Application of a simple lumped kinetic model for the catalytic cracking reaction of \( \textit{n} \)-butane over the HZSM-5 zeolite

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Abstract

A simple lumped kinetic model applied to \( \textit{n} \)-butane catalytic cracking over synthesized HZSM-5 zeolite, with \( \text{SiO}_2/\text{Al}_2\text{O}_3=484 \) in a stainless steel plug flow reactor under various operating conditions developed. To suitably estimate the kinetic parameters of catalytic cracking reactions of \( \textit{n} \)-butane, a lumped kinetic model consisted of 6 reaction steps and 5 lumped compounds considered. The Levenberg-Marquardt algorithm utilized to estimate kinetic parameters using MATLAB R.7.10 software. In order to confirm the significance of optimized parameters, the statistical F-test and variance analysis indicating the accuracy of the calculated data were employed. Furthermore, the validity of the model was confirmed. Ultimately, results from the proposed kinetic model showed excellent agreement with experimental data.

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Keywords: \( \textit{n} \)-butane; lumped kinetic model; HZSM-5 zeolite; catalytic cracking

1. Introduction

A major portion of the worldwide petrochemical industry is involved with the production of light olefin materials and their subsequent use in the production of numerous important chemical products. Propylene is one of the most important feedstocks for the petrochemical industry the demand for which is growing very rapidly, driven primarily by the high growth rate of polypropylene use [1]. Many processes currently used for propene production cannot meet this growing demand [2]. Therefore, a need to fill this gap completely might be felt. Recently, transformation of light paraffins into propylene has become a growing field of research interest again since it contains converting of these low value feeds into an essentially valuable product [3-6].

Due to the simple products distribution, low structural carbon atoms and also high selectivity toward light olefin production in reactions of normal and \( \textit{iso} \)-butane cracking over zeolite catalysts, kinetics of this reaction has been the subject of many investigations[7-14].

Kinetic models are the helpful tool for researchers to study mechanisms of catalytic reactions in detail and simulate the experimental results. Several authors investigated the kinetic modeling of paraffin catalytic cracking over HZSM-5 zeolite using both lumped [15-16] and micro-kinetic models [17-22]. One of the major problems one has to deal with when calculating the constants of rate equations of the micro-kinetic model is the large numbers of chemical equations which have to be written in order to completely describe the effects of all components. In other words, exact prediction of all of these rate constant values needs a great number of experimental data. Furthermore, for simple...
linear paraffins which yield a limited product distribution, using of a complex kinetic model seemed unnecessary. Lumped kinetic model is greatly simpler than micro-kinetic one and contains much lower numbers of compounds in kinetic scheme. Besides, it needs considerably fewer experimental data.

In this study, a simple lumped kinetic model which consisted of 5 lump compounds and 6-steps kinetic scheme which may suitably predict the experimental data in a wide range of various operating conditions utilized. In addition, determination of constants of rate equations might be fruitful for later research to predict behavior of coupled methanol and paraffin cracking reaction [5-6, 15].

2. Experimental

HZSM-5 zeolite with a SiO₂/Al₂O₃ ratio = 484 synthesized, prepared according to the Canadian patent, [23] and catalyst samples were crushed and sieved (to mesh size: 355 μm). Samples of 1g zeolite catalyst were loaded into the reactor for each test.

Physicochemical properties of catalyst sample were presented in Table 1. The results obtained from XRD test and SEM image confirmed HZSM-5 template and cubic shape zeolite with the size between 2 to 20 μm which is represented in Figures 1 and 2, respectively.

<table>
<thead>
<tr>
<th>Table 1. Physicochemical properties of the zeolite samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ / Al₂O₃ molar ratio</td>
</tr>
<tr>
<td>Total acidity, (nmole of NH₃)g⁻¹</td>
</tr>
<tr>
<td>Surface area (m²/g, SBET)</td>
</tr>
<tr>
<td>Total pore volume, Vp (cm³/g)</td>
</tr>
<tr>
<td>Average pore diameter , dp (nm)</td>
</tr>
<tr>
<td>Mean crystallites size , S (μm)</td>
</tr>
</tbody>
</table>

Fig. 1. X-ray diffraction pattern of the HZSM-5 zeolite.  
Fig. 2. The SEM micrograph of the HZSM-5 sample prepared in this work.

3. Catalytic performance

n-Butane cracking reaction over HZSM-5 was conducted in a stainless steel tubular reactor with an inner diameter of 10 mm. All runs were performed under a total pressure of 104 kPa and a 20 kPa n-butane partial pressure. This was obtained by an accurate mixing of the paraffin with N₂ as a diluent gas, utilizing two digital mass flow meters. A schematic diagram of the experimental setup was shown in Figure-3. The Reactor heated and kept under isothermal conditions using a vertical furnace and reactions were performed at 470-530°C and a n-butane GHSV (gas hourly space velocity) of 0.24-2.65 gₜₐₜ(h,gₑₐₜ)⁻¹. The products samples were withdrawn periodically and sent to a gas chromatograph (GC, Varian CP, model 4900) for on-line analysis with Star Toolbar software.
4. Catalytic activity tests

\( n \)-Butane conversion, different product selectivity and yields were defined as follows:

\[
\text{Conversion (\%)} = \frac{F_0 - F_e}{F_0} \\
\text{Selectivity } i \text{ (\%)} = \frac{n_i \times F_{ie}}{4 \times (F_0 - F_e)} \\
\text{Yield}_i \text{ (\%)} = \text{Selectivity } i \times \text{Conversion}
\]

Where \( F_0, F_e \) and \( F_{ie} \) are the inlet and outlet butane molar flow rates, and the exit molar flow rate of compound \( i \), all in \( \text{mol.h}^{-1} \); respectively. The Selectivity value for each compound \( i \) was based on the number of carbon atoms for that compound, \( n_i \) (i.e.; on \( \text{CH}_2 \) basis). The term GHSV is the inverse of the contact time, and is defined as the mass flow rate of \( \text{C}_4 \) in \( \text{g.h}^{-1} \) over the total mass of catalyst; i.e.:

\[
\text{GHSV} = \frac{F_0 \left( \frac{g_{C4}}{g \text{cat} \cdot h} \right)}{W}
\]

Where \( W \) is the weight of the catalyst in grams. GHSV values were widely ranged from 0.24 to 2.65 \( \text{h}^{-1} \).

5. Procedure for the kinetic study

The length of the catalyst bed and radius of the reactor was low and temperature difference along the bed was less than 1°C hence, plug flow was assumed in the isothermal fixed-bed reactor. The total reaction rate for each compound at zero time on stream expressed by \( r_i \) was calculated through the sum of all reaction rates of different steps, \( r_j \) in which that lumped compound was involved. The equation and the unit of \( r_i \) were given by:

\[
r_i = \frac{dX_i}{d\tau} = \frac{W}{F_0} \sum_{j=1}^{n_r} (r_j) \left( \frac{(\text{mol}_i)\text{CH}_2}{\text{g.h}} \right)
\]

Where:

\[
r_j = \frac{W}{F_0}
\]
and \( \nu_{ij} \) is the stoichiometric coefficient of compound \( i \) in the reaction step \( j \). In order to simplify the modeling equation, the concentration, \( X_i \), in the equation of reaction rate was expressed as the molar fraction of each compound on CH\(_2\) basis. Furthermore, based upon the definition of \( X_i \), it may be readily related to partial pressure of each product.

The Adams-Bashforth-Moulton method was used for the integration of the set by using a program in MATLAB (R2010-a) [23]. The kinetic parameters for the proposed model should be optimized in order to minimize the following Multi-objective function established as the sum of squares of the differences between the experimental and calculated values of concentrations [24]:

\[
OF = \sum_{i=1}^{n_l} \sum_{k=1}^{m} \left[ (X_{ik} \text{cal} - X_{ik} \text{cal})^2 \right]
\]  

(7)

where: \( n_l \) is the number of lumps; \( m \) is the number of experimental points excluding repetitions; \( X_{ik} \text{cal} \) is the calculated mole fraction of lump \( i \) for experimental condition \( k \), determined by solving the mass balance of equation (5) utilizing a CH\(_2\) basis (i.e.; corresponding to a given value of contact time and temperature); and \( X_{ik} \) is the experimental mole fraction of lump \( i \) for experimental condition \( k \). Estimated kinetic parameters were obtained by nonlinear regression using the Levenberg-Marquardt algorithm in MATLAB [25]. Kinetic parameters to be optimized included Arrhenius parameters for the rate constant for each reaction step \( j \). In order to reduce the correlation between the frequency factor and activation energy, re-parameterization was applied [15-16, 26-27]. The Arrhenius equation of the rate constant was as follows:

\[
k_j = A_j \exp \left( \frac{-E_j}{RT} \right)
\]

(8)

After introduction of the mean temperature, \( T_m \), rate coefficients for the formation of primary products may be written as follows:

\[
k_j = \exp \left[ \ln A_j - \frac{E_j}{RT_m} - \frac{E_j}{R} \left( \frac{1}{T} - \frac{1}{T_m} \right) \right]
\]

(9)

The expression for \( k_j \) thus becomes:

\[
k_j = k_j^* \exp \left[ -\frac{E_j}{R} \left( \frac{1}{T} - \frac{1}{T_m} \right) \right]
\]

(10)

Consequently, at \( T_m = 500^\circ\text{C} \), the parameters to be optimized are the kinetic constant at a reference temperature and the activation energy for each reaction step \( j \).

In order to test the fit between the model and experimental points, additional statistical F-test was utilized to examine the significance of parameters in a regression model. This test involved partitioning the sum of squares of residuals (SS\(_\text{residual}\)) into two components, “pure error” and “lack of fit”:

\[
SS_{\text{residual}} = (SS_{\text{pure error}}) + (SS_{\text{lack of fit}})
\]

(11)

The sum of squares of pure error (SS\(_{\text{pure error}}\)) was the sum of squares of differences between each experimental mole fraction and the average of all experimental mole fractions under the same operating condition. The sum of squares of lack of fit (SS\(_{\text{lack of fit}}\)) was the weighted sum of squares of differences between the averages of replications of the mole fraction for each lump \( i \) corresponding to the same operating condition and fitted mole fraction. The weight for each experimental point was simply the number of replications of the mole fraction for point \( j \). Statistical functions were presented in Table 2 [28-29]. The variance for the lack of fit and pure error was defined as the ratio of the sum of squares over the degrees of freedom. The degrees of freedom were the number of independent points available to estimate a parameter. Definitions for the degrees of freedom corresponding to the statistical functions provided in Table 2. In order to evaluate the significance of the model, the variances of pure error and the lack of fit were compared. For this comparison, an F-ratio statistic test was performed, which provided a measure of testing the null hypothesis or the statistical significance of the lack of fit defined as the ratio of the variance of lack of fit over the variance of pure error:
Table 2. Statistical functions for the significance of the proposed kinetic model.

<table>
<thead>
<tr>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lack of fit</td>
<td>( \sum_{i=1}^{n} \sum_{j=1}^{m} R_{ij} (x_{ij} - \hat{x}_{ij})^2 )</td>
<td>( v_{LF} = mn_{i} - n_{p} )</td>
</tr>
<tr>
<td>Pure error</td>
<td>( \sum_{i=1}^{n} \sum_{j=1}^{m} \sum_{k=1}^{l} (x_{ik} - \hat{x}_{ik})^2 )</td>
<td>( v_{PE} = \left( \sum_{j=1}^{m} R_{ij} - m \right) n_{i} )</td>
</tr>
</tbody>
</table>

To verify that the kinetic model was appropriate (i.e.; that lack of fit was not statistically significant and that the null hypothesis was established) the test statistic value also had to satisfy the following expression:

\[
F < f(\alpha, v_{LF}, v_{PE})
\]  

Where \( f(\alpha, v_{LF}, v_{PE}) \) was the critical value of the Fischer distribution function for given values of degrees of freedom, \( v_{LF} \) and \( v_{PE} \), and \( \alpha \) were the significance level, usually 0.01 or 0.05. In the present case, a 95% confidence level (i.e.; \( 100(1-\alpha)\% \) or \( \alpha = 0.05 \)) was chosen. Critical values of the Fischer distribution function could be obtained from the Fischer distribution tables [30] or from the command \( \text{finv} \) included in MATLAB.

6. Kinetic Model

As shown in Figure-4, five lumped compounds including \( n \)-butane, olefins (i.e.; sum of all light olefins), paraffins (i.e.; sum of all light paraffins), methane and heavy components (\( C_5^+ \) olefins and paraffins plus aromatics) were considered. The kinetic scheme involved six reaction steps corresponding to the experimental data which considered the fundamental and main stages of the reaction mechanisms including cracking of butane into primary and secondary products like light olefins, methane, paraffins and heavy products as well as; olefins transformation into heavy products and paraffins.

Fig. 4. Kinetic scheme proposed. Butane (normal butane, reactant feed), Olefins (Ethylene, Propylene, Butene), Paraffins (Ethane, Propane, iso butane) and Heavy Products (\( C_5^+ \)).
Based upon the kinetics scheme proposed and experimental data obtained, chemical kinetics constants for the reaction steps of this process were determined. Thus, assuming a second order reaction for steps involving olefins (i.e., regardless of whether the olefin was produced or consumed) and unity for other steps, resulted in the following rate expressions:

\[
\begin{align*}
  r_{n-C4} &= -k_1 X_{n-C4}^2 - k_2 X_{n-C4} - k_5 X_{n-C4} \\
  r_{\text{olefins}} &= k_1 X_{n-C4}^2 - k_6 X_{\text{olefins}}^2 \\
  r_{\text{Methane}} &= k_3 X_{n-C4} \\
  r_{\text{Paraffins}} &= k_2 X_{n-C4} + k_4 X_{\text{olefins}}^2 \\
  r_{\text{Heavy Products}} &= k_5 X_{n-C4} + k_6 X_{\text{olefins}}^2
\end{align*}
\]

(14)

7. Results and Discussions

The estimated parameters of the best fit, including the kinetic constants at reference temperature \(T_m\) and activation energies for the 6 reaction steps are laid out in Table 3.

<table>
<thead>
<tr>
<th>Reaction step, (j)</th>
<th>(k_j^*)</th>
<th>(E_j) (J/mol.K)</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0850</td>
<td>113484.5</td>
<td>mol(\text{CH}_2) gcat(^{-1}) h(^{-1}) (mol(n\text{-C}_4)/mol(^{-2}))</td>
</tr>
<tr>
<td>2</td>
<td>0.0566</td>
<td>40021.79</td>
<td>mol(\text{CH}_2) gcat(^{-1}) h(^{-1}) (mol(n\text{-C}_4)/mol(^{-1}))</td>
</tr>
<tr>
<td>3</td>
<td>0.0072</td>
<td>114.642 8</td>
<td>mol(\text{CH}_2) gcat(^{-1}) h(^{-1}) (mol(n\text{-C}_4)/mol(^{-1}))</td>
</tr>
<tr>
<td>4</td>
<td>0.336</td>
<td>154.6171</td>
<td>mol(\text{CH}_2) gcat(^{-1}) h(^{-1}) (mol(n\text{-C}_4)/mol(^{-1}))</td>
</tr>
<tr>
<td>5</td>
<td>0.0023</td>
<td>170170.6</td>
<td>mol(\text{CH}_2) gcat(^{-1}) h(^{-1}) (mol(n\text{-C}_4)/mol(^{-1}))</td>
</tr>
<tr>
<td>6</td>
<td>0.0004</td>
<td>134168.5</td>
<td>mol(\text{CH}_2) gcat(^{-1}) h(^{-1}) (mol(n\text{-C}_4)/mol(^{-1}))</td>
</tr>
</tbody>
</table>

Table 4 set out the statistical parameters and variance analysis of the kinetic model for \(n\)-butane cracking corresponding to the functions introduced in the Table 2.

<table>
<thead>
<tr>
<th>Statistical Variable</th>
<th>O.F</th>
<th>m</th>
<th>n</th>
<th>(S_{1,F})</th>
<th>(S_{2,F})</th>
<th>(v_{1,F})</th>
<th>(v_{2,F})</th>
<th>(\gamma)</th>
<th>(\eta)</th>
<th>(\phi)</th>
<th>(f(\alpha, v_{1,F}, v_{2,F}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0174</td>
<td>24</td>
<td>5</td>
<td>0.0106</td>
<td>0.0064</td>
<td>108</td>
<td>30</td>
<td>12</td>
<td>9.82 \times 10^{-5}</td>
<td>2.13 \times 10^{-4}</td>
<td>0.461</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.690</td>
</tr>
</tbody>
</table>

The agreement between experimental data and calculated values as a function of \(n\)-butane contact time is represented in Figure 5. The experimental results of lumped components and calculated data from the proposed model are respectively shown by points and solid lines in all three figures that each one corresponded to a temperature. It demonstrated that the proposed kinetic model fitted the experimental data very well (i.e., agreement between predicted and experimental data was practically the same). Furthermore, the value of the objective function (see equation (7) of this work, please) was 0.0174, highlighting the accuracy of the present kinetic model. Finally, results of variance analysis indicated the validity of the proposed kinetic scheme.
Fig. 5. Comparison between the experimental data (points) and calculated values (solid line) for n-butane cracking, partial pressure = 20 kPa at: (a) 470 °C, (b) 500 °C, (c) 550 °C.

Conclusion

The synthesized catalyst with special Si/Al = 484 showed low selectivity for the production of heavy products, which may be due to the low acidity and aluminium content in the zeolite structure. A lumped kinetic model consisting of 5 lumps and 6 reaction steps was proposed, and the corresponding constants from the Arrhenius equation for different rate equations were estimated. The proposed model was simple yet elegantly accurate predicting product distributions from the catalytic cracking of the feed. Second order reactions were found to be the best for reactions involving light olefin production or consumption, while first order reactions were better for all other reactions. The agreement between experimental and predicted mole fractions of different lumped compounds was very satisfactory. The information obtained in this study paved down the road for optimization of the process being considered which is currently undertaken.

References


