{14,15} In practice, this model gives adequate descriptions of cracking behaviour. Four-lump model is characterised by 4 lumps and five kinetic constants (Figure 6).

The main products of catalytic cracking taken into consideration are gas, petrol, and coke. This

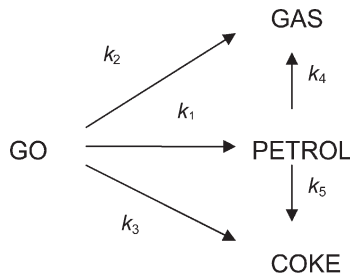


Fig. 6 – Kinetic scheme of 4-lump model

model is described by the following rate equations for gas oil cracking (eq. 1 to 4):

$$r_1 = k(T) \frac{y_1^2}{1 + k_H y_1} \varphi \quad (1)$$

$$r_2 = [k_1 w_1^2 - K w_2] \varphi \quad (2)$$

$$r_3 = [k_3 w_1^2 + k_5 w_2] \varphi \quad (3)$$

$$r_4 = [k_2 w_1^2 + k_4 w_2] \varphi \quad (4)$$

$$k(T) = k_2(T) + k_3(T) + k_4(T) = k_0 \exp \left[-\frac{E_A}{R_g T} \right] \quad (5)$$

$$K = k_4 + k_5 \quad (6)$$

In this work, a second order reaction has been used for gas oil cracking with an inhibition term, incorporated to account for the fact of competitive adsorption.²⁶ The first order reaction has been used for petrol and coke cracking. The applied deactivation function is:

$$\varphi = n A_c t^{n-1} \quad (7)$$

The deposited coke is a function of a catalyst contact time. The formation of coke decreases proportionally with the cracking activity, i.e. cracking rates.

The experiments have been performed in an automated computer-controlled MAT unit. Considering the fixed MAT reactor non-isothermal conditions, plug-flow, non-stationary, applying mass as well as heat balance equations, we have the following equations:

$$\frac{\partial w_1}{\partial t} + u(w_1) \frac{\partial w_1}{\partial z} + r_1(T) = 0 \quad (8)$$

$$\frac{\partial T}{\partial t} + u(w_1) \frac{\partial T}{\partial z} + \frac{\sum (\Delta_r H)_i}{\rho_s c_{ps}} r_1 = 0 \quad (9)$$

$$\frac{\partial w_{2-4}}{\partial t} + u(w_1) \frac{\partial w_{2-4}}{\partial z} + r_{2-4} = 0 \quad (10)$$

The set of the above equations (8–10) is a system of partial differential equations, which could be solved to obtain yield profiles of the reactants and products as a function of reactor length and time. These yields are time-average values measured at the end of the experiments²⁵. The set of above first order hyperbolic equations are replaced by the simpler ones, by introducing new variables, $s = z/u$ and $\theta = t + z/u$ to:

$$\frac{dw_1}{ds} + r_1(T) = 0 \quad (11)$$

$$\frac{dT}{ds} + \frac{\sum (\Delta_r H)}{\rho_s c_{ps}} r_1(T) = 0 \quad (12)$$

$$\frac{dw_{2-4}}{ds} + r_{2-4} = 0 \quad (13)$$

These ordinary differential equations can be solved with well-known numerical procedures.

The kinetic parameters were estimated by the Nelder-Mead method. The chosen criterion was a mean square deviation between the calculated and average experimental values of the component yields. The sequential analytical method was applied, rather than simultaneous regression, because of many parameters contained in the kinetic model.²⁵ The constant reaction heat for each lump (or an average reaction heat for the entire feed) was assumed. It provided a good way to account for the temperature gradient in the reactor.²⁹ The frequency factor, activation energy and the parameter n in deactivation function were estimated. The heat of the overall reaction was taken from the published data as mean values for that type of FCC process.²⁶ The selected criteria were mean square deviation between experimental values of the overall conversion and the end temperature vs. calculated values. After that, the cracking of gas oil to petrol was considered in the first lump, and two kinetic coefficient, k_1 and K , were estimated. These constants were, in fact, mean values valid in the given temperature interval. They seemed preferable over introduction of new parameters through the new heat balances for all subsequent reactions in other lumps. Relative change in the temperature within the given interval, from the beginning to the end of the reaction, amounted to 3 %.

The calculated kinetic constants for Feed 3 are presented for all temperatures in Table 5.

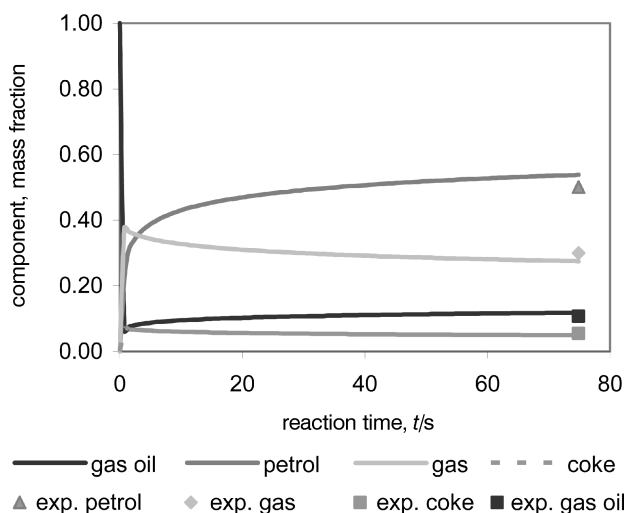
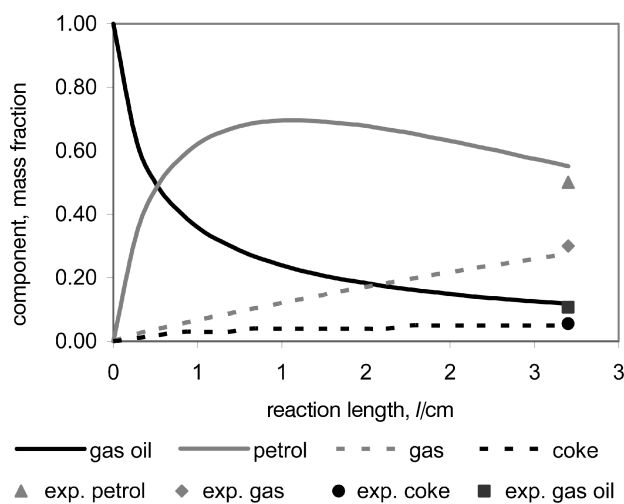
The chosen optimisation criterion was the deviation between experimental yield of petrol and theoretical value. The kinetic coefficients for other lumps were estimated in a similar way. In Table 6, fig. 7 and 8, model predictions on product yields

Table 5 – Typical simulation results (Feed 3)

T, K	$\frac{k_1}{\text{g}^{-1} \text{ cm}^3 \text{ s}^{-1}}$	$\frac{k_2}{\text{g}^{-1} \text{ cm}^3 \text{ s}^{-1}}$	$\frac{k_3}{\text{g}^{-1} \text{ cm}^3 \text{ s}^{-1}}$	$\frac{k_4}{\text{s}^{-1}}$	$\frac{k_5 \cdot 10^{-3}}{\text{s}^{-1}}$	$\frac{k_o}{\text{g}^{-1} \text{ cm}^3 \text{ s}^{-1}}$	$\frac{E_A}{\text{kJ mol}^{-1}}$	$\frac{\Delta H}{\text{kJ kg}^{-1}}$
755	1.803	0.086	0.0385	0.0294	2.226	5805	79.31	330.36
783	1.984	0.120	0.0659	0.0404	0.2273	4872	68.45	334.34
793	2.134	0.148	0.0886	0.0506	0.3183	4562	69.93	354.53
803	2.195	0.113	0.1059	0.0646	0.1406	5870	72.12	375.99
813	2.207	0.122	0.1089	0.0690	0.4581	5279	67.61	385.12

Table 6 – Comparison between the obtained experimental data and those obtained from the kinetic model (Feed 3)

T, K	755		783		793		803		813	
	exp.	model	exp.	model	exp.	model	exp.	model	exp.	model
Conversion, χ / %	80.36	79.47	84.17	84.20	87.74	87.70	88.77	88.84	89.32	89.31
Petrol, w / %	49.99	49.99	50.58	50.58	50.07	50.07	50.02	50.02	50.01	50.01
Gas, w / %	21.32	21.32	25.24	25.24	27.10	27.10	28.50	28.50	30.07	30.07
Coke, w / %	5.01	5.01	5.20	5.19	5.24	5.24	5.42	5.42	5.48	5.49

Fig. 7 – The simulation data (curves) and experimental data (points) for Feed 3, component mass fractions as a function of reaction time at the reactor exit ($T = 813 \text{ K}$)Fig. 8 – The simulation data (curves) and experimental data (points) for Feed 3, component mass fractions as a function of reaction length ($T = 813 \text{ K}$) at the end of reaction

were presented together with experimental results – those are the points labelled with asterisks located at the ends of curves.

The results for all experiments have been confirmed very well. The values of the estimated ki-

netic constants are arbitrary and lumping can be considered as semi-empirical. The proposed model gives accurate predictions in the appropriate range of FCC variables for the used feeds, catalyst, and temperature.

Conclusions

The influence of hydrogen/feed amount ratio (hydrodesulphurisation process parameter) on the catalytic cracking products was analysed. The highest conversion, gas and petrol yields, and the minimum LCO and HCO yields were achieved with the feed obtained under the highest hydrotreating process severity, i.e. H₂/CH amount ratio.

The increase of H₂/CH ratio and temperature, results in the aromatic hydrocarbon increase.

An improved non-isothermal MAT model for the FCC process was developed. The model took into account the temperature drop due to cracking reactions as a function of the reactor length, and it also permitted calculating the volume expansion caused by cracking. Residence time of gas oil could be accurately estimated.

The 4-lump kinetic model for hydrodesulphurised gas oil cracking was applied. The non-isothermal and non-stationary fixed MAT reactor was used for testing and verification of the results. A sequential method of kinetic analysis was chosen. The reliability of parameters was satisfactory – the proposed model gave accurate predictions in the appropriate range of FCC variables for the given feeds, catalyst, and temperature. The product yields predicted by the model indicated an excellent agreement with the experimental data.

Symbols

- A_c – constant in decay function
- c_{ps} – mean heat capacity of gas phase, $\text{kJ kg}^{-1} \text{K}^{-1}$
- C_p – carbon in paraffinic chains
- C_A – carbon in aromatic rings
- C_N – carbon in naphthenic rings
- E_A – activation energy, kJ mol^{-1}
- HCO – heavy cycle oil
- HDS – hydrodesulphurisation
- GO – gas oil
- H₂/CH – hydrogen-to-feed amount ratio, $n_{\text{N}_2}/n_{\text{feed}}$
- K – constant, $k_5 + k_6, \text{s}^{-1}$
- k_0 – frequency factor, $\text{g}_{\text{cat}}^{-1} \text{cm}^3 \text{s}^{-1}$
- $k(T)$ – gas oil cracking kinetic coefficient, reaction (1), $\text{g}^{-1} \text{cm}^3 \text{s}^{-1}$
- $k_{(1-3)}$ – kinetic coefficients, $\text{g}^{-1} \text{cm}^3 \text{s}^{-1}$
- $k_{(4-5)}$ – kinetic coefficients, s^{-1}
- LCO – light cycle oil
- LHSV – liquid hourly space velocity (volume feed flow per unit catalyst volume), $\text{m}_{\text{feed}}^3 \text{m}_{\text{cat}}^{-3} \text{h}^{-1}$
- LPG – liquefied petroleum gas
- n – constant in decay function
- R_g – gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
- $r_{(1-4)}$ – reaction rate, $\text{g cm}^{-3} \text{s}^{-1}$

- s – new variable, s
- T – reactor temperature, $^{\circ}\text{C}$
- T_c – regenerator temperature, $^{\circ}\text{C}$
- t_c – reaction time, s
- u – linear velocity, cm s^{-1}
- WHSV – weight hourly space velocity (mass feed flow per unit catalyst mass), $\text{kg}_{\text{feed}} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$
- $w_{(1-2)}$ – mass fractions of gas oil, 1 and petrol, 2
- X – conversion, %
- Y – yield, %
- z – axial coordinate, cm

Greek letters

- ϕ – catalyst decay function, –
- $\Delta\gamma H$ – heat of cracking reaction, kJ kg^{-1}
- ρ_s – mean vapour density at reactor condition, kg m^{-3}
- θ – new variable, s

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