Dynamic Modeling and Simulation of Industrial Naphta Reforming Reactor
Gholamreza Zahedi, M. Tarin, M. Biglari

Abstract—This work investigated the steady state and dynamic simulation of a fixed bed industrial naphta reforming reactors. The performance of the reactor was investigated using a heterogeneous model. For process simulation, the differential equations are solved using the 4th order Runge-Kutta method. The models were validated against measured process data of an existing naphta reforming plant. The results of simulation in terms of components yields and temperature of the outlet were in good agreement with empirical data. The simple model displays a useful tool for dynamic simulation, optimization and control of naphta reforming.

Keywords—Dynamic simulation, fixed bed reactor, modeling, reforming

I. INTRODUCTION

CATALYTIC reforming of naphta is a major process to produce gasoline with high octane number in refinery and petrochemical industry. In this process paraffins and naphthenes are converted to aromatics by platinum catalyst. The catalytic reforming uses a bifunctional catalyst by which an acidic function (provided by a chlorinated alumina carrier) is combined with a hydrogenation/dehydrogenation function (provided by platinum with a second metal) [1]. The improvement in octane quality is mainly achieved by the formation and concentration of aromatic hydrocarbons as a result of a variety of reactions [2]. A simple model was suggested by Smith [3], in which naphta reforming is considered as a combination of four reactions. Ancheyta et al. [4] presented a kinetic equation which was incorporated in a fixed-bed uni-dimensional pseudo homogeneous adiabatic reactor model. Rahimpour et al. [5] presented kinetics and deactivation models for industrial catalytic naptha reformers, as well.

A dynamic simulation of reforming process with catalyst regeneration and circulation was carried out by Lee et al. [6]. In their modeling, seven CSTRs (Continuous Stirred Tank Reactor) were used for each reactor and to account for catalyst deactivation each CSTR was divided into N fragments. The corresponding models were solved as a series of equations within each CSTR. The lifting gas flow rate was used in the dynamic simulation for controlling catalyst circulation and regeneration rate, and good agreement with plant data was achieved for both steady state and dynamic simulations.

A simulation model for catalytic reforming has been also developed by Padmavathi and Chaudhuri [7] to monitor commercial plant performance. The model involved 35 pseudo components.

Khosrvinapour, Mostafazadeh and Rahimpour [8] presented modeling and simulation of a catalytic membrane naptha reformer. They showed that there are many advantages in using membrane reactors; including a lower temperature than customary fixed-bed reactors which results in longer life of catalysts and higher aromatic generation rate, among other positive effects.

Simulation of the naphta reforming process needs information pertaining to reaction kinetics, as well as mass and heat transfer between gas phase and catalyst surface. Stjepovic et al. [9] presented a series of reliable kinetic data. Several other models have been also reported in the literature for naphta reforming. Yet a critical inspection of the literature discloses that there is sparse amount of information available concerning the use of dynamic models for industrial naphta reforming reactors in the face of catalyst deactivation. Consequently, this paper presents the results of a dynamic simulation of naphta reforming in the presence of catalyst deactivation by a dynamic simulator.

II. PROCESS DESCRIPTION

Use Naphtha reforming process converts low octane gasoline to high octane number. Fig. 1 shows process flow diagram of the naphta reforming process in Kermanshah refinery, Iran. The naphta feed is mixed with rich hydrogen recycle gas and then is heated to desired temperature and enters the first reactor. The molar ratio of H2/HC must be kept at a specific level [10, 7]. Most of the reactions are endothermic and result in temperature drop across the reactor and reduction in the reactions rate. To avoid temperature decline, reactions take place in three reactors instead of one reactor [9]. The effluent of first reactor is reheated and is directed to second reactor in which mostly isomerization reactions take place. Outlet of second reactor after heating is entered to third reactor. In this reactor dehydrocyclization and cracking occur; however, the temperature drop across the third reactor is marginal because of exothermic behavior of the reactions. The outlet of third reactor is then cooled and separated to liquid and gas phases in a high pressure separator drum. The gas phase which is rich in hydrogen is recycled and the liquid phase after stripping from some light gases is sent to gasoline tanks.

G. Zahedi is with Process Systems Engineering Centre (PROSPECT), Faculty of Chemical Engineering, Universiti Teknologi Malaysia, UTM Skudai, 81310 Johor Bahru, Johor, Malaysia (Fax:+(6)-07-5581463; Email: grzahedi@cheme.utm.my, grzahedi@yahoo.com)
M. Tarin graduated from Chemical Engineering Department, Razi University, Iran.
M. Biglari is with Department of Chemical Engineering, Ryerson University, Toronto, Ontario, Canada MSB 2K3

II. PROCESS DESCRIPTION

Use Naphtha reforming process converts low octane gasoline to high octane number. Fig. 1 shows process flow diagram of the naphta reforming process in Kermanshah refinery, Iran. The naphta feed is mixed with rich hydrogen recycle gas and then is heated to desired temperature and enters the first reactor. The molar ratio of H2/HC must be kept at a specific level [10, 7]. Most of the reactions are endothermic and result in temperature drop across the reactor and reduction in the reactions rate. To avoid temperature decline, reactions take place in three reactors instead of one reactor [9]. The effluent of first reactor is reheated and is directed to second reactor in which mostly isomerization reactions take place. Outlet of second reactor after heating is entered to third reactor. In this reactor dehydrocyclization and cracking occur; however, the temperature drop across the third reactor is marginal because of exothermic behavior of the reactions. The outlet of third reactor is then cooled and separated to liquid and gas phases in a high pressure separator drum. The gas phase which is rich in hydrogen is recycled and the liquid phase after stripping from some light gases is sent to gasoline tanks.

G. Zahedi is with Process Systems Engineering Centre (PROSPECT), Faculty of Chemical Engineering, Universiti Teknologi Malaysia, UTM Skudai, 81310 Johor Bahru, Johor, Malaysia (Fax:+(6)-07-5581463; Email: grzahedi@cheme.utm.my, grzahedi@yahoo.com)
M. Tarin graduated from Chemical Engineering Department, Razi University, Iran.
M. Biglari is with Department of Chemical Engineering, Ryerson University, Toronto, Ontario, Canada MSB 2K3

Fig. 1 Process flow diagram for Naphtha reforming [10]
Tables I and II exhibit the characteristics of the studied industrial naphtha reforming reactor.

### TABLE I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (wt%)</td>
<td>0.3</td>
</tr>
<tr>
<td>Re (wt%)</td>
<td>0.3</td>
</tr>
<tr>
<td>Void fraction of bed</td>
<td>0.36</td>
</tr>
<tr>
<td>Density of bed catalyst (kg.l(^{-1}))</td>
<td>0.3</td>
</tr>
<tr>
<td>Catalyst diameter (mm)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

### TABLE II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha (kg/h)</td>
<td>30.41×10(^3)</td>
</tr>
<tr>
<td>(\text{H}_2/\text{HC}) molar ratio</td>
<td>4.74</td>
</tr>
<tr>
<td>Mole percent of (\text{H}_2) in recycle</td>
<td>69.5</td>
</tr>
<tr>
<td>Diameter and Length of first reactor (M)</td>
<td>1.52, 6.29</td>
</tr>
<tr>
<td>Diameter and Length of second reactor (M)</td>
<td>1.67, 7.13</td>
</tr>
<tr>
<td>Diameter and Length of third reactor (M)</td>
<td>1.98, 7.89</td>
</tr>
</tbody>
</table>

### III. REACTION KINETICS

There were few kinetic models with industrial application. Among the models the kinetics proposed by smith [3] was employed in our study. In this kinetic model, naphtha reforming is summarized as the main fractions of aromatics, paraffins and naphthenes. Four main reactions are dehydrogenation on naphthenes, dehydrocyclization of paraffins, hydrocracking of naphthenes and hydrocracking of paraffins. The four reactions are given as the following [3]:

\[
\text{Naphthenes} \rightarrow \alpha \text{H}_2 + 3 \text{H}_2 \quad (1)
\]

\[
\text{Paraffins} + \frac{n}{3} \text{H}_2 \rightarrow \frac{n}{15} \text{C}_1 + \frac{n}{15} \text{C}_2 + \frac{n}{15} \text{C}_3 + \frac{n}{15} \text{C}_4 + \frac{n}{15} \text{C}_5 \quad (2)
\]

\[
\text{Naphthenes} + \frac{n}{3} \text{H}_2 \rightarrow \frac{n}{15} \text{C}_1 + \frac{n}{15} \text{C}_2 + \frac{n}{15} \text{C}_3 + \frac{n}{15} \text{C}_4 + \frac{n}{15} \text{C}_5 \quad (3)
\]

\[
\text{Paraffins} + n \text{H}_2 \rightarrow \frac{n}{15} \text{C}_1 + \frac{n}{15} \text{C}_2 + \frac{n}{15} \text{C}_3 + \frac{n}{15} \text{C}_4 + \frac{n}{15} \text{C}_5 \quad (4)
\]

Accordingly, the rates of reactions are determined as follows [3, 8]:

\[
R_1 = \frac{k_1}{K_1}(P_n - P_i) \quad (5)
\]

\[
R_2 = \frac{k_2}{K_2}(P_n - P_i) \quad (6)
\]

\[
R_3 = \frac{k_3}{P_i}(P_n - P_i) \quad (7)
\]

\[
R_4 = \frac{k_4}{P_i} \quad (8)
\]

Where \(R_1, R_2, R_3\) and \(R_4\) are reaction rates of naphtha reforming respectively. \(P_i\) (\(i = \text{paraffins, aromatics, naphthenes and H}_2\)) is a partial pressure of component \(i\). \(k_1, k_2, k_3\) and \(k_4\) are the rate coefficient of reaction, respectively, while \(K_1, K_2, K_3\) and \(K_4\) are equilibrium constants of the reactions, respectively. The expressions of these parameters are given as below [3]:

\[
K_1 = 1.04 \times 10^3 \exp(46.15 - 50784 / 1.8T) \quad (9)
\]

\[
K_2 = 9.87 \exp(-7.12 + 8000 / 1.8T) \quad (10)
\]

\[
k_1 = 9.87 \exp(23.21 - 34750 / 1.8T) \quad (11)
\]

\[
k_1 = 9.87 \exp(35.98 - 59600 / 1.8T) \quad (12)
\]

\[
k_1 = (49.97 - 62300 / 1.8T) \quad (13)
\]

### IV. MATHEMATICAL MODEL

The catalyst deactivation gives unsteady state behavior to the process and the reactors; therefore, in order to build dynamic model of the reactor the following assumptions were made:

1) One dimensional plug flow is considered.
2) Axial dispersion of heat is neglected compared to convection term.
3) There are no radial concentration and temperature gradients.

Fig. 2 shows an element along the reactors bed for applying governing equations.

![Fig. 2 An element of length \(\Delta z\), in the tubular reactor](image-url)
A. Deactivation Model

The catalyst deactivation model for commercial naphtha reforming has been used from Ref. [11] as:

$$\frac{da}{dt} = -k_{\text{Act}} \exp \left( -\frac{E_{\text{Act}}}{RT} \left( 1 - \frac{1}{T} \right) \right) a^n$$  \hspace{1cm} (20)

B. Heat and Mass Transfer Coefficients

Mass transfer coefficient between gas phase and solid phase is given by the following equation [12]:

$$k_p = \frac{0.458}{\varepsilon_b} (\text{Re}_{\text{f}})^{-0.407} (0.123 \rho m_d / \mu)^{0.458}$$  \hspace{1cm} (21)

And heat transfer coefficient between gas phase and solid phase was obtained from Ref. [13] as below:

$$h_i = 0.2G C_i \text{Re}_i^{0.6} \text{Pr}^{0.6}$$  \hspace{1cm} (22)

C. Numerical Solution

In order to investigate effect of process parameters on production rate, the set of partial differential equations, ordinary differential equations of deactivation model, non linear algebraic equations of reaction rates and auxiliary correlations should be solved numerically. In this case, the equations initially were solved based on our previous experience on the process steady state model by setting time derivatives in Equations 14-17 to zero and considering the activity to be unity.

So by using backward finite difference method the steady state simulation are converted to nonlinear algebraic equations [14]. The reactor was separated into several segments and then Gauss–Newton method was used to solve the nonlinear algebraic equations in each segment [14]. The consequence of the steady state simulation was utilized as the initial conditions for dynamic state equations in each node of the reactor. In order to solve a dynamic simulation the set of equations have been separated in axial coordinate on the nodes so partial differential equations are altered to ordinary differential equations. The 4th order Runge–Kutta approximation was used to solve ordinary differential equations. All programs were carried out in MATLAB 7.5 software [15].

V. RESULTS AND DISCUSSIONS

A. Steady-state Module

In order to investigate the validation of steady state model, the consequence of steady state simulation and plant data at zero time are given in Table III. Fig. 3 to 7 display the mole fraction of reactants, products and temperature for gas phase along the reactor resulting from steady state simulation. From Fig. 3 and Fig. 4, paraffin and naphthen mole fractions decrease while in Fig. 5 and Fig. 6, aromatic and hydrogen mole fractions increase along the reactor. Fig. 7 shows temperature profile of gas phase along the reactor.

**TABLE III**

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Outlet Temperature (K)</th>
<th>Aromatic in Reformate (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant</td>
<td>Simulation</td>
<td>Plant Simulation</td>
</tr>
<tr>
<td>1</td>
<td>759</td>
<td>760</td>
</tr>
<tr>
<td>2</td>
<td>765</td>
<td>766</td>
</tr>
<tr>
<td>3</td>
<td>772</td>
<td>769.5</td>
</tr>
</tbody>
</table>

![Fig. 3 Paraffin mole fraction profile along the reactor axis for fluid phase under steady state condition](image1)

![Fig. 4 Naphthen mole fraction profile along the reactor axis for fluid phase under steady state condition](image2)

![Fig. 5 Aromatic mole fraction profile along the reactor axis for fluid phase under steady state condition](image3)
B. Dynamic Module

Table V indicates validation of dynamic model for reformate production rate. It was illustrated that, there is a good agreement between dynamic simulation results and historical process data from [10]. Fig. 8 to 12 shows the three dimensional gas phase components and activity of the catalyst along the reactor during operation time of naphtha reforming reactors. Fig. 8 and 9 illustrate the aromatic and hydrogen mole fractions versus time and length for naphtha reforming reactors, respectively. The mole fractions of aromatics and hydrogen increase along the reactor, while they decrease as time passes due to catalyst deactivation.

Table IV

<table>
<thead>
<tr>
<th>Day</th>
<th>Industrial data (ton/day)</th>
<th>Simulation result (ton/day)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>225.90</td>
<td>212.70</td>
<td>5.8</td>
</tr>
<tr>
<td>34</td>
<td>224.25</td>
<td>216.32</td>
<td>3.5</td>
</tr>
<tr>
<td>62</td>
<td>229.65</td>
<td>220.15</td>
<td>3.8</td>
</tr>
<tr>
<td>97</td>
<td>229.65</td>
<td>223.60</td>
<td>4.1</td>
</tr>
<tr>
<td>125</td>
<td>229.65</td>
<td>226.04</td>
<td>2.6</td>
</tr>
<tr>
<td>160</td>
<td>211.60</td>
<td>205.71</td>
<td>1.6</td>
</tr>
<tr>
<td>188</td>
<td>222.75</td>
<td>218.07</td>
<td>2.1</td>
</tr>
<tr>
<td>223</td>
<td>233.05</td>
<td>226.10</td>
<td>2.9</td>
</tr>
<tr>
<td>243</td>
<td>228.65</td>
<td>221.70</td>
<td>7.8</td>
</tr>
<tr>
<td>321</td>
<td>227.64</td>
<td>222.33</td>
<td>2.3</td>
</tr>
<tr>
<td>398</td>
<td>317.30</td>
<td>3.6.64</td>
<td>3.3</td>
</tr>
<tr>
<td>425</td>
<td>317.94</td>
<td>308.95</td>
<td>2.8</td>
</tr>
<tr>
<td>461</td>
<td>317.94</td>
<td>309.26</td>
<td>2.7</td>
</tr>
<tr>
<td>490</td>
<td>317.94</td>
<td>301.23</td>
<td>5.3</td>
</tr>
<tr>
<td>524</td>
<td>317.94</td>
<td>302.70</td>
<td>3.1</td>
</tr>
<tr>
<td>567</td>
<td>317.94</td>
<td>304.39</td>
<td>4.3</td>
</tr>
<tr>
<td>610</td>
<td>313.90</td>
<td>304.65</td>
<td>2.9</td>
</tr>
</tbody>
</table>
VI. CONCLUSIONS

An industrial naphtha reforming reactor was modeled and also simulated by the heterogeneous model. The proposed model has been solved numerically using the 4th order Runge–Kutta approach. Alteration of components and temperature, with time and reactor length was evaluated. Moreover, the model was validated with a typical plant industrial data. The model performed satisfactorily well at industrial conditions and a good agreement between the plant data and the simulation results was obtained.

ACKNOWLEDGMENT

Financial support of Universiti Teknologi Malaysia under RUG no Q.J130000.2525.00H81 is gratefully acknowledged.

REFERENCES


NOMENCLATURE

ΔHᵢ  enthalpy change of reaction i (kJ/mol)
aₑ  external particle surface area per unit of reactor volume (m²,m⁻¹)
a  activity of catalyst (-)
cₚₑ  Specific heat of the gas at constant pressure (kJ.mol⁻¹. K⁻¹)
cₚₛ  Specific heat of the solid at constant pressure (kJ.kg⁻¹. K⁻¹)
cᵢ  total concentration (mole.m⁻³)
Eₐct  activation energy used in the deactivation model (j.mole⁻¹)
G  Superficial gas flow rate (m.h⁻¹)
hᵢ  gas inside heat transfer coefficient (kJ.m⁻².K⁻¹.h⁻¹)
Kᵦᵢ  deactivation model parameter constant (h⁻¹)
Kᵦᵢ  mass transfer coefficient for component i (m.h⁻¹)
adSORB  dissociative adsorption constant of H₂O(-)
Kᵢᵢ, Kᵢᵢ  equilibrium constant (MPa⁻¹) for reaction (1) and (MPa⁻¹)
Kᵢᵢ  equilibrium constant of reaction 2(-)
kᵢᵢ  forward rate constant (kmol.h⁻¹.kg⁻¹.MPa⁻¹) for reaction (1) and (kmol.h⁻¹.kg⁻¹.MPa⁻²) for reaction (2) and (kmol.h⁻¹.kg⁻¹) for reactions (3) and (4)
n  sintering order(-)
pᵢ  Partial pressure of component i(bar)
R  universal gas constant (j.mol⁻¹.K⁻¹)
Rᵢᵢ, Rᵢᵢ  rates of reactions 1, 2 and 3 (kmole.kg⁻¹.hr⁻¹)
Reᵢᵢ  Reynolds number of tube(-)
Reᵢᵢ  Reynolds number of particle(-)
T  temperature of gas on the solid surface (K)
Tᵢᵢ  temperature of gas phase (K)
t  time (h)
u  superficial velocity (m.h⁻¹)
yᵢᵢ  bulk gas phase mole fraction for component i (-)
yᵢᵢ  Surface mole fraction of ith component in the solid phase (-)
Z  axial reactor coordinate (m)

Greek letters

εᵦ  void fraction of catalytic bed (m³,g⁻¹)
εₛ  solid particles’ void fraction (m³,m⁻³)
ρ  density of gas mixture(Kg. m⁻³)
ρᵦ  bed density of catalyst(Kg. m⁻³)
µ  Viscosity of gas mixture(kg.m⁻¹.h⁻¹)

Superscripts and subscripts

0  inlet conditions
s  initial conditions


