

Thermal-oxidative Cracking Modeling Procedure Involving Model Components

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Abstract— A procedure and an algorithm for computer modeling of the thermal-oxidative cracking process have been developed. A distinctive feature of the developed procedure and algorithm is that for modeling both light and heavy fractions, we propose using specific model components and involving them in chemical process flow description, as well as in component balances and kinetic equations for specific components. The adequacy of the developed model has been tested with the example of computer simulation of the process of oxidative degradation of tar, which suggests that it can be used to simulate similar processes.

Key words— *model; modeling; cracking; procedure; model component*

I. INTRODUCTION

At present, the deep processing of heavy oil residues is widespread, and the initiated thermo-oxidative cracking in particular. Initiated thermo-oxidative cracking is a complex process when initially heavy hydrocarbons interact with oxygen to form a hydroperoxide, which subsequently decomposes forming radicals and fragments of molecules, followed by the rearrangement of these fragments to form new molecules of lighter hydrocarbons [1–2]. The most important stage in the development of resource-effective initiated thermal-oxidative cracking process is its modeling. The procedure of this process modeling is proposed in several papers, particularly in [3–5]. It is suggested in [3–4] to write down the component balances for each fraction, and there are no specific stoichiometric schemes of processes. The author in [5] proposed to model a gasoline fraction by one model component, while products are modeled by true components. However, the author of this work did not simulate the processes of oxidative cracking of heavier hydrocarbon mixtures. We have developed a new procedure for modeling the cracking process for heavy hydrocarbons, the distinctive feature of which is selecting the specific components for the modeling of fractions (both light and heavy hydrocarbons) and the chemical

process diagram developing using selected model components that characterize the fractions properties. We also propose using the specific model components for component balances.

II. THERMOXIDIZING CRACKING PROCESS WITH MODEL COMPONENTS MODELING PROCEDURE

The proposed procedure consists of the following steps:

A. Analysis of experimental data.

B. Determination of the model components characterizing the fractions and chemical behavior of the process written down for these model components (the so-called "approximated" chemistry), based on the experimental data analysis. The experience of approximate chemistry using for modeling the aromatization process is described in [6]. We propose the following chemical scheme:

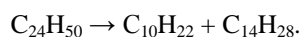
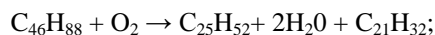


Table 1 shows the model components proposed for modeling the initiated cracking of heavy oil fractions (tar).

C. Development of a laboratory reactor computer model and finding kinetic constants. For this, it is necessary to select the kind of divergence criterion for the calculated and experimental data and to minimize it. We propose to use the computer mathematics system (SCM) MATLAB. The mathematical description of the thermal-oxidative cracking process in a laboratory reactor has the following form:

TABLE I. SUGGESTED MODEL COMPONENTS FOR HEAVY OIL FRACTIONS INITIATED CRACKING SIMULATION

Feed	Empirical formula	Name
Initial mixture for destruction (tar)	C ₄₆ H ₈₈	Trifenylylene, octadecahydroctacosane
	C ₂₁ H ₁₈	Trimethyltriphenylene
Destruction products		
Gaseous products	CH ₄ ; C ₂ H ₆ ; C ₃ H ₆	Methane, ethane and propylene
Fraction with boiling temperature < 200°C	C ₈ H ₁₈	Octane
	C ₈ H ₁₄	Octine
Fraction with boiling temperature > 200°C and < 350°C	C ₁₀ H ₂₂	Decane
	C ₁₄ H ₂₈	Tetradecene
Fraction with boiling temperature > 350°C (dark residue)	All hydrocarbons with the number of carbon atoms greater than 20: C ₄₆ H ₈₈ ; C ₂₁ H ₁₈ ; C ₂₅ H ₅₂ ; C ₂₁ H ₃₂ ; C ₂₂ H ₃₈	

$$\frac{dn_{C_{46}H_{88}}}{d\tau} = G(-k_1 c_{C_{46}H_{88}} c_{O_2} - k_2 c_{C_{46}H_{88}});$$

$$\frac{dn_{O_2}}{d\tau} = -Gk_1 c_{C_{46}H_{88}} c_{O_2};$$

$$\frac{dn_{H_2O}}{d\tau} = 2Gk_1 c_{C_{46}H_{88}} c_{O_2};$$

$$\frac{dn_{C_{22}H_{38}}}{d\tau} = G(k_2 c_{C_{46}H_{88}} - k_3 c_{C_{22}H_{38}});$$

$$\frac{dn_{C_{24}H_{50}}}{d\tau} = G(k_2 c_{C_{46}H_{88}} - k_4 c_{C_{24}H_{50}} - k_5 c_{C_{24}H_{50}} - k_6 c_{C_{24}H_{50}});$$

$$\frac{dn_{C_{25}H_{52}}}{d\tau} = Gk_1 c_{C_{46}H_{88}} c_{O_2};$$

$$\frac{dn_{C_{21}H_{32}}}{d\tau} = Gk_1 c_{C_{46}H_{88}} c_{O_2};$$

$$\frac{dn_{H_2}}{d\tau} = G(8k_3 c_{C_{22}H_{38}} - 14k_4 c_{C_{24}H_{50}});$$

$$\frac{dn_{C_{21}H_{18}}}{d\tau} = Gk_3 c_{C_{22}H_{38}};$$

$$\frac{dn_{CH_4}}{d\tau} = G(k_3 c_{C_{22}H_{38}} + 12k_4 c_{C_{24}H_{50}});$$

$$\frac{dn_{C_2H_6}}{d\tau} = 3Gk_4 c_{C_{24}H_{50}};$$

$$\frac{dn_{C_3H_6}}{d\tau} = 2Gk_4 c_{C_{24}H_{50}};$$

$$\frac{dn_{C_8H_{18}}}{d\tau} = 2Gk_5 c_{C_{24}H_{50}};$$

$$\frac{dn_{C_8H_{14}}}{d\tau} = Gk_5 c_{C_{24}H_{50}};$$

$$\frac{dn_{C_{10}H_{22}}}{d\tau} = Gk_6 c_{C_{24}H_{50}};$$

$$\frac{dn_{C_{14}H_{28}}}{d\tau} = Gk_6 c_{C_{24}H_{50}};$$

$$0 \leq \tau \leq \tau_R$$

The residence time in the reactor τ_R is taken from the experimental results on an initiated cracking laboratory reactor, borrowed from [1].

To find the kinetic constants, the following divergence criterion is minimized:

$$S = \sum_{i=1}^{12} [(\omega_{H_2O}^{calc.} - \omega_{H_2O}^{exp.})^2 + (\omega_{gas}^{calc.} - \omega_{gas}^{exp.})^2 + (\omega_{C_5-C_9}^{calc.} - \omega_{C_5-C_9}^{exp.})^2 + (\omega_{C_{10}-C_{20}}^{calc.} - \omega_{C_{10}-C_{20}}^{exp.})^2 + (\omega_{dr.}^{calc.} - \omega_{dr.}^{exp.})^2]$$

Experimental data are also borrowed from [1]. The Nelder-Mead method was used [7–8] for the criterion minimization. Minimization of this criterion determines the coefficients of temperature dependences equations of chemical reactions rate constants:

$$k_1(T) = \exp(16 - 1500/T) \quad k_2(T) = \exp(5.3 - 670/T)$$

$$k_3(T) = \exp(5.3 - 500/T) \quad k_4(T) = \exp(2.4 - 3000/T)$$

$$k_5(T) = \exp(24 - 18000/T) \quad k_6(T) = \exp(45 - 32000/T)$$

Fig. 1 shows the comparison of the calculated and experimental values of the mass fractions of the fraction $200 < t_B < 350$ °C for different residence times in the reactor.

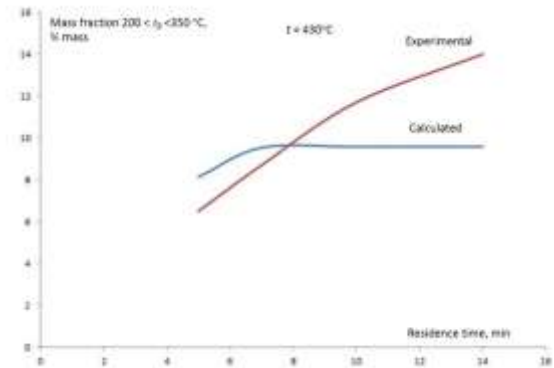


Fig. 1. Comparison of the calculated and experimental mass fractions for different residence times (productivities)

Also, the effect of temperature in a laboratory reactor on the yield of a fraction of $200 < t_B < 350$ °C (hydrocarbons C₁₀–C₂₀) at two different capacities for raw material (tar) had been studied. The result of this study is shown in Fig. 2.

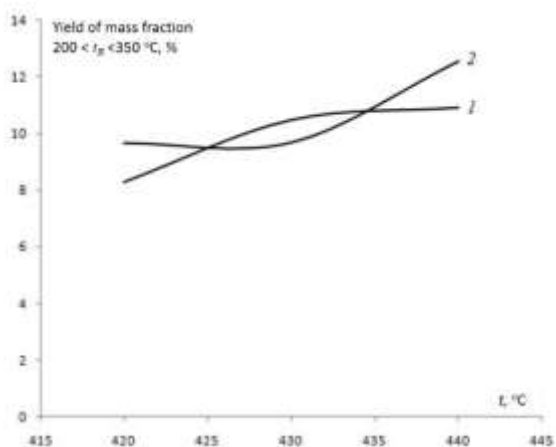


Fig. 2. Dependence of the yield of the fraction $200 < t_B < 350$ °C on the temperature at two different capacities for raw materials: 1 – $G = 90$ g / min; 2 – $G = 70$ g / min.

D. Development of a model of an experimental and / or semi-industrial reactor using SCM MATLAB, and determination of the base reagents conversion degree.

E. Development of a model of an experimental and / or semi-industrial reactor using the modeling programs package CHEMCAD.

The developed procedure is practically applied in [9].

III. CONCLUSIONS

1. The scope of works on the thermo-oxidative cracking of hydrocarbons modeling is reviewed.
2. A computer modeling procedure of the heavy hydrocarbons thermo-oxidative cracking has been developed.

3. A distinctive feature of the proposed procedure is that to simulate both light and heavy fractions, we propose using specific substances and involving them in chemical process flow description and writing the component balances equations for specific components.

REFERENCES

- [1] Shvets V.F., Sapunov V.N., Kozlovsky R.A., Makarov M.G., Gartman T.N., Lugansky A.I., Sovetin F.S., Suchkov Y.P., Gorbunov A.V. Some options of oil refining deepening. *Journal of Applied Chemistry*. 2016. Ed. 11. Vol. 89, Pp. 1806-1815. (in Russian)
- [2] Sovetin F.S., Gordiyevskaya Y.I., Gartman T.N., Novikova D.K. Analytical review of approaches to modeling the processes of initiated cracking. *Chemical Industry Today*. 2017. No. 1. Pp. 3-15. (in Russian)
- [3] Mircea C., Agachi S., Marimoiu V. Simulation and Model Predictive Control of a Universal Oil Products Fluid Catalytic Cracking. *Chemical Engineering and Processing*. 2003. V. 42. Pp. 67-91.
- [4] Pashayeva B.A. Synthesis of the oil catalytic cracking control system using the predictive model. *The Don engineer's messenger*. 2013. V. 24. No. 1 (24). Pp. 12-21. (in Russian)
- [5] Goncharov D.V. A small-size reactor for the process of thermo-oxidative cracking of hydrocarbon liquid fuel. Dissertation for the degree of candidate of technical sciences. 05.17.08. Moscow. MSU-IE (MIHM). 2005. (in Russian)
- [6] Gartman T.N., Sovetin F. S., Proskuro E. A., Shvets V. F., Kozlovskiy R. A., Suchkov Y.P., Sapunov V.N., Loktev A. S., Levchenko D. A., Dedov A.G. Computation of the Solid Catalyzed Gas Phase Reactions with a Simultaneous Choice of the Scheme of the Reactions for Different Composition of the Initial Reaction Mixture. *Chemical engineering transactions*. 2014. Vol. 39. Pp.1009-1014.
- [7] Gartman T.N., Klushin D.V. Basics of computer modeling of chemical-technological processes. Moscow. Publ. Akademkniga. 2008. 416 p. (in Russian)
- [8] Formaliev V.F., Revisnikov D.L. Numerical methods. Moscow. Physmatlit. 2004. 400 p. (in Russian)
- [9] Gartman T.N., Sovetin F.S., Podsedkina Y.I., Shvets V.F., Kozlovsky R.A., Sapunov V.N. Kinetic Simulation of Initiated Cracking of Tar. *Theoretical Foundations of Chemical Engineering*. 2018. Vol. 52. No. 1. Pp. 57-63. (in Russian)