Modeling, Simulation and Optimization of Dehydrogenation and Dehydrocyclization Reactions

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Abstract

Catalytic reforming of heavy naphtha is an essential process in oil industries. A mathematical model isconstrcteded to describe the reactions inside the reactorsand to be applicale for an industrial catalytic reformer unit.The industrial reformer reactor is considered as an ideal plug flow reactor. The reaction network consisted of naphthenedehydrogenation and paraffin dehydrocyclization reactions which are the main reactions that take place in the reforming process.Themodel describe conservation equations of mass and energyused to determine the outlet concentrations of paraffins, naphthenes and aromatics for the main reactions in the reformer. This model includes four sequencing moving beds of catalyst at the steadystate condition which is based on components aggregation into one group (C_7). This model is used to estimate the outlet temperatures from the first and the second reactor by using the computer program Matlab. The estimated outlet concentrations and temperatures agrees very well withtheindustrial data which were shown by small percent deviation. Based on the model of the whole reforming process and process variable analysis;sensitivity analysis is conducted. the process is optimized. Therefore, the model can be used in monitoring the performance of similar reactors.

Keywords: *Catalytic Reforming, Modeling, imulation,dehydrogenation ,dehydrocyclization*

I. INTRODUCTION

Catalytic reforming of naphtha is one of the most important processes for high octane gasoline manufacture and aromatic hydrocarbons production [1]. This process is classified into three types; semi-regenerative fixed bed reactor, cyclic fixed bed reformer and continuous reformers[2]. There are four major reactions that take place during reforming. They are: (1) dehydrogenation of naphthenes to aromatics, (2) dehydrocyclization of paraffins to aromatics, (3) isomerization, and (4) hydrocracking [3]. The bifunctional metal–acid catalysts are generally porous oxides with acid properties that have a small amount of a metal supported on them. The acid function of the support and the metal function may be tuned to promote the desired reaction selectivity by the addition of promoters [4]. The entire reactor charge is heated and passed through the catalytic reformers, which are designed with four adiabatically, operated reactors and 4 furnaces (heaters) between the reactors to keep the reaction temperature at design levels [5].

Many articles have been published about the modeling of naphtha reforming process. The earlier studiess of reforming are about radial and axial flow, spherical fixed bed reactors, which study the effect of pressure and temperature on conversion and hydrogen production [6-10], some researches were about semi-regenerative naphtha catalytic reforming process [11,12], other research studied the effect of catalyst activity on reformat production and RON using CCR moving bed reactor [13-16]. This work aims to simulate the model of the CCR reforming unit in the axial direction in case of mass and energy, which indicates the degree of completion of the chemical reactions, using Matlab program to solve the differential equations.

II. MODEL DEVELOPMENT

The steam reforming unit modeled is shown in Fig. (1). The unit consists of four reactors; each
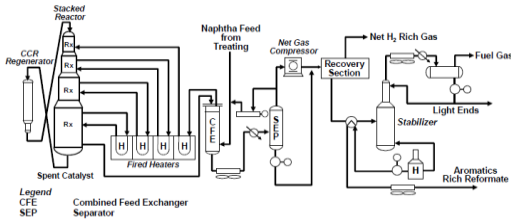
Fig.1 Flow Sheet of a Continuous Catalytic Reforming Process.[18]

Reactor consists of two perforated coaxial cylinders between which the catalyst moves slowly downwards under the gravity force. The catalyst is progressively coked as it moves through the reactors. [1].

The model of moving-bed catalytic reforming reactor is presented by a system of equations of material balance for components and the equation of heat balance as follows [1]:

$$G.\frac{\partial C_i}{\partial z} = -u.\frac{\partial C_i}{\partial R} - \varphi\frac{\partial C_i}{\partial l} + \frac{1}{l}.\int_0^l r_j(l)a_j(l)dl \qquad (1)$$

The right hand side describe the component concentration C_i change with the volume of raw material processed in the reactor The left hand side represent the component concentration change along the two directions redial and axial. The third term describe the integral reactions rate for component i; including catalyst activity distribution through the catalyst bed length in the reactor with a moving bed.

$$\rho^m.C_p^m.G.\frac{\partial T}{\partial z} = -u.\rho^m.C_p^m.\frac{\partial T}{\partial R} - \varphi.\rho^{cat}.C_p^{cat}.\frac{\partial T}{\partial l}$$
$$+ \sum Q_j.\frac{1}{l}.\int_0^l r_j(l)a_j(l)dl(2)$$

The right hand side is the change of the hydrocarbons' temperature T, change with the volume of raw material processed in the reactor

The left hand side represent the change of the hydrocarbons' temperature change along the two directions redial and axial. The third term describe the reaction heat, which is assumed to be constant within eachhomological group (normal alkanes, isoalkanes, aromatic hydrocarbons, cyclopentanes, cyclohexanes).

The boundary conditions are:

At=0, $C_i = C_{i, 0}$;$T = T_{en}$;
Atl=0, $C_i = C_{i, 0}$ (at the *reactor entrance*);$T = T_{en}$;
Atr=0, $C_i = C_{i, 0}$;$T = T_{en}$;

For the mathematical description of hydrodynamic and energy balance of catalytic reforming reactor some assumptions are accepted:

1. The operation is adiabatic for each reactor.
2. The thermal conductivity in the axial dimension was found to be of small magnitude ;somass and heat transport occurs by means of convection.
3. The radial component of the velocity vector was found to be of smallmagnitude;therebythe change of composition in the radial dimension is neglected.[PhD]
4. All components of heavy naphtha are presented by one compound (C_7).

So equations 1 & 2 will be reduced to be

$$G.\frac{\partial C_i}{\partial z} = -\varphi\frac{\partial C_i}{\partial l} + \frac{1}{l}.\int_0^l r_j(l)a_j(l)dl \quad (3)$$

$$\rho^m.C_p^m.G.\frac{\partial T}{\partial z} = -\varphi.\rho^{cat}.C_p^{cat}.\frac{\partial T}{\partial l}$$
$$+ \sum Q_j.\frac{1}{l}.\int_0^l r_j(l)a_j(l)dl \quad (4)$$

With the boundary conditions

Atz=0, $C_i = C_{i, 0}$;$T = T_{en}$;
Atl=0, $C_i = C_{i, 0}$ (at the *reactor entrance*);$T = T_{en}$;
at$l$= L , $\frac{\partial C_i}{\partial l} = 0$, $\frac{\partial T}{\partial l} = 0$

In this model consideration of the catalyst deactivation is a major issue, which changes with catalyst layer's dimensions (length and radius) and also with time because of the coke lay down.

The catalyst activity is inversely proportional to the coke formation rate, thus the catalyst activity depends on the catalyst circulating factor (h_{cir}) by the following equation [1]:

$$a_j = A_0 . e^{-\alpha_j.C_{coke}/h_{cir}} \qquad (5)$$

The values of A_0 and α for each reforming reaction are

Compound	A	B	C	D
Heptane	-5.14E+0	6.76E-1	-365E-4	7.65E-8
Methylcyclohex-ane	-6.19E+1	7.84E-1	-4.43E-4	936E-8
Toluene	-2.34E+1	5.12E-1	-2.76E-4	4.91E-8

included in the table (1)

Table 1:the values of Experimentally Defined A_0 and α for the Main Types of Reactions. [1]

Reactions	α	A_0
Cycloalkanes dehydrogenation	5.7	59.77
Alkanes hydrocracking	0.3	3.14
Alkanes isomerization	0.4	3.69
Alkanes dehydrocyclization	0.8	21.84

And h_{cir} is calculated from the following equation

$$h_{cir} = u.\rho^m/(\varphi.\rho^{cat}) \qquad (6)$$

Reactions of catalytic naphtha reforming are elementary and Hougen-Watson Langmuir-Hinshelwood type of reaction rate expressions are used to describe the rate of each reaction. Rate expressions of this type explicitly account for the interaction of chemical species with catalyst and contain denominators in which characteristic terms of adsorption of reacting species are presented. The reaction rate coefficients obey the Arrhenius law [19]:

$$r = ke^{\frac{-E}{RT}}\frac{(P_{nP} - P_N P_{H_2}/K_{nP\to N})}{(P_{H_2}\Gamma)^2} \qquad (7)$$

$$r = ke^{\frac{-E}{RT}}\frac{(P_{nP} - P_A P_{H_2}^3/K_{N\to A})}{(P_{H_2}\theta)^2} \qquad (8)$$

Equation (7) represents the reaction rate of paraffin dehydrocyclization and equation (8) represents the reaction rate of naphthenes dehydrogenation.
Adsorption terms of the metal function (θ), and for the acid function (Γ), are defined as follows (Van Trimpont, Marin and Froment, 1988) [19]:

$$\Gamma = (P_{H_2} + 107P_{C_{6-}} + 21.9(P_{iP} + P_{nP} + 659P_N + 0.703P_{H_2}P_A)/P_{H_2} \qquad (9)$$

$$\theta = (1 + 0.0027P_N + 8,314\exp\left(-\frac{11658.6}{T}\right)P_N \times 10^{11}/P_{H_2} \qquad (10)$$

For the calculations of heat capacity of each component in the heat balance equation the following equation can be used which show dependence of heat capacity on temperature [12]:

$$Cp_i = A_i + B_i T + C_i T^2 + D_i T^3 \qquad (11)$$

Table 2 :properties of pure compounds contained in reforming feed and products.[12]

To solve these model equations mathematically using the operation data in table (2), reactor specifications in table (3) and catalyst specifications in table (4) a computer program that is Matlab version 7.10 (R2010a) was developed for the numerical solution of the equations.

Table 3: Naphtha Feed And Operation Conditions

Parameter	Value
Heavy naphtha feed stock	86 m^3/hr
Naphtha feed density (vapor phase)	5.04 kg/m^3
Catalyst mass flow rate	238.5 kg/hr
Reactor inlet temperature	525 ^{o}C
Pressure	4.5 kg/cm^2
Feed Composition (% mole) :	
n-Paraffins	21.62
iso-Paraffins	21.42
Olefins	0.54
Naphthenes	37.57
Aromatic	18.85

Table 4: Reactor Specification

Reactor	Length (m)	Diameter (m)	Catalyst load (Ton)
Reactor 1	4.8	1.85	4.3
Reactor 2	5.7	1.85	5.4
Reactor 3	6.25	1.85	5.6
Reactor 4	5.9	2.1	8.3

Table 5: Catalyst Specifications

Catalyst Properties	Value
Density	670 kg/m^3
Diameter	1.6 mm
Surface area	170 m^2/g
Heat capacity	850 J/kg.K
Pt	0.25 %wt

III. RESULTS AND DISCUSSION

The model studies the kinetics of the main reforming reactions (dehydrogenation and dehydrocyclization) which produce aromatic to post the octane number. In order to ensure that the mathematical model can be used in commercial CCR reformer testing, simulated results are tested against measured

data from industrial unit in two different views; composition concentration change and temperature change.

The measured data were obtained from the industrial CCR reforming unit of an Egyptian refinery.

A. Mass Balance Model

A noticeable characteristic of these plots is that the change of components (paraffins, naphthenes, aromatics) concentrations are almost linear along the reactor axial length. Because it was difficult to follow the changes in feed composition along the reactor experimentally, it is assumed that the four reactors act as one stacked reactor.
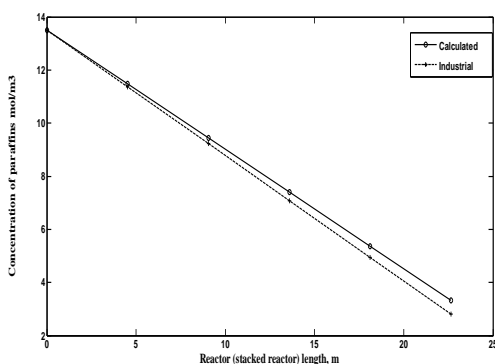
Fig.2 Change of N-Paraffins Concentration With Reactor (Stacked Reactors) Length
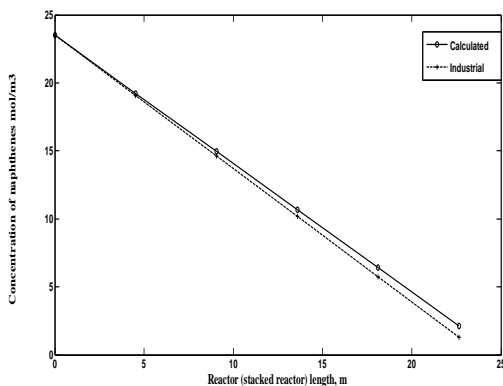

Fig.3 Change of Naphthenes Concentration With Reactor (Stacked Reactors) Length
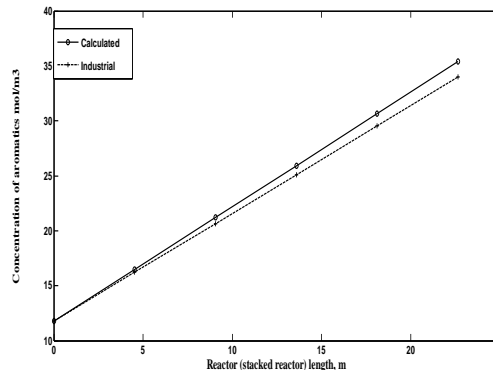

Fig.4 Change of Aromatics Concentration with Reactor (Stacked Reactors) Length

Figures (2) & (3) show the change of n-paraffins and naphthenes concentrations against reactor length. It is clear that paraffins and naphthenes concentrations decrease linearly along the stacked reactor length because of the reforming reations (dehydrogenation and dehydrocyclization)which consume them. The deviation between estimated and industrial results increase along the reactor with the decreasing in components (paraffins and naphthenes) concentrations.The mean deviation is 3.3% for paraffins and 3.39% for naphthenes.

Figure (4) shows the change of aromatic concentration against the stacked reactor length. It is clear that aromatic concentration increase linearly along the reactor lengthbecause it is the main product of reforming reactions. The deviation between estimated and industrial confirms the good predictions of the presented model.witha mean deviation of 3.06%.

B. Energy Balance Model

Since the naphthenedehydrogenation and paraffin dehydrocyclization reactions take place primarily in the first two reactors, so the change in temperature for the first two reactors will be studied in those reactors.
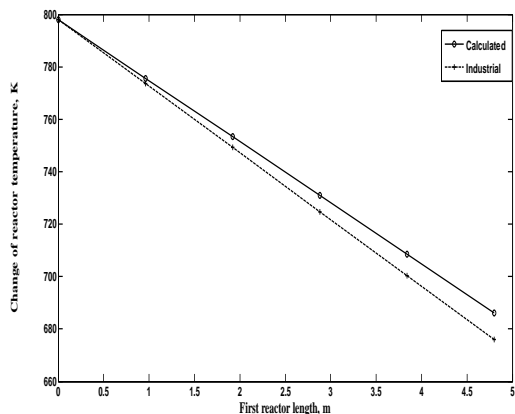
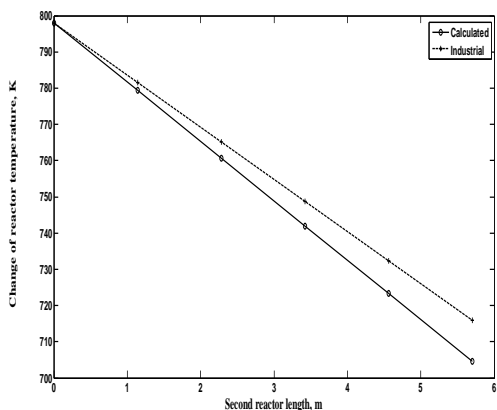**Fig.5 Effect of First Reactor Length on Gas Stream Temperature**

Fig.6 Effect of Second Reactor Length on Gas Stream Temperature

Figures (5) & (6) show the change of first and second reactors feed stream temperatures respectively against their lengths. It is clear that the temperatures decrease linearly with the catalyst bed length because of the dehydrogenation and dehydrocyclization reactions which are highly endothermic and mainly occur in the first and second reactors. It is clear also from calculated and industrial data that the deviation between them increases along the first and second reactors' axis up to 0.015%, 0.0159% for the first and the second reactor respectively. The mean deviation observed along the first reactor is 0.0069% and 0.0075% along the second one.

IV. SENSITIVITY ANALYSIS

A. Concentration Analysis

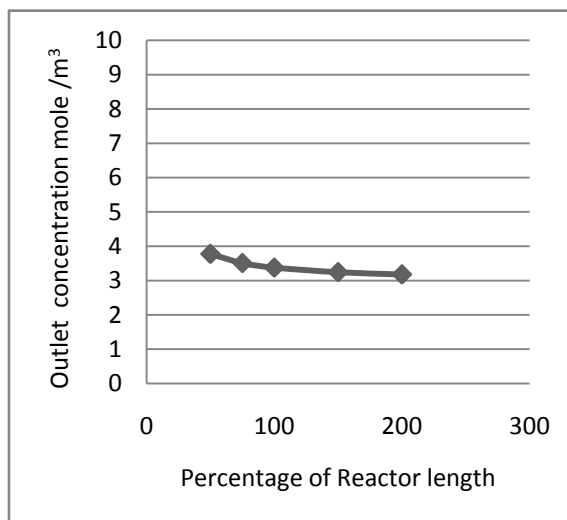#### 1) Paraffin Concentration

Fig.7 Paraffins Concentration Predictions

Figure 7 shows a slight decrease in outlet concentration of n-paraffins with the increase of the reactor length up to 200% of its original value.
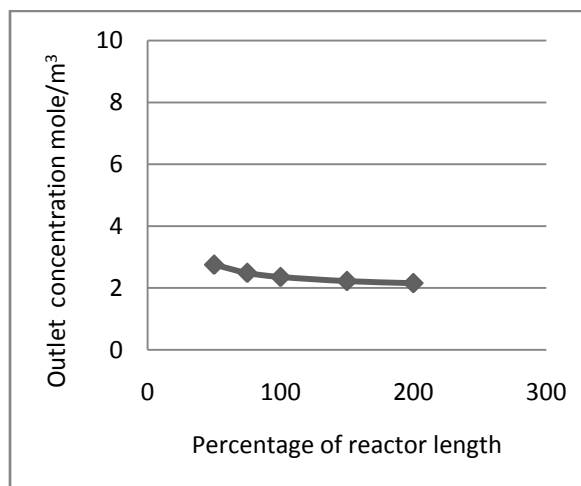
2) Naphthenes Concentration

Fig.8 Naphthenes Concentration Prediction

Figure 8 shows a slight decrease in outlet concentration of naphthenes with the increase of the reactor length up to 200% of its original value.
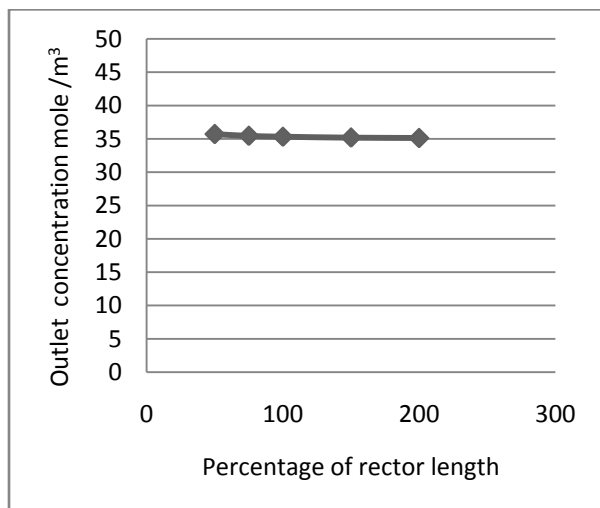
3) Aromatics Concentration

Fig.9 Aromatics Concentration Predictions

Also figure 9 shows a slight change of Aromatics outlet concentration with the increase of the reactor length up to 200% of its original value.

B. Temperature Analysis

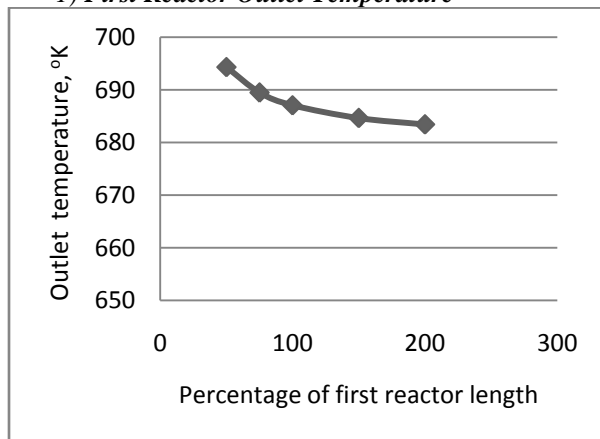### 1) First Reactor Outlet Temperature

Fig.10 First Reactor Outlet Temperature Predictions

Figure 10 shows a considerable decrease of the outlet temperature from the first reactor on increase its length up to 200% of its original value.
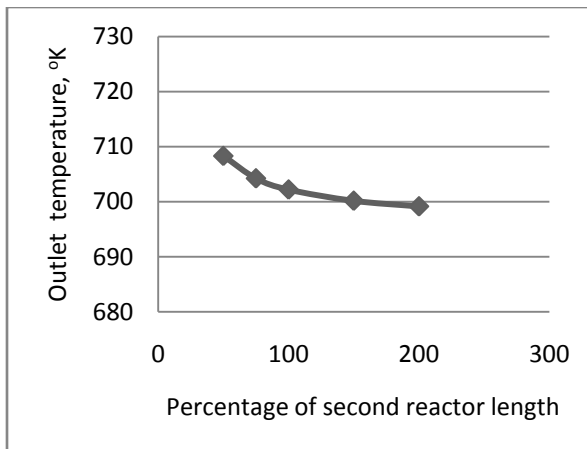
4.2.2-Second Reactor Outlet Temperature

Fig.11 Second Reactor Outlet Temperature Predictions

On the other hand, in case of the second reactor the decrease of outlet temperature is not as noticeable as in the case of the first reactor as shown in figure 11 on increase of its length up to 200% of its original value.

V. CONCLUSIONS AND RECOMMENDATIONS

A mathematical model has been developed which gives estimated results for outlet concentration with maximum deviation 18.5%, 79.3%, 4.18% for paraffins, naphthenes and aromatics respectively. The second model gives estimated results with maximum deviation 2.6%, 5.5% for outlet temperature from first and second reactors.

Sensitivity analysis shows that an increasing the reactor length up to 200% of its value a slight effect on outlet concentration of all components (paraffins, naphthenes and aromatics) was observed.

On the other hand, in case of outlet temperature from either first or second reactor, the decrease of temperature in the range 50-100 % of reactor length are noticeable; while on a further increase in reactor length (up to 200%) of reactor the effect of length is less noticeable.

Finally… the given results were close to the industrial data, but this model may be resolved using different assumptions or more complexity to give more reasonable results in case of mass balance and energy balance.

Nomenclature

a	Catalyst activity
A_0	Experimentally defined coefficient, a linear component determining the number of catalyst active centers.
C_{coke}	Mass fraction of coke on the catalyst
C_i	Concentration of component i, mol/m3
$C_{i,0}$	Inlet concentration of component i, mol/m3
C_p^m	Heat capacity of hydrocarbons mixture, j/(kg k)
C_p^{cat}	Heat capacity of catalyst, j/(kg k)
G	Raw material flow rate, m^3/h
h_{cir}	Catalyst circulating factor, m^3/m
i	Numerator
j	Numerator
k	Rate constant, hr^{-1}
l	Length of reactor, m
Q_j	jth reaction heat, j/mol
r	Reaction rate, mol/(m3 h)
R	Time, h
t	Temperature, k
T	Inlet temperature, k
T_{en}	Hydrocarbons flow rate, m/h
u	Hydrocarbons flow rate, m/h
v_i	Stoichiometric coefficient in gross-equation of chemical reaction
z	Volume of raw material processed in the reactor

Greekletters

α_j	Experimentally defined coefficient of catalyst poisoning – nonlinear component that determines different extent of angle and edge atoms deactivation due to coking
ρ^m	Density of hydrocarbons mixture, kg/m^3
ρ^{cat}	Density of catalyst, kg/m^3
φ	Catalyst flow rate, m/h

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