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Thermodynamically consistent kinetic models for simulation of complex oil refinery processes. Case study: modelling of the naphtha reforming process

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Highlights
- Detailed but simple kinetic models for complicated reaction systems are considered
- Use of thermodynamic potentials in kinetic equations increases the model efficiency
- Proposed model accurately describes naphtha reforming in wide range of conditions
- Proposed model is one of the most detailed and, at the same time, one of the simplest

1. Introduction

The prediction and application efficiency of kinetic models for the complicated reaction systems, such as petrochemical process, is defined by optimal relation between the level of reaction and reactants detailization and the number of kinetic parameters in the model. Development of the new approaches giving the way to create accurate but simple models, appropriate for application in reaction engineering purposes is an important task in the area.

2. Methods and approach

Earlier [1], we proposed the approach based on reasonable lumping of reactants and reactions into homologue groups with description of difference between individual reaction rates within the group by account of thermodynamic potentials (first of all, free Gibbs energy of corresponding reactions) in the value of the apparent activation energy of the given reaction. It was shown that the rates of aromatization of all normal paraffins and naphtenes into corresponding alkylbenzenes might be described by one common equation with just 3 kinetic parameters (pre-exponent, activation energy and correlation coefficient):

$$W_j = k_{01}(1-\theta)\exp\left(-\frac{E_{a1}+\beta\Delta G_j}{R\,T}\right)\left(P_{NPi}-\frac{P_{ARi}P_{H_2}^4}{K_{Pj}}\right)$$

where k_0 – pre-exponent, E – activation energy, ΔG_j – free Gibbs energy for j-th reaction, P – partial pressures of reactants, K_{pj} – equilibrium constant for j-th reaction, β - empiric correlation coefficient.

The given research was dedicated to further development of the approach.

The experimental study was performed in the lab setup in the isothermal plug flow reactor, providing accurate attribution of obtained results to temperature and reactor type. Kinetic experiments included variation of the feed type (2 types), temperature (350-490°C), pressure (3.5-10 bar), feedstock LHSV (1.5-3.0 h^{-1}), HCG recirculation ratio (500-2000) – in total over 100 experiments.

The earlier proposed list of reactants and possible reactions considered was expanded to 64 individual and lumped compounds with 230 possible reactions.

3. Results and discussion

In the given study, it was shown that the rates of all paraffins hydrocracking/hydrogenolysis reactions may be described by one common equation using the enthalpy of each specific reaction ΔH_j as the measure of the

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bond energy of the C-C bond to be cracked. It made possible to use one equation with only three parameters for all 135 reactions of this type (instead of 270 parameters in the conventional approach).

$$W_j = k_o \exp\left(-\frac{E + \beta`\Delta H_j}{RT}\right)$$

This gave the possibility to obtain the accurate information on the composition of gas (C1-C4) product, not described in majority of existing models. In general, the model provides qualitatively adequate and quantitatively accurate description of experimental data, with one set of parameters for wide range of conditions (including pressure and feedstock type variation, usually requiring adjustment of parameters in conventional models). Examples of description are given in Fig.1.
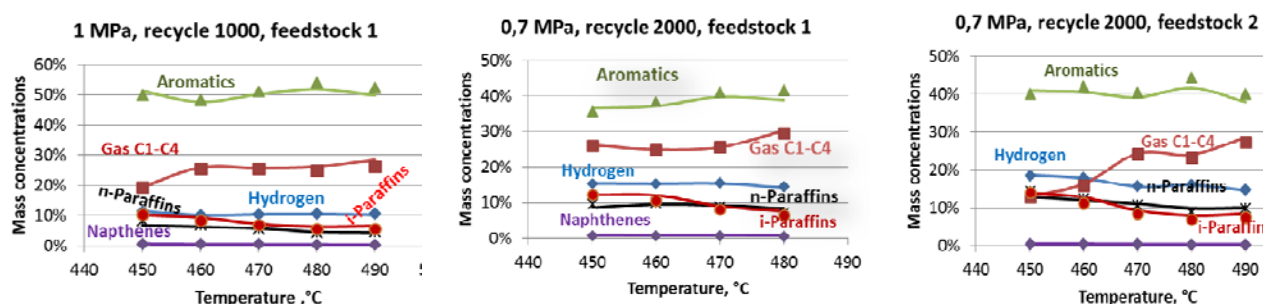

Figure 1. Comparison of experimental (points) and simulated (lines) reformate composition in experiments with variation of temperature, pressure, hydrogen recycle ration and feedstock type.

The proposed model is one of the most detailed among those published in literature. At the same time, it is one of the simplest, it uses only 26 kinetic parameters to be defined from experiments (see Fig.2).
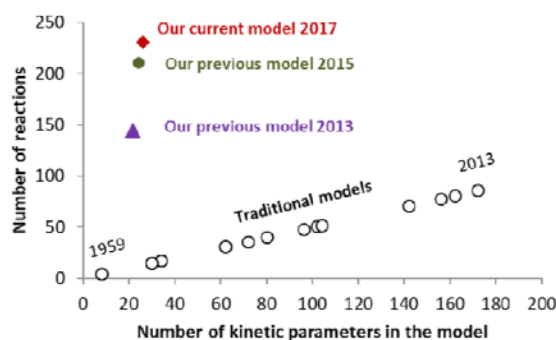

Figure 2. Comparison of accuracy/complexity ratio for traditional kinetic models for naphtha reforming process [2] and models based on the use of the thermodynamic potentials

4. Conclusions

Use of thermodynamic potentials and construction of the thermodynamically consistent kinetic models may provide the efficient simulation of the catalytic processes of oil refinery and petrochemistry in the wide range of their application conditions with quantitative prediction of their key operation parameters. In our mind, the proposed approach, except the naphtha reforming case, may be expanded to other petrochemical processes such as hydrotreatment, isomerization, hydrocracking etc.

References

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[2] M.R.Rahimpour, M.Jafari, D.Iranshahi, Applied Energy 109 (2013), 79.