Improving of Design Parameters of an Industrial Continuous Catalytic Reforming Reactors

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Abstract

Catalytic reforming of naphtha occupies an important issue in refineries for obtaining high octane gasoline and aromatic compounds, which are the basic materials of petrochemical industries. In this study, a novel of design parameters for industrial continuous catalytic reforming reactors of naphtha is proposed to increase the aromatics and hydrogen productions. Improving a rigorous mathematical model for industrial catalytic reactors of naphtha is studied here based on industrial data applying a new kinetic and deactivation model. The optimal design variables are obtained utilizing the optimization process in order to build the model with high accuracy and such design parameters are then applied to get the best configuration of this process by new design variables. New results related to aromatic and hydrogen production have been obtained (the highest hydrogen and aromatic) in comparison with those reported in the literature and with the conventional method.

Key words: naphtha reforming, continuous catalytic reactors, kinetic model, regeneration.

Introduction

In order to achieve environmental regulations, octane number of the produced gasoline should be increment to an acceptable level. Continuous catalytic reforming (CCR) operation is regarded as a proper choice to fulfill this goal. Continuous catalytic reforming (CCR) of naphtha is a significant operation to produce high octane gasoline called reformate, aromatic feedstock and hydrogen in petrochemical industries [1-3]. For designing new plants and optimizing the existing ones, a suitable mathematical model to simulate the industrial CCR reactor is required. The naphtha feedstock is a very complex containing many components and each of them undergoes different reactions. A detailed model with taking into accounts all the components and reactions in addition to the catalyst deactivation is a hard task and thus an appropriate lumping of the components by carbon number based on similar properties and kinetic behavior should be more convenient [4-6]. Therefore, efforts have made for modelling CCR reactors of naphtha by considering kinetic lumps (groups of components) in reforming reactions. Such progress is observed in illustrating better kinetic

and deactivation mechanisms with higher predictive ability and presenting more efficient reactor setups to improve the production yield and operating conditions [7-10].

The aim of the present study is to improve the design parameters for naphtha continuous catalytic reforming (CCR) reactors based on the industrial data obtained by a real plant to achieve the optimal design and operations of such process. The model introduced is firstly investigated by employing the optimization process to obtain the optimum decision variables with a big challenge, which is getting a high agreement between industrial data and the model results (with average absolute error less than 1% among all results). Secondly, the model is then used to maximize the production rate (higher hydrogen and aromatic production than those reported in the literature and obtained in the industrial plant). Modeling, simulation and optimal design via optimization of the

industrial CCR reactor are carried out by gPROMS (**g**eneral **PR**ocess **M**odeling **S**ystem) package.

Process Description of CCR Reactor
An industrial scheme of a continuous catalytic reforming process is shown in Figure 1. The industrial process consists of a series of four separate reactors (the first one is the smallest and the last reactor is the largest) and a regeneration system. Regenerated catalysts is entered the top of the 1st reactor and is moved axially through the reactor then exit from the bottom of the reactor. The catalyst is moved from the bottom of the 1st reactor to the top of the next reactor and such behavior is repeated up to the last reactor. The catalyst will be withdrawn from the last reactor and is sent to the regenerator. After that, the regenerated catalyst is sent to the 1st reactor again, where gas-lift method is employed for catalyst circulation between the reactors and the regenerator.
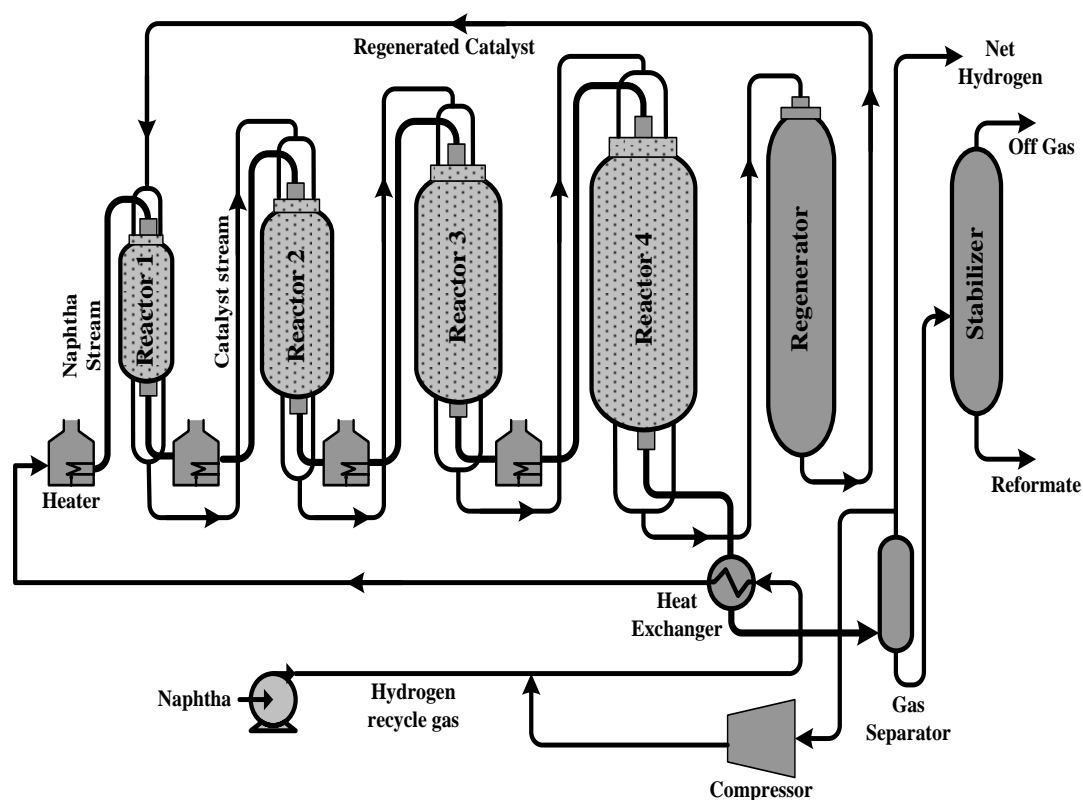

Fig. 1: Industrial scheme of a continuous catalytic reforming process

The feedstock is passed through all reactors and the liquid product obtained by the last reactor will be sent to the separator (where hydrogen rich gas is separated from hydrocarbons). Then, products are passed to the stabilizer and the exit reformate obtained via the bottom of the stabilizer will be sent to storage for gasoline blending. Table 1 shows the characterization of the industrial CCR process (feedstock, catalyst, reactors) taken from a real industrial CCR plant reported in the literature [11].

Table 1: Characterization of the Industrial CCR Process

Property	Values			
Feedstock				
Feed (naphtha)	233637.01 (kg/hr)			
Hydrogen to hydrocarbon (mole ratio)	2.193			
H_2 in recycle (mole %)	0.83			
Catalyst				
Particle diameter	1.8 (mm)			
Specific surface area	220 (m^2/g)			
Void fraction	0.36			
Bulk density	680 (kg/m^3)			
Platinum (Pt)	0.3 (wt %)			
Tin (Sn)	0.3 (wt %)			
Industrial Reactors				
	First Reactor	**Second Reactor**	**Third Reactor**	**Fourth Reactor**
Catalyst distribution (wt %)	12	18	25	45
Reactor length to reactor diameter (L/D)	3.88	4.40	4.78	5.33
Outlet temperature (°C)	434	452	470	488
Outlet pressure (kPa)	581	535	490	446
Hydrogen production (kg/h)	14030	16435	18560	20340
Aromatic production (kg/h)	69230	107785	142660	174600
Naphthene production (kg/h)	23000	12036	7172	3960
Paraffine production (kg/h)	164085	128780	89790	52220

Mathematical Modeling

In this study, hard efforts have been made to improve the design parameters to obtain an accurate mathematical model of the industrial continuous catalytic reforming reactors of naphtha based on the industrial data reported in the literature [12, 13]. In order to develop the industrial reactor model for CCR process with high accuracy, mass and energy balances are required in addition to the catalyst deactivation, pressure drop, thermodynamic and kinetic relations. The overall continuous catalytic reforming reactors model introduced in this work are assembling the mass and energy balance on the system of reforming reactions, kinetic models for reforming reaction and catalyst deactivation model that has not been taken widely into considerations for such reactors as well as Ergun's equation to calculate the pressure drop in the differential format. The following assumptions are made during the modelling of such reactors: The reactors are operated in steady-state conditions, heat loss is negligible, a homogeneous catalyst moving bed is considered and the gas mixtures are considered to be ideal.

Mass Balance

The mass flow rate of each component through the CCR reactor containing catalyst is calculated by the following equation:

$$\frac{dF_i}{dW} = \sum_{j=1}^{n_r} \gamma_{i,j}\, r_j, i = 1,2,3 \dots, 26 \quad \dots(1)$$

Where, n_r is the number of reactions, F_i is the molar flow rate of the component i ($kmol/h$), r_j s the rate of reaction j ($kmol.kg_{cat}^{-1}.h^{-1}$), W is the catalyst weight (kg), $\gamma_{i,j}$ is the stochiometry coefficients of species i in reaction j.

Energy Balance

The energy balance equation for the CCR reactor containing catalyst is evaluated by the following correlation:

$$\frac{dT}{dW} = \frac{\sum_{j=1}^{n_r}(-\Delta H_{r_j})r_j}{\sum_{i=1}^{26}(F_i Cp_i)} \qquad \text{...(2)}$$

Where, T is the temperature (K), Cp_i is the heat capacity of component i ($kJ/kmol.K$), ΔH_j is the heat of reaction of reaction j ($kJ/kmol$).

Pressure Drop

The pressure drop through the reactors can be calculated by using the Ergun's equation as presented in the following equation [3]:

$$\frac{dP}{dW} = -\frac{G}{\rho d_p \varphi^3}(\frac{150(1-\varphi)\mu}{d_p} + 1.75\,G)\frac{1}{A_c \rho_c} \qquad \text{...(3)}$$

Where, P is the total reactor pressure (bar), ρ is the density of the gas mixture (kg/m^3), A_c is the cross sectional area of the bed (m^2), μ is the viscosity of the gas mixture (cP), d_p is the diameter of the catalyst particle (m), ρ_c is the density of the catalyst (kg/m^3), φ is the void fraction of catalyst bed (-), G is the superficial mass velocity of gas mixture ($kg/m^2.s$).

Chemical Reaction Network

The naphtha feedstock and reforming products are included as 26 hydrocarbon lumps characterized by naphthenes (alkylcyclohexanes (ACH) and alkylcyclopentanes (ACP)), normal paraffins (NP), isoparaffins

(IP), and aromatic (A) lumps with carbon numbers ranging from C_6 to C_9^+ with 47 reforming reactions. The impact of pressure drop is also considered [4, 8]. In this model, the lumps of hydrocarbons related to the main reforming reactions network can be described as follows [1,5,11,14]:

- Dehydrogenation Reactions

The formation of aromatics by dehydrogenation of cyclohexanes is an endothermic reaction leading to an increase in the octane number. Such reaction is the fastest among all the reforming reactions, therefore equilibrium state is quickly occurred. The reaction rate equations for this reaction are stated as:

$$ACH_n \leftrightarrow A_n + 3H_2$$
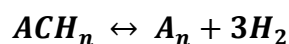
$$r_{1n} = k_{1n}\left(P_{ACH_n} - \frac{P_{A_n} P_{H_2}^3}{K_{1n}}\right) \qquad \text{...(4)}$$

$$k_{1n}(kmol.kg_{cat}^{-1}.h^{-1}.kPa^{-1}) = exp\left(a - \frac{E}{RT}\right) \qquad \text{...(5)}$$

$$K_{1n}(kPa^3) = \exp\left((A - \frac{B}{T}\right) \qquad \text{...(6)}$$

- Dehydrocyclization Reactions

In the reforming process, dehydrocyclization of paraffins to naphthenes and aromatics is a desirable reaction due to induce the most considerable increment in octane number among the naphtha reforming reactions. The most reactions of dehydrocyclization are endothermic and promoted by high temperature, low pressure and by both metallic and acidic functions of the catalyst. The needed reactions with the reaction rate equations are written as follows:

$$ACH_n + H_2 \leftrightarrow NP_n$$
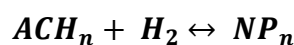
$$r_{2n} = k_{2n}\left(P_{ACH_n} P_{H_2} - \frac{P_{NP}}{K_{2n}}\right) \qquad \text{...(7)}$$

$k_{2n}(kmol.kg_{cat}^{-1}.h^{-1}.kPa^{-2}) = exp\left(a - \frac{E}{RT}\right)$ …(8)

$K_{2n}(kPa^{-1}) = \exp\left(A - \frac{B}{T}\right)$ …(9)

$ACH_n + H_2 \leftrightarrow IP_n$
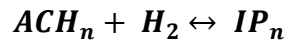
$r_{3n} = k_{3n}\left(P_{ACH_n}P_{H_2} - \frac{P_{IPn}}{K_{3n}}\right)$ …(10)

$k_{3n}(kmol.kg_{cat}^{-1}.h^{-1}.kPa^{-2}) = exp\left(a - \frac{E}{RT}\right)$ …(11)

$K_{3n}(kPa^{-1}) = \exp\left(A - \frac{B}{T}\right)$ …(12)

$NP_n \leftrightarrow ACP_n + H_2$

$r_{4n} = k_{4n}\left(P_{NP_n} - \frac{P_{ACP_n}P_{H_2}}{K_{4n}}\right)$ …(13)

$k_{4n}(kmol.kg_{cat}^{-1}.h^{-1}.kPa^{-1}) = exp\left(a - \frac{E}{RT}\right)$ …(14)

$K_{4n}(kPa) = \exp\left(A - \frac{B}{T}\right)$ …(15)

$IP_n \leftrightarrow ACP_n + H_2$

$r_{5n} = k_{5n}\left(P_{IP_n} - \frac{P_{ACP_n}P_{H_2}}{K_{5n}}\right)$ …(16)

$k_{5n}(kmol.kg_{cat}^{-1}.h^{-1}.kPa^{-1}) = exp\left(a - \frac{E}{RT}\right)$ …(17)

$K_{5n}(kPa) = \exp\left(A - \frac{B}{T}\right)$ …(18)

• Isomerization Reactions
Isomerization reactions are regarded as important reactions owing to the branched hydrocarbons that have a high octane number compared with others and such reactions are promoted via acid catalyst function. In the reforming process, the isomerization reactions are endothermic reaction and paraffins and naphthenes compounds are isomerized. The following
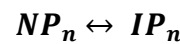
equations are used to describe the isomerization reactions:

$ACP_n \leftrightarrow ACH_n$
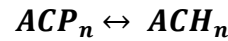
$r_{6n} = k_{6n}\left(P_{ACP_n} - \frac{P_{ACP_n}}{K_{6n}}\right)$ …(19)

$k_{6n}(kmol.kg_{cat}^{-1}.h^{-1}.kPa^{-1}) = exp\left(a - \frac{E}{RT}\right)$ …(20)

$K_{6n}(-) = \exp\left(A - \frac{B}{T}\right)$ …(21)

$NP_n \leftrightarrow IP_n$

$r_{7n} = k_{7n}\left(P_{NP_n} - \frac{P_{IP_n}}{K_{7n}}\right)$ …(22)

$k_{7n}(kmol.kg_{cat}^{-1}.h^{-1}.kPa^{-1}) = exp\left(a - \frac{E}{RT}\right)$ …(23)

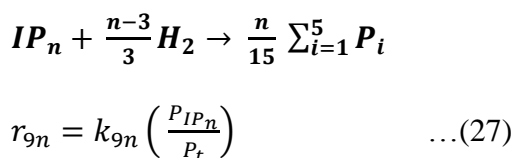$K_{7n}(-) = \exp\left(A - \frac{B}{T}\right)$ …(24)

• Paraffins and Naphthenes Cracking Reactions
In this process, carbons bonds are breaking in the reformer reactors at any positions along the hydrocarbon chain. The aim of these reactions is to reduce the low octane number paraffins and naphthenes from reformate leading to produce lighter hydrocarbons having higher octane in the products. Such reactions are catalyzed via acidic or metallic function of the catalyst. Reaction with the rate equations for hydrocracking of paraffins are shown below as follows:
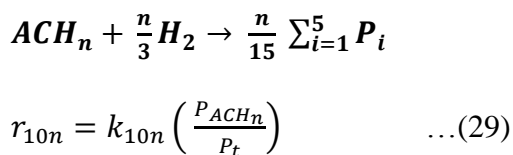
$NP_n + \frac{n-3}{3}H_2 \rightarrow \frac{n}{15}\sum_{i=1}^{5}P_i$
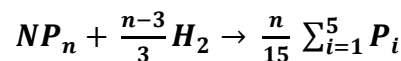
$r_{8n} = k_{8n}\left(\frac{P_{NP_n}}{P_t}\right)$ …(25)

$k_{8n}(kmol.kg_{cat}^{-1}.h^{-1}) = exp\left(a - \frac{E}{RT}\right)$ …(26)

$$IP_n + \frac{n-3}{3} H_2 \rightarrow \frac{n}{15} \sum_{i=1}^{5} P_i$$

$$r_{9n} = k_{9n} \left(\frac{P_{IP_n}}{P_t} \right) \qquad \ldots(27)$$

$$k_{9n}(kmol.kg_{cat}^{-1}.h^{-1}) = exp\left(a - \frac{E}{RT} \right) \qquad \ldots(28)$$

$$ACH_n + \frac{n}{3} H_2 \rightarrow \frac{n}{15} \sum_{i=1}^{5} P_i$$

$$r_{10n} = k_{10n} \left(\frac{P_{ACH_n}}{P_t} \right) \qquad \ldots(29)$$

$$k_{10n}(kmol.kg_{cat}^{-1}.h^{-1}) = exp\left(a - \frac{E}{RT} \right) \qquad \ldots(30)$$

$$ACP_n + \frac{n}{3} H_2 \rightarrow \frac{n}{15} \sum_{i=1}^{5} P_i$$

$$r_{11n} = k_{11n} \left(\frac{P_{ACP_n}}{P_t} \right) \qquad \ldots(31)$$
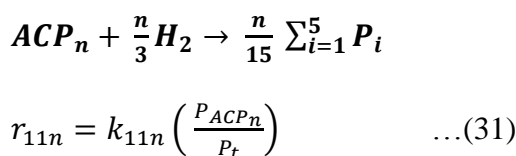
$$k_{11n}(kmol.kg_{cat}^{-1}.h^{-1}) = exp\left(a - \frac{E}{RT} \right) \qquad \ldots(32)$$

- Hydrodealkylation Reactions

In these reactions, the branched radical of aromatic ring is cleavage in the presence of hydrogen. This reaction is considered the slowest of the reforming reactions, which is catalyzed by the metallic function of the catalyst and is favored at high temperature and pressure reactions. The needed chemical reactions with the rate equation for hydrodealkylation process are given as follows:

$$A_{n+1} + H_2 \rightarrow A_n + CH_4$$

$$r_{12n} = k_{12n}\left(P_{A_{n+1}}.P_{H_2}^{0.5} \right) \qquad \ldots(33)$$
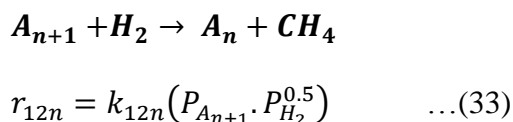
$$k_{12n}(kmol.kg_{cat}^{-1}.h^{-1}.kPa^{-1.5}) = exp\left(a - \frac{E}{RT} \right) \qquad \ldots(34)$$

Catalyst Deactivation

Coke deposition on the catalyst is an undesirable by-product in the CCR process and coke formation is a significant issue for catalyst deactivation. Catalyst deactivation is primarily a function of coke deposition on the catalyst leading to block the active sites and reducing the yield of product therefore controlling coke deposition is equivalent to control the catalyst deactivation [15]. This deactivation effect is compensated by increasing the operating temperature so that the yields of primary products are kept constant. However, there is a limit for increasing the temperature after a certain value that can not yield reformate of desired quality. Then the catalyst has to be regenerated for using in the next cycle of operation [4]. The perfect model should accurately be predicted the rates of coke formation and the catalyst deactivation on the reactor performance as a function of operating conditions [16-18]. Therefore, the following equations related to the catalyst deactivation have taken into accounts in this work as presented below, where the rate of reaction over a spent catalyst can be evaluated via multiplying the activity of the catalyst and the rate of reaction over fresh catalyst:

$$r_i = \beta_i r_i^\circ \quad , \quad 0 \leq \beta_i \leq 1 \qquad \ldots(35)$$

$$\beta_i = \exp(-\emptyset_i C_{c_i}) \qquad \ldots(36)$$

Where, r_i° is the rate of ith reaction of fresh catalyst (coke content is zero), r_i is the rate of ith reaction of spent catalyst, β_i is the catalyst activity (which is a function of deposited coke), $\emptyset_i$ is the deactivation constant, C_{c_i} is the coke weight fraction.

The related reaction rate constants, equilibrium constants, activation energies, frequency factors, heat of reactions, heat capacities, etc.) can be found elsewhere [1, 4, 12, 19].

Case Studies

Case 1: The minimization of the sum of the squared production (SSP) between the industrial data and estimated yields of hydrogen, aromatics, naphthene and paraffine components at the end of each reactor under the same characterization of the industrial CCR reactors (operating conditions, catalyst distribution and properties, feedstock, reactors) is used as an objective function in the optimization process to evaluate the optimal decision variables. Non-linear regression is employed to optimize the control variables (inlet reaction temperature and pressure for each reactor simultaneously) including the outlet temperature, the outlet pressure, hydrogen production, aromatic production, naphthene production and paraffine production of the industrial unit as process constraints and the average absolute error must not exceed 1% among all results. The following equation is employed for this purpose:

$$SSP = \sum_{i=1}^{nc}(F_i^{ind} - F_i^{cal})^2 \qquad …(37)$$

Case 2: The optimization process in case 2 is aimed to maximize the productivity of hydrogen and aromatics, where the optimal outlet temperature and pressure, catalyst distribution and hydrogen to hydrocarbon ratio for each reactor is obtained. The optimal design parameters obtained in case 1. are utilized in case 2 as constraints. The following objective function for case 2 can be introduced as follows:

$$Productivity(PR) = [F_{H_2}] + [F_{Aromatic}] \qquad …(38)$$

Optimization Problem Formulation

Mathematically, the optimization problem for case 1 can be described as:

$Min \quad SSP$

$T_{in,i}, \ P_{in,i} \ , \qquad i=1,..no. \ of \ reactors$

Subject to $\qquad y(w, m(w), u(w),$
$g(w), q)= 0,$

$$T_{in,i}{}^L \leq T_{in,i} \leq T_{in,i}{}^U$$
$$P_{in,i}{}^L \leq P_{in,i} \leq P_{in,i}{}^U$$
$$T_{out,i}{}^L \leq T_{out,i} \leq T_{out,i}{}^U$$
$$P_{out,i}{}^L \leq P_{out,i} \leq P_{out,i}{}^U$$
$$PR_{H2}{}^L \leq PR_{H2} \leq PR_{H2}{}^U$$
$$PR_{aromatic}{}^L \leq PR_{aromatic} \leq PR_{aromatic}{}^U$$
$$PR_{Naphthene}{}^L \leq PR_{Naphthene} \leq PR_{Naphthene}{}^U$$
$$PR_{Paraffine}{}^L \leq PR_{Paraffine} \leq PR_{Paraffine}{}^U$$

While, the optimization problem for case 2 is stated as:

$Max \quad PR$

$T_{out,I} \ , \ P_{out,i} \ , \ Cat_{dis} \ , \qquad i=1,..no. \ of \ reactors$

$$T_{out,i}{}^L \leq T_{out,i} \leq T_{out,i}{}^U$$
$$P_{out,i}{}^L \leq P_{out,i} \leq P_{out,i}{}^U$$
$$Cat_{dis}{}^L \leq Cat_{dis} \leq Cat_{dis}{}^U$$
$$H_2/H_c \geq H_2/H_c{}^*$$
$$Cat_{act}{}^L \leq Cat_{act} \leq Cat_{act}{}^U$$
$$[P_{R1(in)} - P_{R4(out)}] < [P_{R1(in)} - P_{R4(out)}]^*$$
$$PR_{H2} > PR_{H2}{}^*$$
$$PR_{aromatic} > PR_{aromatic}{}^*$$

$y(w, m(w), u(w), g(w), q)= 0$ represents the system model described above, where w is the independent variable (catalyst distribution), $m(w)$ denotes the set of all differential and algebraic variables, $u(w)$ represents the derivative of differential variables with respect to catalyst distribution, q gives the design variables, and $g(w)$ is the control variables. PR_i is the productivity of component i, Cat_{dis} is the catalyst distribution, Cat_{act} is the catalyst activity, P_R is the reactor pressure, L and U is the lower and upper bound, respectively.

Results and Discussion

Optimal Design Parameters for Case 1

The effect of optimized parameters of the industrial CCR reactor has been investigated here. The optimal design parameters for the industrial continuous catalytic reforming (CCR) reactors are reported in Table 2 based on the industrial data obtained by a real

plant for getting the optimal design and operations of such process.

Table 2: Optimization problem results for case study 1

Decision variables	Optimal Values			
	1st Reactor	2nd Reactor	3rd Reactor	4th Reactor
Inlet temperature (°C)	Tin$_1$=518.03	Tin$_2$=516.31	Tin$_3$=515.07	Tin$_4$=514.11
Inlet pressure (kPa)	Pin$_1$=595.02	Pin$_2$=550.21	Pin$_3$=505.34	Pin$_4$=460.15
Outlet temperature (°C)	Tout$_1$=434.01	Tout$_2$=451.98	Tout$_3$=470.11	Tout$_4$=488.09
Outlet pressure (kPa)	Pout$_1$=580.8	Pout$_2$=535.6	Pout$_3$=490.4	Pout$_4$=445.7
Hydrogen production (kg/h)	14033.202	16430.400	18591.453	20342.362
Aromatic production (kg/h)	69234.866	107786.297	142668.738	174600.000
Naphthene production (kg/h)	230·0.279	12036.027	7172.520	3961.580
Paraffine production (kg/h)	164087.056	128780.230	89788.789	52219.1360
Catalyst activity (%)	0.950	0.943	0.938	0.918
Absolute Error of the Industrial Product Compositions and Present Study				
Hydrogen production (%)	0.023	0.028	0.169	0.012
Aromatic production (%)	0.007	0.001	0.006	0.000
Naphthene production (%)	0.001	0.008	0.007	0.039
Paraffine production (%)	0.001	0.000	0.001	0.002

As can be seen from these results, a very good agreement is obtained by using the optimization process. Where, the optimum decision variables with the target values among all results between the industrial data and model results have been achieved with average absolute error less than 1% under process conditions and constraints. The best inlet reaction temperature that should be applied for getting the actual temperature of the industrial naphtha CCR reactors are optimized to be 518.03 °C, 516.31 °C, 515.07 °C and 514.11 °C for reactor 1, 2, 3 and 4, respectively. Whereas, The best inlet reaction pressure that should be utilized for getting the actual pressure for the industrial naphtha CCR reactors are optimized to be 595.02 kPa, 550.21 kPa, 505.34 kPa, and 460.15 kPa, for reactor 1, 2, 3 and 4, respectively.

The optimal decision variables presented above have been obtained under process limitations for each reactor (outlet temperature, outlet pressure, Hydrogen production, aromatic production, naphthene production and paraffine production). Such new results can be attributed to the accuracy of the model studied here under process conditions and constraints, where all the necessary design parameters, reaction rate equations as a function of operating conditions (obtained based on the experimental data, mass and energy balance, hydrodynamic parameters, physiochemical properties in addition to the catalyst activity that ignored in the literature) have taken into considerations here. Such design and kinetic parameters can effect on the process leading to reduce the sensitivity analysis of the process and giving high deviation and as a results the performance and the behaviour of the process can not be predicted confidently in addition to the advanced solution method utilized here (Successive quadratic Programming (SQP)).

Based on the results presented above, a clear indication is observed that the accuracy of the mathematical model related to the design parameters can now be applied with high trusted for modifying such design parameters by changing the decision variables in order to improve quality and quantity of the process via maximizing the hydrogen and aromatic production.

Optimal Design Parameters for Case 2

After getting the optimal results of case 1, the optimization process is applied for case 2 in order to obtain the maximum productivity of hydrogen and aromatic. The optimal results related to case study 2 are given in Table 3. As noted from this table, the highest hydrogen production is optimized to be 20821.857 kg/h (while 20342.362 kg/h for conventional process) and aromatic production of 191428.973 kg/h (whereas 174600.0 kg/h for conventional process). Such new results have got utilizing the optimization technique of the decision variables simultaneously (not individually for each variable as presented in the literature). Where, the best outlet temperature and pressure is 444 °C and 476.4 kPa, 462 °C and 544.2 kPa, 482 °C and 496.6 kPa, and 497 °C and 451.3 kPa for reactor 1, 2, 3 and 4, respectively. Also, the new catalyst distribution and H_2/Hc should be ordered simultaneously beside temperature and pressure as follows: 21.4 wt% and 2.193, 22.2 wt% and 2.898, 26.8 wt% and 3.491, and 29.6 wt% and 4.857 for reactor 1, 2, 3 and 4, respectively, under process constraints (the catalyst activity, pressure difference and the productivity of hydrogen and aromatic).

Table 4 shows the comparison results obtained from this study and those obtained by previous studies related to the production increasing of hydrogen and aromatic. It is clearly observed from this table that the production increasing of hydrogen (by 481.857 kg/h) and aromatic (16828.973) is higher than conventional method and those obtained in the literature, which becomes a considerable amount per year. This new results is attributed to the improvement of design parameters investigated here (outlet temperature, outlet pressure, catalyst distribution and process constraints) in addition to the solution method (SQP) employed in this study depending on the modified model. Where, this method used here to maximize the production of hydrogen and aromatic is better than the methods used with all previous works (that used different solution methods for maximizing the objective function to get the optimal design of CCR reactor) in this field. Such approach utilized having high accuracy in evaluating the control variables of the process within gPROMS package (advanced languages and formalisms for model improvement, which allow the description of difficult differential and algebraic models and has several features that make it an attractive tool and suitable for the modelling, simulation and optimization of any plant process). Furthermore, this approach is a highly trusted method for solution of such mathematical models, which means that this model can be applied confidently to reactor design, operation and control leading to get higher profit (higher quality and quantity).

Table 3: Optimization problem results for case study 2

Decision variables	Optimal Values			
	1st Reactor	2nd Reactor	3rd Reactor	4th Reactor
Outlet temperature (°C)	Tout$_1$=444.0	Tout$_2$=462.0	Tout$_3$=482.0	Tout$_4$=497.0
Outlet pressure (kPa)	Pout$_1$=576.40	Pout$_2$=544.2	Pout$_3$=496.6	Pout$_4$=451.3
Catalyst distribution (wt %)	21.4	22.2	26.8	29.6
H_2/Hc	2.193	2.898	3.491	4.857
Catalyst activity (%)	0.943	0.937	0.927	0.912
P_{R1}(in) − P_{R4} (out) (kPa)	147.8			
Hydrogen production (kg/h)	14673.069	17606.492	19768.371	20821.857
Aromatic production (kg/h)	86759.027	136484.659	173364.538	191428.973

Table 4: Comparison results between this work and previous studies

Authors (year)	Production Increasing of Hydrogen (kg/h)	Production Increasing of Aromatic (kg/h)
Rahimpour et al. (2011)	54.432	414.600
Iranshahi et al. (2013)	322.560	6633.600
Karimi et al. (2014)	383.040	9535.800
This study (2016)	481.857	16828.973

The Performance of the Industrial CCR Reactor

The effect of optimized parameters on industrial CCR performance has been investigated and compared with the performance of the non-optimized operations in the Figures 2-8. The reaction side temperature profiles of industrial (conventional) and recuperative reactors are illustrated in Figure 2. Owing to the predominant reactions in the naphtha reforming process are highly endothermic, temperature drop along the reaction side is expected and the temperature drops using the optimized parameters (case 2) are lower than the industrial method (case 1).
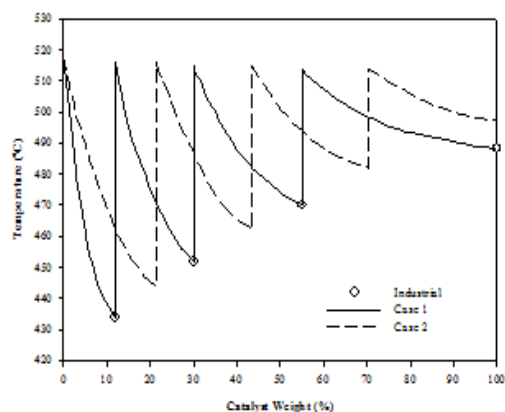

Fig. 2: Temperature profiles along four CCR reactors for case studies

This reduction in temperature drop can be attributed to heat transfer from exothermic side. In the first reactors, concentration of naphthenes is high and dehydrogenation, which is very rapid and endothermic reaction, takes place. Hence, very sharp temperature drop occurs in this reactor. While in the last reactors, naphthenes concentration decrease and hydrocracking and hydrodealkylations occur, which are very slow and exothermic reactions, thus, temperature drop is lower. As well as, the hydrogen content of the recycled gas decreases in the optimized configurations and the molar flow rate of the recycled gas will be increased by increasing in H_2/HC molar ratio. Using the optimized design parameters, more recycled gas enters the reactors, which acts as a thermal source and leading to less temperature drop. Due to the relationship between the temperature gradient and the molar flow rate, the sum of the fresh naphtha feed and recycled gas, the temperature drop along the optimized reactors is the least due to an increase in the molar flow rate [1, 12].

One of the advantages of the CCR reactor is to reduce the pressure drops in the reactors allowing to use of smaller catalyst particle with high efficiency and the reaction rate and conversion increase with decreasing the pressure drop. So, other significant design parameter that influences the performance of naphtha reforming process is operating pressure. Figure 3 shows the pressure profile for industrial and both case studies. As can be observed from this Fig., the pressure drop in the industrial reactors is higher than the optimized reactors (case 2) due to the design parameters of such reactor in which the catalyst distribution reactors is longer than that of conventional process. The sudden pressure drops during the passage of stream through the reactors are due to

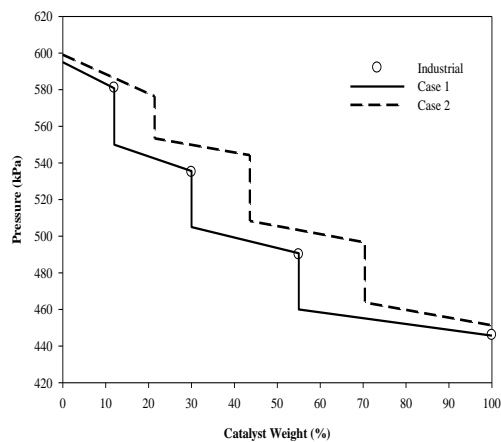piping and employing intermediate instruments such as furnaces [11].

Fig. 3: Pressure profiles along four CCR reactors for case studies

The hydrogen and aromatic yield vs. the catalyst distribution for both case studies is illustrated in Figure 4 and 5, respectively. One of the positive impacts of the proposed modifications can clearly be observed in these figures. Hydrogen is regarded the most the source of hydrocracking, hydrotreating and hydroprocessing units in the refineries.
Hydrogen is a product in the dehydrogenation and dehydrocyclization reactions in addition to the reactant in the hydrocracking and hydrodealkylation reactions.
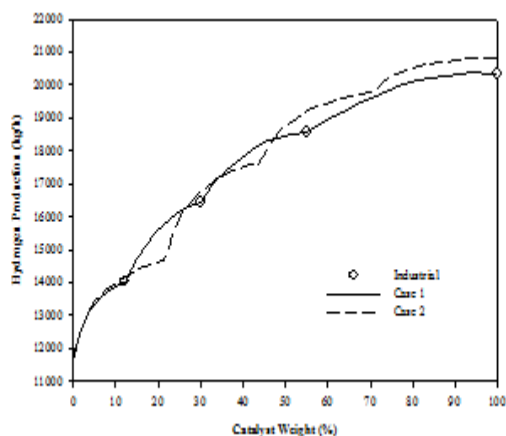

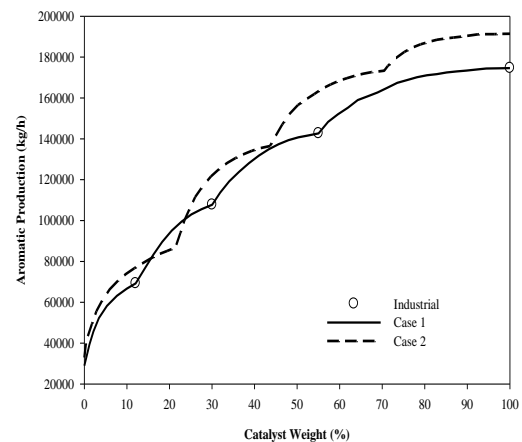Fig. 4: Hydrogen production along four CCR reactors for case studies

Fig. 5: Aromatic production along four CCR reactors for case studies

In the first two reactors, the high production rate is observed, because dehydrogenation and dehydrocyclization are dominant reactions, while in the last two reactors, production rate decreases owing to presence of hydrogen consumer reactions. As noticed, in the optimized configuration owing to supply the copious heat for dehydrogenation and dehydrocyclization reactions, hydrogen production rate has increased, which is one of the main goals in the modified configuration.
Aromatic production with high octane number is the main aim of reforming process hence, the aromatic yield should be increased in the proposed configuration. Almost all reactions proceed more rapidly at higher temperatures hence, the aromatics and hydrogen yields increase in both optimized reactors due to a lower temperature drop compared with conventional method. Moreover, the pressure drop in the reactors is considerably less than that in the conventional, so that the product yield increases as a result of increasing in reaction rates. These factors lead to higher aromatic production in the modified process configuration (case 2) compared with the traditional process (case 1). The amount of

aromatic flow rate has increased as the stream passes through the reactors owing to aromatic producing reactions such as dehydrogenation and dehydrocyclization of paraffins to aromatics. As well as, higher aromatic production is achieved employing case 2 configuration and consequently, high octane gasoline can also be produced in this configuration. Where, the rate of aromatics production is higher than those produced by the conventional method due to the dehydrogenation of naphthenes to aromatics [1].

The naphthenes and paraffins production rates are illustrated in Figure 6 and 7, respectively for both case studies. Naphthenes and paraffins constitute the main part of naphtha. Since dehydrogenation of naphthene is the major source of aromatic production and octane number enhancement, naphthenes play a very important role in naphtha reforming process. Since naphthenes are consumed in the naphtha reforming process and their flow rates decline along the catalyst distribution of the reactors. Owing to hydrogenation reaction in naphtha reforming reactors, more heat is available for the dehydrogenation of naphthens, which is endothermic and its yield increases by consuming more heat.
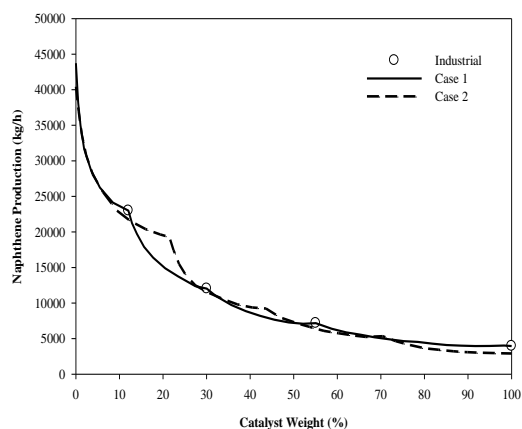

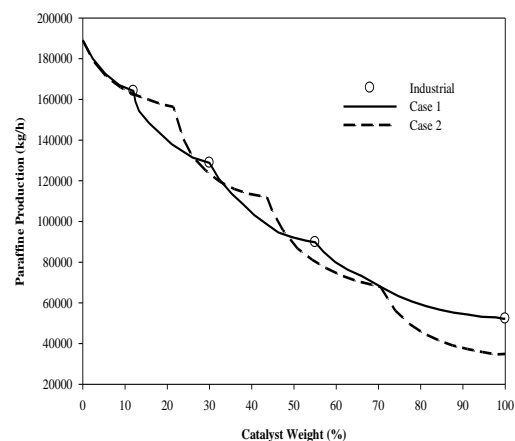Fig. 6: Naphthene production along four CCR reactors for case studies

Fig. 7: Paraffin production along four CCR reactors for case studies

Also, hydrocracking as another naphthene consumer reaction is favored at high temperature thus, the highest conversion of naphthene is observed in optimized design parameters (modified configuration − case 2) that operate at higher temperature. As well as, the paraffins production declines continuously along the catalyst distribution inside the reactors owing to dehydrocyclization and hydrocracking reactions. Using the optimized parameters, more heat is accessible leading the dehydrocyclization toward consuming more paraffins. On the other hand, hydrocracking is favored at high temperature and it can progress further in the modified configuration having a higher operating temperature. Therefore, a lower position in comparison with the conventional configuration [11, 12] is observed.

The catalyst activity along the catalyst distribution for both case studies is shown in Figure 8. The catalyst activity has a reverse relationship with temperature and the catalyst activity is increased as proceeding along the reactors due to a decrease in temperature. As clearly observed, the catalyst activity deteriorates considerably owing to coke deposition on the catalyst surfaces and sintering

phenomena. It is worth mentioning that the catalyst activity itself does not convey any independent judgment, and its effect on the production rate should be investigated. One of the main goals is to keep the catalyst activity as high as possible under process conditions with taking into considerations the optimal design parameters that should be modified.
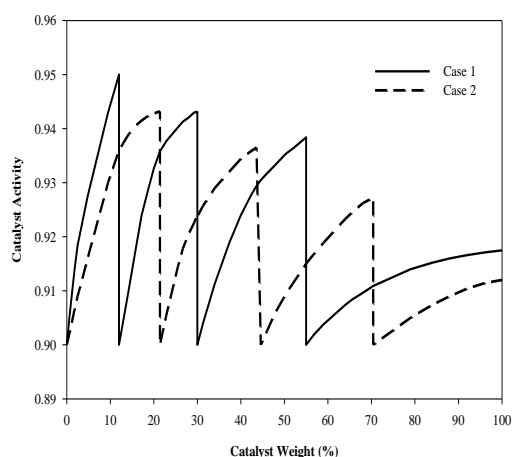

Fig. 8: Catalyst activity along four CCR reactors for case 1 and case 2

Conclusions

A new configuration of industrial continuous catalytic reforming reactors of naphtha is studied by improving the design parameters of such process in order to boost the aromatics and hydrogen productions as a result of increasing the efficiency of the reformers. A rigorous mathematical model for CCR reactors of naphtha is investigated here depending on industrial data with taking into account the deactivation model. The optimal design variables have obtained employing the optimization process in order to build the model with high accuracy (with average absolute error less that 1% among all results between the industrial data and model results). Then, such design parameters have been employed for getting the best configuration of the process by improving the design parameters. The

results of the modified design parameters showed about 16828.973 and 481.857 kg/h have increase in the aromatics and hydrogen production, respectively, compared with those reported in the literature and obtained with the conventional method. Such new results have clearly indicated that the modified design parameters of CCR reactors can cause excellent configuration in comparison with the conventional system.

Nomenclature

a	constant
A	constant
B	constant
CCR	continuous catalytic reactor
n	number of carbon atom
P_t	total pressure (kPa)
P_{An}	partial pressure of n carbon aromatic (kPa)
P_{ACHn}	partial pressure of n carbon alkyl- cyclohexane (kPa)
P_{ACPn}	partial pressure of n carbon alkyl-cyclopentane (kPa)
P_{H2}	partial pressure of hydrogen (kPa)
P_{IPn}	partial pressure of n carbon iso-paraffin (kPa)
P_{NPn}	partial pressure of n carbon normal-paraffin (kPa)
SQP	successive quadratic programming
SSP	sum of the squared production .3
R	gas constant (J mol^{-1}K^{-1})
T	temperature (K)
*	the target final value
in	inlet
out	outlet

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