Kinetic model and Simulation Analysis for Propane Dehydrogenation in an Industrial Moving Bed Reactor

Chin S. Y., Radzi, S. N. R., Maharon, I. H. and Shafawi, M. A.

Abstract—A kinetic model for propane dehydrogenation in an industrial moving bed reactor is developed based on the reported reaction scheme. The kinetic parameters and activity constant are fine tuned with several sets of balanced plant data. Plant data at different operating conditions is applied to validate the model and the results show a good agreement between the model predictions and plant observations in terms of the amount of main product, propylene produced. The simulation analysis of key variables such as inlet temperature of each reactor (T_inrx) and hydrogen to total hydrocarbon ratio (H2/THC) affecting process performance is performed to identify the operating condition to maximize the production of propylene. Within the range of operating conditions applied in the present studies, the operating condition to maximize the propylene production at the same weighted average inlet temperature (WAIT) is \( \Delta T_{\text{inrx1}} = -2 \), \( \Delta T_{\text{inrx2}} = +1 \), \( \Delta T_{\text{inrx3}} = +1 \), \( \Delta T_{\text{inrx4}} = +2 \), and \( \Delta H2/\text{THC} = -0.02 \). Under this condition, the surplus propylene produced is 7.07 tons/day as compared with base case.

Keywords—kinetic model, dehydrogenation, simulation, modeling, propane

I. INTRODUCTION

In order for a company to remain world-class competitive it will be necessary to run the plant with less operating cost and at the same time, increase productivity. To realize this level of performance, it is crucial to simulate and optimize the entire process and plant. This requires a new level of understanding which includes the microkinetic models of each catalytic step. If entire processes are understood at this level, it will be possible to increase the output of most of our reactor systems between 50 and 100% and even up to 200 to 300% sometimes.

Dehydrogenation is a highly endothermic, equilibrium-controlled reaction. Equilibrium conversion and reaction rate increases with temperature, they are likewise favored at lower pressures because the volume of products exceeds that of reactants.

In order to achieve reasonable economic conversion per pass (separation costs of unreacted paraffins are high), temperatures exceeding 550 °C are a prerequisite. High reaction temperature means magnification of side reactions. The stability of paraffins and olefins becomes critically influenced by the several side reactions. Oligomerization to heavier compounds, cracking to lighter hydrocarbons, skeletal isomerization, aromatization, alkylation of the formed aromatic rings, eventually leading to coke formation, lower the yields. Removal of hydrogen from the products improves the equilibrium extent and rate of dehydrogenation. However, recycle of hydrogen helps reduce the coke formation on the catalyst [1].

In view of the reaction characteristics as stated above, the optimum operating condition of the dehydrogenation reactor represents a compromise among the critical factors. In view of this, an accurate model and simulation tool is crucial in identifying the optimum operating condition of the plant [2].

In the present study, several type of kinetic and reactor models was validated using the inter reactor sample data. The best model was identified and rigorous simulations were performed to determine the operating condition for maximizing the production of propylene from dehydrogenation of propane.

II. PROCEDURE

A. Type of Reactor Model Used

In the present study, all the chemical reactions possibly occurred in the reactor were incorporated into the reactor model for simulation. However, isomerization of iso-butane and dehydrogenation of iso-butane and n-butane were ignored due to its’ negligible amount in the exit composition and unpredictable trend. Due to the lack of information, the rate expression to describe coke formation was not included in the present study. The amount of coke formed was assumed to be constant as long as the weighted average inlet temperature remained unchanged.

Since the slow moving bed reactors are employed, the reactors were modeled using plug flow reactor (PFR). In PFR or tubular flow reactor the feed enters at one end of a cylindrical tube and the product exits at the other end. The PFR model used in in-house software assumes there is no mixing in the axial direction and complete mixing in the radial direction. The PFR model is governed by the mole balances and design equations, rate law, stoichiometry, pressure drop
correlations and energy balances equations. The flowsheet in Figure 1 shows the important steps of performing simulation using PFR in the in-house software.

B. Reaction Kinetics

The reaction schemes used in the present study is mainly based on the one developed by Loc et al. [3-4] and Lobera et al. [5-6] in addition to the side reactions proposed based on the inter reactor composition. The kinetic scheme for the propane reactions over the Platinum on Alumina catalyst are parallel network as below:

i. Main reaction (dehydrogenation reaction)

\[
C_3H_8 \leftrightarrow C_3H_6 + H_2
\]

(C3) \hspace{1cm} (= C3) \hspace{1cm} (H2)

ii. Side reaction (cracking reaction)

a. \[C_3H_8 + H_2 \rightarrow C_3H_6 + CH_4\]

(C3) \hspace{1cm} (H2) \hspace{1cm} (C2) \hspace{1cm} (C1)

b. \[C_3H_6 + H_2 \rightarrow C_2H_6 \]

(= C2) \hspace{1cm} (H2) \hspace{1cm} (C2)

c. \[2C_3H_6 + H_2 \rightarrow C_2H_4 \]

(= C3) \hspace{1cm} (H2) \hspace{1cm} (C6)

d. \[C_2H_6 + iC_4H_{10} \rightarrow CH_4, C_2H_4 + 4H_2\]

(= C3) \hspace{1cm} (iC4) \hspace{1cm} (T) \hspace{1cm} (H2)

e. \[C_3H_6 \rightarrow C_2H_4 + CH_4\]

f. \[C_2H_6 + H_2 \rightarrow C_2H_4 + CH_4\]

III. KINETIC PARAMETERS ESTIMATION

A. Rate law developed by Loc et al. [3-4]

The equation describing the main reaction for propane dehydrogenation (reaction I) is taken from Loc et al. [3-4] and it is shown in (1):

\[
r_I = a \times k \left( \frac{1 - P_{C_3H_8}P_{H_2}}{P_{C_3H_8}K_{eq}^{\text{eq}}} \right) \frac{P_{C_3H_8}}{P_{H_2}^{0.5} + K_{C_2H_4}P_{C_3H_8}} \text{kmol/(s.m³)}
\]

(1)

Where \(K_{eq}\) is the equilibrium constant of reaction I

\[K_{eq} = 8.49e + 8 \exp(-118707/(RT)) \text{kPa} \]  (2)

and \(k_0 \) and \(K_{C_2H_4}\) are

\[k_0 = 0.378 \times 10^4 \exp(-2950/T) \text{kmol/(s.m³.kPa)} \]  (3)

\[K_{C_2H_4} = 3.4785 \times 10^4 \exp(7200/T) \text{(kPa)} \]  (4)

Due to the lacking of information on the physical properties of catalyst, the dimensionless catalyst activity, \(a\) is fine tuned using the composition of the reactor inter stage sample. \(a\) for the 1st reactor is 0.34 while for the 2nd, 3rd and 4th reactors is 0.38.

Based on the literature, most of the rate law describing side reactions can be expressed in power law [3-6]. All the activation energy side reactions was taken from the literature while the pre-exponential factor of the Arrhenius equation was fine tuned based on the composition of the inter stage samples. Table I shows the rate laws for all the possible side reactions after fine tuning.

Figure 1: Steps involved in the PFR simulations.

Under tab “Summary”, add and configure a specific conversion, selectivity or yield as a signal port to the PFR.

Under tab “Summary”, add information about the configuration of the PFR. This info is the energy stream out of/into, pressure drop, inner diameter, length and volume.

Under tab “Summary”, add information about the inlet stream. This info is the mass/molar flowrate, temperature, pressure and composition of the stream.

Under reactions tab, click the Add/Edit button to bring up the form where reactions can be added or edited. The reactions tab will display the stoichiometric coefficient matrix for the reactions as soon as they are configured.

The Kinetics tab is where the reaction kinetics are added and/or edited. Check box that enables the use of advanced kinetics, which allows the user to input a set of custom reaction kinetics. The advanced reaction kinetics used in the present study is shown in the section III.

Add/ edit the important data

Solve the model

Obtain simulation results

Fig. 1 Steps involved in the PFR simulations.
B. Rate law developed by Lobera et al. [5-6]

The equation describing the main reaction for propane dehydrogenation (reaction 1) is taken from Lobera et al. [4-5] and it is shown in (5):

$$r_1 = a k_1 \left( P_{C_3} \left( P_{C_5}/K_{eq} \right) \right) \frac{1}{1+ \left( P_{C_3}/K_{eq} \right)}$$

Where $K_{eq}$ is the equilibrium constant of reaction 1

$$K_{eq} = 8.49 e^{8e(-118707/(RT))} \text{ kPa}$$

and $k_1$ and $K_{eq}$ is

$$k_1 = 5.15 e^{-5e(-34570/(1-793.15))} \text{ (kmol/s·m}^3\text{·kPa)}$$

$$K_{eq} = 349 e^{85817/(1-793.15)} \text{ kPa}$$

Due to the lacking of information on the physical properties of catalyst, the dimensionless catalyst activity, $a$ is fine tuned using the composition of the reactor interstage sample. The $a$ for the 1st, 2nd, 3rd and 4th reactors are 0.33, 0.47, 0.55 and 0.68 correspondingly.

Similar with the previous section, the reaction kinetics describing side reactions were fine tuned and it is shown in Table II.

In order to distinguish the PFR model incorporated with 2 different reaction kinetics, PFR model incorporated with reaction kinetics developed by Loc et al. [3-4] is labeled as PFR_Loc Model, whereas the PFR model incorporated with reaction kinetics developed by Lobera et al. [5-6] is labeled as PFR_Lobera Model.
simulation. The simulation was done solely based on the axial variations.

Fig. 3 Product and reactant compositions of the main reaction in the reactor exit stream

Exit composition of Rx 1

Exit composition of Rx 2

Exit composition of Rx 3

Exit composition of Rx 4

(a)

(b)

(c)

(d)

Fig. 4 Product compositions of the side reactions in the reactor exit stream
TABLE IV AARE FOR THE MODELS USED IN EXIT COMPOSITION PREDICTION.

<table>
<thead>
<tr>
<th>Component</th>
<th>Base Case AARE</th>
<th>Case 1 AARE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFR_Loc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>0.69%</td>
<td>0.65%</td>
</tr>
<tr>
<td>C3=</td>
<td>5.39%</td>
<td>4.18%</td>
</tr>
<tr>
<td>H2</td>
<td>20.63%</td>
<td>7.14%</td>
</tr>
<tr>
<td>C1</td>
<td>8.20%</td>
<td>7.83%</td>
</tr>
<tr>
<td>C2</td>
<td>13.62%</td>
<td>5.97%</td>
</tr>
<tr>
<td>C2=</td>
<td>11.48%</td>
<td>11.97%</td>
</tr>
<tr>
<td>BTX +</td>
<td>8.77%</td>
<td>18.43%</td>
</tr>
<tr>
<td>Heavies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AARE</td>
<td>9.83%</td>
<td>8.02%</td>
</tr>
<tr>
<td>PFR_Lobera</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>0.65%</td>
<td>0.42%</td>
</tr>
<tr>
<td>C3=</td>
<td>6.07%</td>
<td>4.09%</td>
</tr>
<tr>
<td>H2</td>
<td>20.54%</td>
<td>7.31%</td>
</tr>
<tr>
<td>C1</td>
<td>7.56%</td>
<td>7.50%</td>
</tr>
<tr>
<td>C2</td>
<td>11.08%</td>
<td>8.40%</td>
</tr>
<tr>
<td>C2=</td>
<td>11.48%</td>
<td>13.17%</td>
</tr>
<tr>
<td>BTX +</td>
<td>12.35%</td>
<td>22.16%</td>
</tr>
<tr>
<td>Heavies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AARE</td>
<td>10.03%</td>
<td>9.01%</td>
</tr>
</tbody>
</table>

Figure 5 shows the yield per pass profiles of the entire reactor system. The increase in temperature from reactor 1 to 4 has increased the conversion as more propane is converted to the main and side products. Nevertheless, the selectivity from reactor 1 to 4 is suppressed by the increase of temperature because high temperature favors the formation of side products. As a whole, the yield per pass was increasing throughout the entire reactor system, as can be seen from Figure 5. Since PFR_Loc model could predict the composition of propane and propylene with smaller absolute relative error of <5.5% as shown in Table IV, the yield per pass is also better described by this model.

B. Model Validation with Different Cases

In order to test the consistency of the models, the operating conditions were varied. For Case 1, the inlet temperature of the Reactor 1 was decreased 1 deg. C while the inlet temperature of Reactor 4 was increased 1 deg. C. The operating condition and composition of the product were the average value of 5 days (25 Nov 2010, 6 Dec 2010, 10 Dec 2010, 13 Dec 2010 and 16 Dec 2010). The same models were adopted for the simulations and AARE for all the models in exit composition prediction of both cases is compared in Table IV. It is found that all the models could predict the composition of case 1 with lower AARE and PFR_Loc Model offers the least AARE. In addition to the composition validation under different cases, the best model, PFR_Loc Model also was tested using the archive data in terms of its consistency in predicting the amount of propylene produced. Table V shows the operating conditions of all the cases selected for the study.

TABLE V OPERATING CONDITIONS OF ALL THE SELECTED CASES FOR THE VALIDATION OF THE AMOUNT OF PROPYLENE PRODUCED.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>Inlet temperature difference, $\Delta T_{inrx}$</th>
<th>H2/THC molar ratio difference, $\Delta$H2/THC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rx 1</td>
<td>-1.33 -0.05 -0.05 1.42 0.00</td>
<td></td>
</tr>
<tr>
<td>Rx 2</td>
<td>-0.07 -0.21 -2.95 0.03 0.00</td>
<td></td>
</tr>
<tr>
<td>Rx 3</td>
<td>0.24 0.22 0.36 0.44 0.04</td>
<td></td>
</tr>
<tr>
<td>Rx 4</td>
<td>-0.02 -0.16 -0.09 0.06 0.05</td>
<td></td>
</tr>
<tr>
<td>Rx 5</td>
<td>0.11 -0.16 -0.10 0.42 0.06</td>
<td></td>
</tr>
</tbody>
</table>

*Due to its’ confidentiality, all the number in the table is given as the difference with base case.

From Table VI, the deviation of the predicted amount of propylene produced from plant data is approximately 4.41% (absolute relative error, ARE). The results also show that the changes predicted by the model is identical to the changes generated from the plant data. These changes are referring to the changes of propylene flow rate in liquid product as compared with the base case. In case 2, more propylene has been produced with a decrease in inlet temperature of the 1st reactor and an increase in the inlet temperature of the 4th reactor. In case 3, a reduction in the inlet temperature of the 3rd reactor has caused a reduction in the propylene production. From case 4 to case 6, the increase in the H2/THC ratio has reduced the amount of propylene in the liquid product. All these changes are observed due to the nature of the dehydrogenation reaction, which is endothermic equilibrium limited. Higher temperature and lower H2/THC ratio shift the reaction to the forward direction. Hence, more propylene is produced.

C. Simulation Analysis

1. Effect of reactor inlet temperature

The inlet temperature of each reactor in the entire reactor system was varied by ±2 °C while the H2/THC ratio, inlet flow rate and inlet stream composition were kept constant. The simulation results show that reactor system with higher WAIT will produce more propylene and vice versa if it is operated at lower WAIT as compared with base case. Higher temperature favors the forward reaction of the highly endothermic dehydrogenation reaction and hence more
propylene will be produced. Part of the simulation results under the same WAIT have been sorted out and tabulated in Table VII.

### Table VI
**COMPARISON OF THE AMOUNT OF PROPYLENE PRODUCED BETWEEN PLANT DATA AND RESULTS PREDICTED BY THE MODEL SIMULATION**

<table>
<thead>
<tr>
<th>Case No.</th>
<th>Propylene in liquid product, kg/hr</th>
<th>ARE, %</th>
<th>Rx 1</th>
<th>Rx 2</th>
<th>Rx 3</th>
<th>Rx 4</th>
<th>Changes in propylene flow rate as compared with base case, kg/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.99 4.15</td>
<td>66.79</td>
<td>0.01</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>-0.65</td>
</tr>
<tr>
<td>3</td>
<td>4.54 4.15</td>
<td>-557.02</td>
<td>0.01</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>-0.97</td>
</tr>
<tr>
<td>4</td>
<td>4.49 4.15</td>
<td>-169.05</td>
<td>0.01</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>-1.15</td>
</tr>
<tr>
<td>5</td>
<td>4.34 4.15</td>
<td>-289.52</td>
<td>0.01</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0.66</td>
</tr>
<tr>
<td>6</td>
<td>4.70 4.15</td>
<td>-199.23</td>
<td>0.01</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1.02</td>
</tr>
</tbody>
</table>

**+** represents surplus, - represents shortage

Base on the data no. 4-6, 9-10, 12, 16-18, 21-22 and 24 in Table VII, the amount of propylene reduced due to the decrease of inlet temperature of one reactor can be compensated by the amount of propylene produced by the following reactor with the increase of temperature. As compared with the base case, surplus propylene can be produced under these operating conditions because of the difference in the degree of sensitivity of equilibrium conversion to reactor temperature (S). Based on the data given by Cavani and Trifiro [10], the equilibrium conversion is most sensitive to the temperature when the temperature is ranged at 600-650 °C. Therefore, S of the reactor system is ranked as $S_{4th\, reactor} > S_{3rd\, reactor} > S_{2nd\, reactor} > S_{1st\, reactor}$. An increase of 1 °C in the inlet temperature of 4th reactor could produce more propylene if comparing with an increase of 1 °C in the inlet temperature of 1st, 2nd and 3rd reactors.

Under the identical WAIT, the maximum amount of propylene could be produced when the inlet temperature differences from the base case for 1st, 2nd, 3rd and 4th reactor are -2 °C, +1 °C, +1 °C and +2 °C respectively. The amount of propylene produced is an additional 6.5 tons/day as compared to the base case. The reduction of the inlet temperature of the 1st reactor has reduced the amount of main and side products. Nevertheless, the amount of propylene and side products produced by the reactor system is more as compared with base case because the reduction in the 1st reactor has been compensated by the increment in the 2nd, 3rd and 4th reactors with the increase of inlet temperature.

### Table VII
**SIMULATION RESULTS FOR THE STUDY OF EFFECT OF INLET TEMPERATURE**

<table>
<thead>
<tr>
<th>No.</th>
<th>$\Delta T_{inrx1}$</th>
<th>$\Delta T_{inrx2}$</th>
<th>$\Delta T_{inrx3}$</th>
<th>$\Delta T_{inrx4}$</th>
<th>Difference in mass flow rate as compared with base case, tons/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>*0.02</td>
<td>-0.58</td>
<td>0.00</td>
<td>0.00</td>
<td>0.56</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>-0.29</td>
<td>0.00</td>
<td>0.00</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
<td>0.29</td>
<td>-0.01</td>
<td>-0.01</td>
<td>*0.02</td>
</tr>
<tr>
<td>4</td>
<td>-0.01</td>
<td>0.29</td>
<td>-0.01</td>
<td>-0.01</td>
<td>*0.02</td>
</tr>
<tr>
<td>5</td>
<td>-0.02</td>
<td>0.56</td>
<td>-0.01</td>
<td>-0.01</td>
<td>*0.02</td>
</tr>
</tbody>
</table>

**Due to its’ confidentiality, all the H2/THC in the table is given as the difference with base case.

### Table VIII
**EFFECT OF H2/THC RATIO**

<table>
<thead>
<tr>
<th>No.</th>
<th>$\Delta H2/THC$</th>
<th>Difference in mass flow rate as compared with base case, tons/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>*0.02</td>
<td>-0.58</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>-0.29</td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>-0.01</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>-0.02</td>
<td>0.56</td>
</tr>
</tbody>
</table>

**Due to its’ confidentiality, all the H2/THC in the table is given as the difference with base case.

2. Effect of H2/THC Ratio

The H2/THC ratio of the entire reactor system was varied by ±0.02 while the inlet temperature, inlet flow rate and inlet stream composition were kept constant. From Table VIII, the simulation results show that reactor system with lower H2/THC ratio will produce more propylene and vice versa if it is operated at higher H2/THC ratio as compared with base case. The reactor system operates at H2/THC ratio difference of -0.02 (data no. 5 in Table VIII) gives maximum surplus of propylene production as compared with the base case, which is 0.56 tons/day. Lower H2/THC ratio shifts the reaction equilibrium to the product side and hence more propylene will be produced.

3. Effect of the combination of reactor inlet temperature and H2/THC ratio

The H2/THC ratio and inlet temperature of the entire dehydrogenation system were varied by ±2 °C and ±0.02 respectively, while the inlet flow rate and inlet stream composition were kept constant. The simulation results show that the operating condition that maximize the production of propylene is $\Delta T_{inrx1} = -2, \Delta T_{inrx2} = +1, \Delta T_{inrx3} = +1, \Delta T_{inrx4} = +2$.
and $\Delta H_2/\text{THC} = -0.02$. Under this condition, the surplus propylene produced is 7.07 tons/day.

V. CONCLUSION

Among the models studied, model PFR_Loc offers the least AARE for the composition prediction of the dehydrogenation system under various operating conditions. Model PFR_Loc is robust to predict the changes in composition when there are changes in the operating conditions.

Higher temperature and lower H2/THC shifts the dehydrogenation reaction to the product side and hence more propylene will be produced.

In the reactor system at the same WAIT, it is preferably to increase the temperature of the reactors which operate at higher range of temperature to obtain more surplus propylene as compared with the base case (e.g., increase the temperature of reactor 2 could have more surplus propylene as compared with increasing the temperature of reactor 1; increase the temperature of reactor 3 could have more surplus propylene as compared with increasing the temperature of reactor 2).

Within the range of operating conditions applied in the present study, the operating condition to maximize the propylene production is $\Delta T_{\text{inrx1}} = -1$, $\Delta T_{\text{inrx2}} = +1$, $\Delta T_{\text{inrx3}} = +1$, $\Delta T_{\text{inrx4}} = +2$ and $\Delta H_2/\text{THC} = -0.02$. Under this condition, the surplus propylene produced is 7.07 tons/day as compared with base case.

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REFERENCES