Detailed description of the mathematical modeling of the catalytic naphtha reforming process dynamics

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Abstract. This work is dedicated to the construction of a kinetic model for the naphtha reforming process. By assembling the components into reactivity based lumps, a new reaction network model rooted on 33 lumps and 101 reactions was studied. The tabu search algorithm was used to determine the global optimal solution. The experimental data from the laboratory scale isothermal reactor was used to investigate the kinetics. By comparing with the test data, the average deviation of the reformed products calculated from the proposed model reached 2.5%.

1. Introduction
Catalytic naphtha reforming is practiced extensively in the petroleum-refining industry to convert petroleum naphtha for use as high-performance gasoline fuel. Naphtha is a low octane cut from atmospheric distillation of crude oil from the topping plant usually in the range between 30°C and 200°C, and constitutes typically from 15% to 30% by weight of the crude oil.  This cut contains some impurities such as sulphur, oxygen, and nitrogen compounds. As a high-octane gasoline blending component, reformed gasoline has reached 1/3 of the gasoline pools of developed countries such as Europe and the United States. Zhou Xiang developed a detailed kinetic model of the CCR process through KMT software, depicting the paraffin and naphthene isomers up to the C9 component, while the aromatic isomers are fully described up to C10. The coking kinetics and the corresponding deactivation of the catalyst are integrated into the model. Wei designed an economic model predictive control (EMPC) and production mode conversion strategy through economic model predictive control (EMPC) and established a dynamic process model to simulate the naphtha reforming process.

2. Chemistry of the Process
The main reactions during the reforming process are shown in Figure 1. The key to a successful simulated catalytic reforming process is to establish a well-developed description of the naphtha reforming kinetics. The reforming process follows pathbelow. (1) Dehydrogenation of a cycloalkane to an aromatic hydrocarbon. (2) Paraffin in naphtha is cyclized to a cycloalkane or converted to an isoparaffin. (3) Dehydrogenation of aromatic hydrocarbons or paraffin. Under typical naphtha reforming conditions, these reactions realize the conversion to aromatics.
3. Experiment

3.1. Research reform response
The commercial platinum stannum bimetallic catalyst Pt-Sn/γ-Al2O3 was used as the reforming catalyst.

3.2. Study detailed kinetics using laboratory-scale reactor experiments
The kinetic study instrument generally includes the section of the preparation and supply of the raw materials, the reactor, and the detection unit. The preparation of the raw materials is to highly purify the raw materials and control the content of harmful substances. The reactor is the key part of the kinetics assay.

![Figure 1. Process flow scheme for the reforming process.](image)

According to the method provided above, the process includes two main stages: (1) reaction stage, and (2) regeneration stage. The reaction stage can be determined as the core of the catalytic reforming process.[5]

3.3. Raw material and product distribution analysis
The operating conditions during the investigation and the basic properties of raw material were summarized in Table 1. The raw materials were analyzed on a PIONA column using a gas chromatograph (GC) to determine their detailed composition.

|     | n-paraffins | i-paraffins | olefins | naphthenes | aromatics |
|-----|-------------|-------------|---------|------------|-----------|
| C4  | 0.007       | 0.000       | 0.003   | 0.000      | 0.000     |
| C5  | 1.167       | 0.422       | 0.000   | 0.325      | 0.000     |
| C6  | 3.792       | 3.492       | 0.000   | 4.396      | 0.228     |
| C7  | 5.236       | 4.155       | 0.000   | 11.884     | 1.371     |
| C8  | 5.824       | 5.508       | 0.000   | 12.312     | 2.976     |
4. Kinetics Scheme Construction

4.1. Dynamics of the reforming process

4.1.1 Method
This study built mathematical model for kinetic reactions, using laboratory data. The main purpose is to predict output parameters and detect contours to improve process performance. A tabu search algorithm is implemented to simulate existing processes in the study,[6, 7] while MATLAB program task is used to accomplish the task. The kinetic model developed was an extension of Badiea’s work,[8] which utilized the aggregated representation of the reaction.

4.1.2 Dynamic model of the reform process
From our view, there are three major drawbacks that may exist in the existing kinetic models.[9] (a) The lack of detail of the naphthenic reaction network leads to the inability to correctly predict the five-membered naphthenes and six-membered naphthenes, which may lead to erroneous calculations of process energy balance. (B) Excessive simplification of the list of components, in particular, Tri-methyl-benzene and methyl-ethylbenzene, which may lead to the incorrect predictions of the aromatics value of the reformat. (C) Incomplete reactor model caused by different reactor flow patterns.

In our study, we tried to overcome the above shortcomings. In order to consider the predictability of better naphtha composition, the following modifications were made to the original model.

Figure 2. Reaction network scheme for the naphtha reforming process.
The rate of chemical reaction of naphtha depends on several factors, such as activation energy, temperature, pressure, and the factors that influence the effects of pressure, temperature and pressure on the kinetic parameters can be expressed as follows

\[ k_j = k_{0j} \exp \left( \frac{-E_{0j}}{RT} \right) \]

Where \( k_{0j} \) represents the frequency factor, \( E_{0j} \) represents the activation energy (KJ/Kmol), \( b_{0j} \) represents the activation energy, \( R \) represents the gas constant (KJ/Kmol k), and \( T \) represents the temperature (K).

4.1.3 Model Parameter Estimation Based on Tabu Search Algorithm

The tabu search algorithm is used to optimize the estimated kinetic parameters to determine the minimum error of the model output and laboratory data. Considering the same conditions as the operating conditions of the laboratory in the model, estimating the frequency factor \( k_0 \) for each reaction in the reaction network is a very important step.\(^{[10]}\)

According to Arrhenius's law, there are usually three kinetic parameters. To verify the proposed kinetic model, the predicted data of the kinetic model needs to be compared with the real data, and the kinetics of each reaction is estimated in the kinetic reaction network. The estimation of parameters is very important.\(^{[11]}\) According to the Arrhenius's law, a total of 300 kinetic parameters, including 100 reaction activation energy factors \((E_1, ..., E_{100})\), and 100 correction factors \((k_1, ..., k_{100})\) need to be determined. These parameters can be used to minimize the difference of results between the predictions and the experiments by using the methods of the objective function. And by applying the optimization algorithm to get the best convergence function, the dynamic parameter objective function \((KPOF)\) is as follows

\[ KPOF = \left( \frac{F_{i,\text{out,cal}} - F_{i,\text{out,act}}}{F_{i,\text{out,cal}}} \right)^2 \]

\( F_{i,\text{out,cal}} \) represents the molar flow rate of the component \((i)\) calculated by the kinetic model and \( F_{i,\text{out,act}} \) represents the molar flow rate of the actual evaluation data component \((i)\) obtained by the laboratory evaluation device. The algorithm source of the kinetic parameters is determined by the tabu search method, and the convergence speed is accelerated by the tabu search optimization algorithm (TS).

5. Results and discussion
Figure 5. The combined effect of temperature and pressure on product distribution

Figure 6. The combined effect of temperature and pressure on product distribution

It can be seen from Figures 3 to 6 that since the pressure is about 0.5 MPa at a low temperature, the hydrocracking reaction is not fast enough to compete with the isomerization reaction. Similarly, it can be seen that the normal paraffin reduction rate is low before 470°C. At lower pressures, the higher the carbon number, the faster the rate of hydrocracking and cyclization. However, as the carbon number of paraffin gets lower, the content is unchanged. The pressure reduction contributes to the dehydrogenation of naphthenes to aromatics. It conforms to the law of catalytic reforming reaction.

6. Conclusion
A process model for the naphtha reforming reaction was established, which was developed to predict the behavior of the CCR and SR process reactions. The modeling process mainly took those aspects into consideration: (1) changes in operating conditions; (2) changes in the molar flow rate of the feedstock; (3) changes in the molar composition of the feedstock. The proposed model is a new network of various reactions, consisting of 33 blocks and 101 reactions. A tabu search algorithm with multiple initial features was used to determine the global optimal solution, and the estimated parameters obtained from the model were tested for different experimental data. The reformate composition and temperature profile were obtained to provide a degree of conversion for each of the reactors. The simulation results are in good agreement with the plant data, with an average deviation of less than 2.5%. Also, the distribution and characteristics of the reformate are described based on material mass balance.

7. Appendices
KPOF dynamic parameter objective function. TS tabu search optimization algorithm. \( Y_N \) Naphthenic component content. \( Y_A \) Aromatic hydrocarbon component content. \( K_{eq} \) Reversible reaction constant. \( Y_{np} \) Normal paraffin content. \( Y_{ip} \) Isoparaffin content - \( F_{i,\text{out}, \text{cal}} \) molar flow rate of the component (i) calculated by the kinetic model. \( F_{i,\text{out}, \text{act}} \) molar flow rate of the actual evaluation data component (i) obtained by the laboratory evaluation device. \( k_0 \) frequency factor. \( E_{0j} \) activation energy, \( kj/kmol \). \( b_{0j} \) activation energy. \( R \) gas constant, \( kj/kmol \cdot K \). \( T \) temperature, K

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