

Optimization of Semi Regenerative Catalytic Naphtha Reforming Unit to Enhance Octane Number and Reformate Yield

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ABSTRACT

Catalytic naphtha reforming is one of the most important processes in which low quality naphtha is converted into high octane motor gasoline. In this study, a mathematical model was developed and used for investigation of the effect of temperature, pressure, hydrogen to hydrocarbon ratio on the octane number, the yield of product, and the undesirable phenomena of coke deposition in a semi regenerative catalytic reforming unit. The result of the model was compared to the plant data to verify the model accuracy. Then, the model was used to find the optimal condition for the maximum value of octane number and yield of product and the minimum value of coke deposition. The optimum condition of the process was estimated using a genetic algorithm optimization method as an efficient optimization method. In the optimal condition, the octane number and the yield of product improved by 0.3 % and 1.23 %, respectively, and the coke deposition reduced by 2.1 %.

1. Introduction

Catalytic naphtha reforming is one of the most critical processes in the oil refinery industries. The process consists of three consecutive adiabatic reactors, and the objective is to convert virgin naphtha cuts with the boiling point range of 30 to 200 °C into high octane gasoline, called reformate. In addition, hydrogen as a desirable product is produced in this process [1-2]. Hydrogen will be a requisite energy source in the upcoming future. Furthermore, due to environmental protection rules, sulfur and nitrogen removal

is one of the main purposes of refineries [3]. The best way to remove nitrogen and sulfur in the whole world from refined petroleum products and natural gas is through hydrodesulphurization and hydrodenitrogenation in the presence of a catalyst, converting them into hydrogen sulfide and ammonia. Hydrodesulphurization (HDS) is a catalytic chemical process widely used to remove sulfur (S) from natural gas and from refined petroleum products. Hydrodenitrogenation (HDN) is an industrial process for the removal of nitrogen from

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petroleum. Although organonitrogen compounds occur at low levels, they are undesirable because they cause poisoning of downstream catalysts. To achieve this goal, refineries use up hydrogen in large quantities for removing these contaminants [4-5]. Hence, attempts are made to enhance hydrogen production rate and hydrogen purity in refineries. According to the importance of hydrotreating and hydrocracking techniques, studies should be focused on upgrading naphtha reforming process, which supplies a large quantity of required hydrogen for refineries. Pursuant to the nature of the reactions, the reforming process also produces light ends (gases) such as propane and butane [6]. In the last decade, due to the wide economic importance of naphtha reforming process, researchers have focused on finding new ways for upgrading naphtha reforming process. Rahimpour et al. used the DE (differential evolution) optimization technique as a powerful tool to find the best operating parameters (such as gasoline octane boosting) in the thermally coupled naphtha reforming heat exchanger reactor [7]. Juarez et al. investigated the modeling and simulation of commercial reforming unit consisting of a series of four catalytic reactors for prediction of the temperature and reformat composition profiles [8].

Weifeng et al. proposed a multi-objective optimization strategy for an industrial naphtha continuous catalytic reforming process to enhance aromatics production rate. The process model is based on a 20-lumped kinetics reaction network and has been proved to be quite effective in terms of industrial application [9]. Rahimpour et al. used the differential evolution (DE) method to optimize the operational conditions of a radial flow spherical reactor containing the naphtha

reforming reactions. In this reactor configuration, the space between the two concentric spheres is filled by catalyst. The dynamic behavior of the reactor has been taken into account in the optimization process [10]. In addition, many studies have been done formerly on the new catalyst provision, showing better resistance against sintering and coke deposition on the catalyst. Benitez et al. and Boutzeloit et al. investigated the performance of catalytic reforming process, through monometallic, bimetallic, and trimetallic catalysts [11-12]. Some researchers, such as Mazzieri et al. and Sugimoto et al., investigated the coke formation and regeneration of catalyst pending the catalytic reforming process [13-14]. The most popularly used type of naphtha reforming unit is semiregenerative reformer, which consists typically of 3 to 4 consecutive fixed bed reactors. A simplified schematic for the semiregenerative naphtha reforming process is shown in Fig.1, and specific properties of the feed and operational conditions of naphtha reforming reactors are presented in Table 1. The main idea of the process is to convert paraffins and naphthenes into aromatics. Treated naphtha is combined with a recycled gas stream containing 60-90 mol % hydrogen; then, it is heated to desired temperature and passes through three consecutive adiabatic reactors and heaters between the reactors to reheat the stream into reaction temperature at design levels, before entering the next reactor [15-16]. The product of the last reactor is separated into liquid and gas phases in reactor product separator. The flashed gas phase, which is rich in hydrogen, is recycled; the liquid phases that chiefly consist of aromatics compounds and light ends are sent to a separation system to remove light gases from aromatics products.

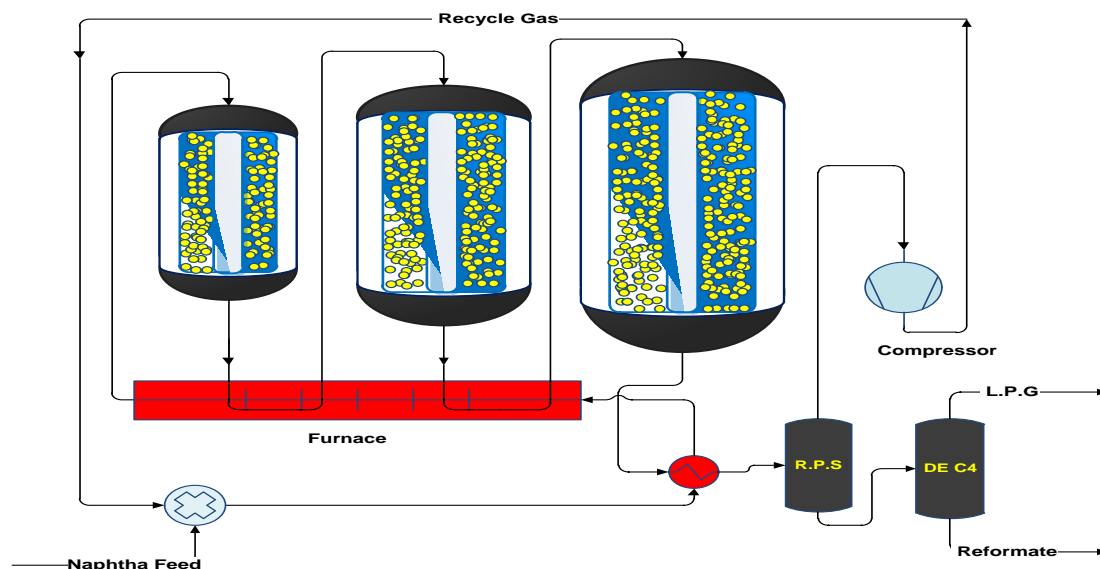


Figure 1. A schematic diagram of semi-regenerative catalytic reforming process.

Table 1
Specifications of feed and product.

TBP (true boiling point)	Naphtha feed	Reformate
IBP	98	37
10 %	110	70
30 %	120	101
50 %	129	122
70 %	143	141
90 %	158	164
FBP	170	188
Parameter	Value	Unit
Feed	56	m ³ /h
H ₂ /HC	4.8	-
LHSV	1.92	h ⁻¹
Mw _{ave}	108.47	gr/mol
Feed stock (Mol %)		
Paraffin		49
Naphthene		36
Aromatic		15

This process is described by a continuous operation over long periods, decreasing catalyst activity due to coke deposition. The optimum reforming cycle length or the time between catalyst regenerations is determined by factors such as declining in reformate yield, specified amount of hydrogen decline, and refinery or reformer economics [15-16]. In order to maintain the conversion at a desired value, the temperature of the reactor is

raised over time as the activity of catalyst decreases. The reforming operation is shut down, and the catalyst is regenerated approximately once each 6-24 months. The research octane number (RON) that can be achieved in semi-regenerative reforming is generally in the range of 85-100, depending on the feed stock quality, gasoline quality, and quantity as well as the operating conditions. Table 2 shows the

characterizations of naphtha reforming Shiraz oil refinery.
reactors and properties of the catalyst used in

Table 2
Reactors and catalyst characterizations.

Parameter	1 st Reactor	2 st Reactor	3 st Reactor
dis (wt %)	20.26	30	49.74
d (m)	1.524	1.676	1.981
A (m ²)	1.36	1.70	2.49
H (m)	4.35	5.11	5.87
V (m ³)	5.9	8.69	14.63
W (kg)	4148	6142	10185
L _D (Kg/m ³)	703	706.8	696.2
d _b (mm)	1380	1530	1830
Typical properties of catalyst			
Parameter	Value	Unit	
d _p	1.2	mm	
Pt	0.3	wt %	
Re	0.4	wt %	
S _a	220	m ² g ⁻¹	
ρ _b	0.3	Kg l ⁻¹	
P _v	0.6	cm ³ g ⁻¹	
ε	0.36	-	

2. Mathematical modeling

A heterogeneous mathematical model is developed by assembling the mass and energy balance on the naphtha reforming system. The mass balance provides the variation of the concentrations, and the energy balance provides the variation of temperature along the reactors. In addition, one of the main functions in naphtha reforming is to consider the pressure drop through the catalyst bed. The Sabri Ergun pressure drop equation considers viscous and kinetic energy changes for wide flow rates to account for the pressure drop through the reforming reactors [17-18].

The following assumptions are considered during the modeling step:

- 1) Ideal gas behavior is applicable.
- 2) Plug flow pattern is considered.
- 3) All the reactors work under adiabatic condition.
- 4) Axial dispersion of heat is neglected.

By considering component material balances as well as energy balance on a differential element 'dw' of catalyst bed, the mass and energy balance are obtained as follows [19]:

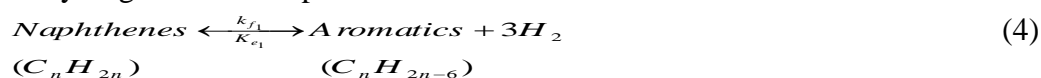
$$\text{Mass balance: } \frac{dF_i}{dw} + \sum_{j=1}^n \gamma_{i,j} \cdot r_j = \frac{\varepsilon}{\rho_b} \frac{d(c_i)}{dt} \quad (1)$$

$$\text{Energy balance: } \frac{dT}{dt} = \frac{-\left(\sum_{i=1}^{n_c} F_i C_{p_i}\right) \frac{dT}{dw} \sum_{j=1}^{n_c} r_j \left(\sum_{i=1}^{n_c} H_i \gamma_{i,j}\right)}{C_{p_{cat}} + \frac{\varepsilon}{\rho_b} \sum_{i=1}^{n_c} c_i C_{p_i}} \quad (2)$$

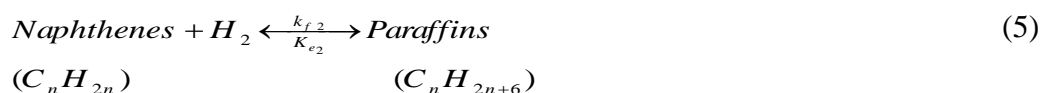
$$\text{Ergun equation: } \frac{dP}{dw} = -\frac{G}{\rho d_p \varepsilon^3} \left(\frac{150(1-\varepsilon)\mu}{d_p} + 1.75 \right) \frac{1}{A_c \rho_c} \quad (3)$$

The kinetic model of Bommanna et al. based on Smith's model is used, which contains four governing reactions as follows [20-21]:

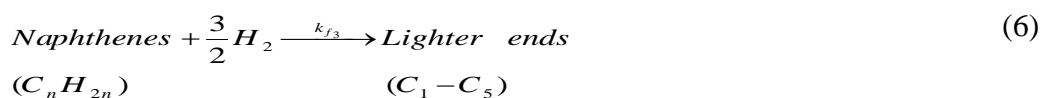
Dehydrogenation of naphthenes to aromatic:



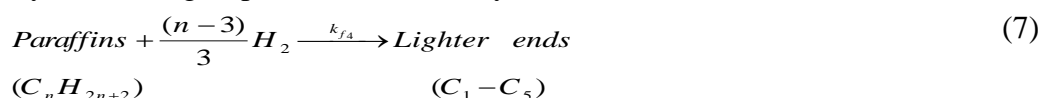
Dehydrocyclization of paraffins to naphthenes:



Hydrocracking of naphthenes to lower hydrocarbons:



Hydrocracking of paraffins to lower hydrocarbons:



$$r_1 = \left(\frac{\text{k}_{f1}}{\text{K}_{e1}}\right)(\text{k}_{e1} P_n - P_a P_h^3) \quad (8)$$

$$r_2 = \left(\frac{\text{k}_{f2}}{\text{K}_{e2}}\right)(\text{k}_{e2} P_n P_h - P_p) \quad (9)$$

$$r_3 = \left(\frac{\text{k}_{f3}}{P_t}\right) P_n \quad (10)$$

$$r_4 = \left(\frac{\text{k}_{f4}}{P_t}\right) P_p \quad (11)$$

The rate constants and heat of reactions are listed in Table 3.

Table 3

Rate constants and heat of reactions for naphtha reforming.

Rate constant *	A	B	E (J.mol ⁻¹)	ΔH (J.mol ⁻¹) (298 K)
k _{f1} (kmol.h ⁻¹ .kg _{cat} ⁻¹ .MPa ⁻¹)	9.87	23.21	36350	71038.06
k _{f2} (kmol.h ⁻¹ .kg _{cat} ⁻¹ .MPa ⁻¹)	9.87	35.98	58550	-36953.33
k _{f3} (kmol.h ⁻¹ .kg _{cat} ⁻¹)	1	42.97	63800	-51939.31
k _{f4} (kmol.h ⁻¹ .kg _{cat} ⁻¹)	1	42.97	63800	-56597.54
k _{e1} (MPa ⁻¹)	1.04×10 ⁻³	46.15	46045	-
k _{e2} (MPa ⁻¹)	9.87	-7.12	8000	-

*k=Aexp(B-(E/RT))

3. Results and discussion

3.1. Model validation

The operating data of Shiraz oil refinery were used as evaluative criteria. The comparison of outlet temperature, research octane number,

and yield between plant data and simulation results demonstrated the ability of the model to predict the desired outputs, as shown in Figs. 2 and 3. Then, the model was applied to investigate the effect of operative variables on

the process. The main process variables that have the greatest effects on the naphtha reforming process are temperature, pressure,

and hydrogen partial pressure. The effects of these parameters on the process are investigated in the following sections.

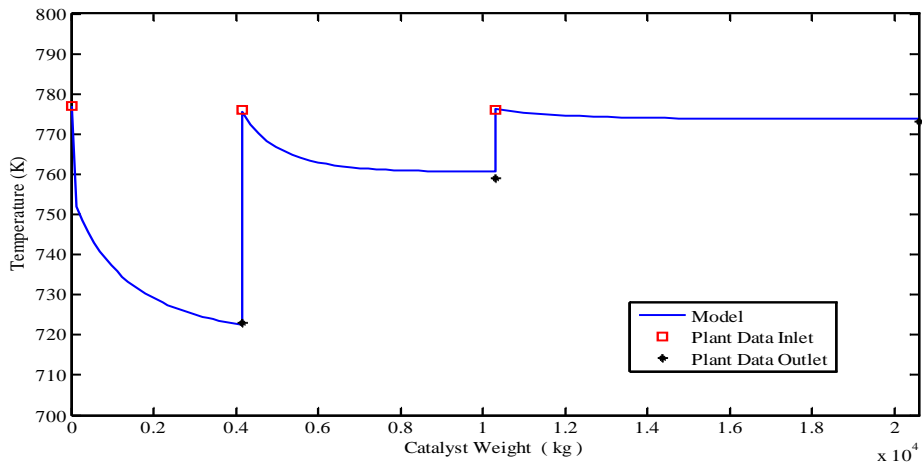


Figure 2. Temperature profile along the reactors, a comparison between model and plant data for semi-regenerative reforming at 3000 kPa.

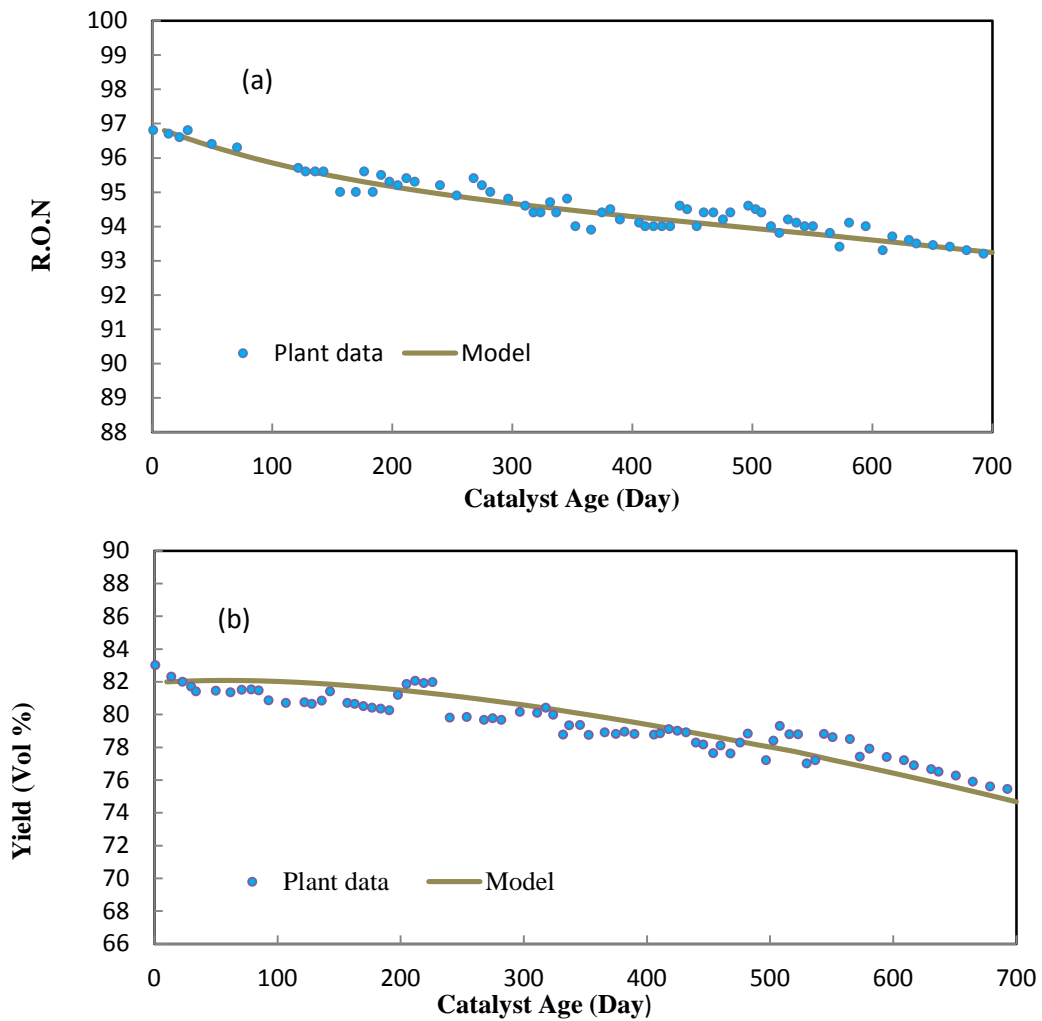
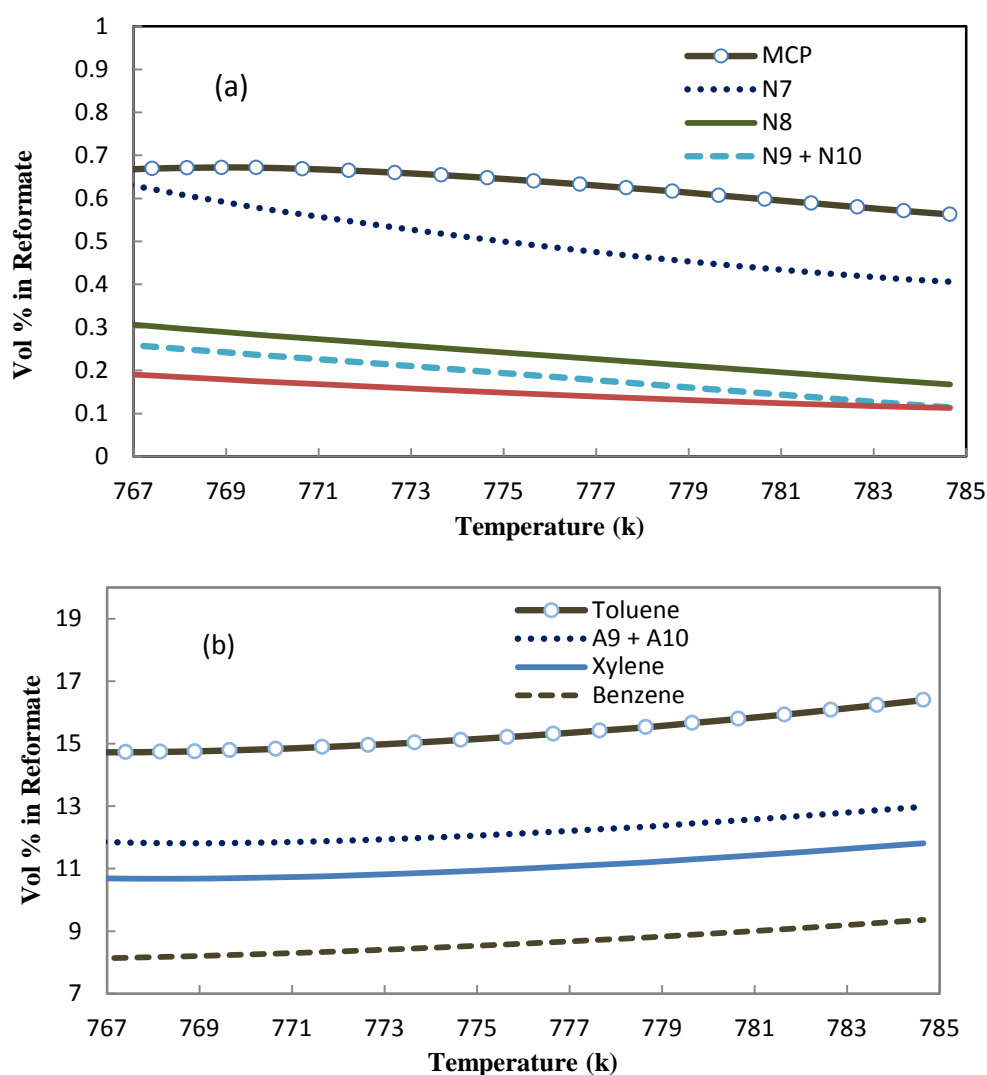


Figure 3. A comparison between model and plant data (a) research octane number versus catalyst age, (b) yield of reformate versus catalyst age.

3.2. Effect of temperature

The most important operating variable to control product quality and yields is the reactor inlet temperature. Since reformers are designed with three or more reactors in series and each reactor may contain a different quantity of catalyst, it is commonly accepted to consider the weighted average inlet temperature (WAIT). In a conventional semi-regenerative unit, the loss of activity of catalyst results in a decrease in product octane as well as the reformate yield and recycle gas purity. As is shown in Fig. 4, an increase in the reactor WAIT results in increasing conversion of the non-aromatic compounds in

the feed to aromatic, although the hydrocracking reaction is more favored than the cyclization of paraffins. In addition, light ends compounds increase, and reformate yield and coke deposit increase. It is worth mentioning that the difference in the effect of temperature on the yield of the products is due to the difference in the heat of reactions. For instance, the naphthenic production (Fig. 4a) decreases with increasing the inlet temperature, because it is an exothermic reaction, while the aromatic production increases with temperature due to its endothermic nature.



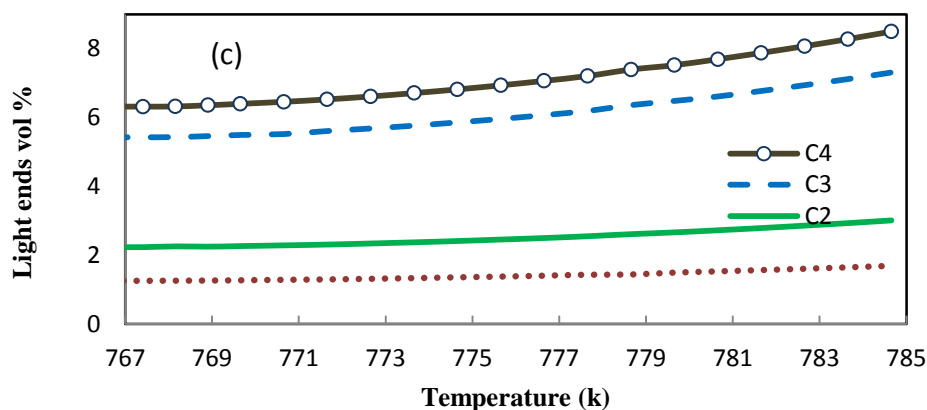


Figure 4. Effect of WAIT on (a) volume percent of naphthenic production, (b) volume percent of aromatics production, and (c) volume percent of light ends.

3.3. Effect of pressure

Hydrogen partial pressure is a basic variable in the naphtha reforming unit because of its inherent effect on reaction rates; however, for the sake of clarification, the total reactor pressure can be used. The lower the pressure is, the higher the yield of both reformate and hydrogen for a given octane number will be. The pressure reduction leads to an increase in the coke deposition on the catalyst and results in shorter cycle life. Higher pressures cause

higher rates of hydrocracking, and more hydrocracking causes the loss of a reformate yield for a given octane number. At higher pressures, coking of the catalyst decreases, resulting in longer cycle life. The real incentive for reducing pressure in reformer reactors is more reformate yield with the added benefit of the hydrogen increase. Fig. 5 represents the effect of pressure on R.O.N and yield in the naphtha reforming process.

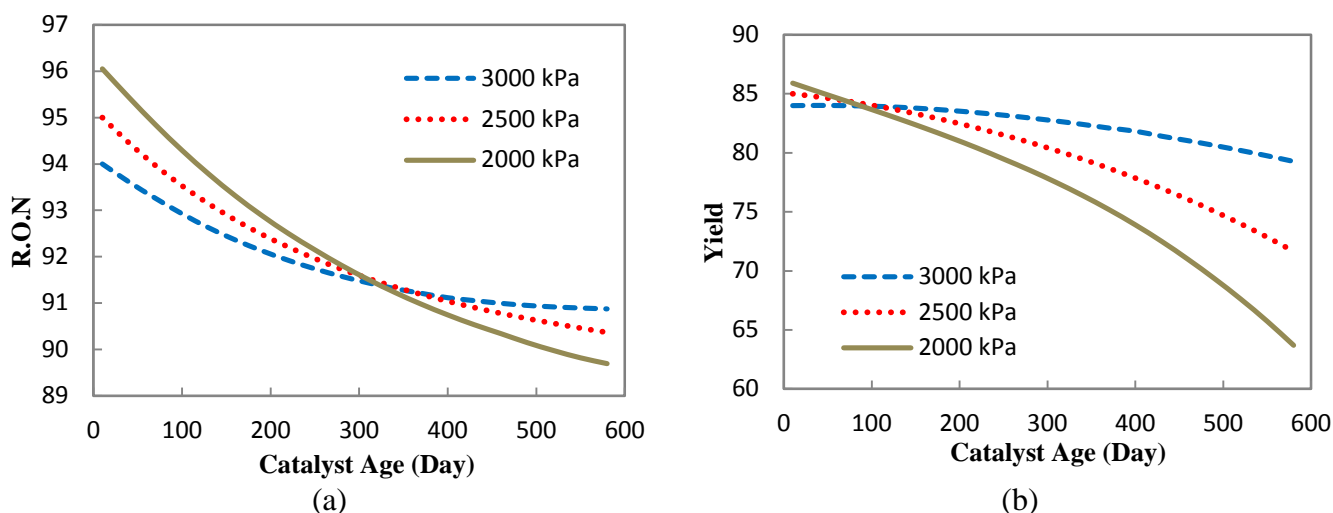


Figure 5. Effect of pressure on (a) research octane number, (b) yield versus catalyst age.

3.4. Effect of hydrogen to hydrocarbon ratio

The profile of coke deposition on the catalyst in each reactor in various H_2/HC ratios is illustrated in Fig.6. Recycled hydrogen is

necessary in the reformer operation for purposes of catalyst stability. The hydrogen reacts with coke precursors and, thus, removes it from the catalyst before forming polycyclic aromatics, which ultimately

deactivated the catalyst. An increase in H_2/HC ratio will move the naphtha through the reactors at a faster rate and supply a greater heat sink for the endothermic heat of reaction. At lower H_2/HC , the hydrogen partial pressure decreases and the coke

formation increases. The H_2/HC ratio has little influence on product quality or yields. Hydrogen partial pressure is set by an economic balance between equipment sizing and energy saving heaters as well as recycle gas compressor and cycle duration.

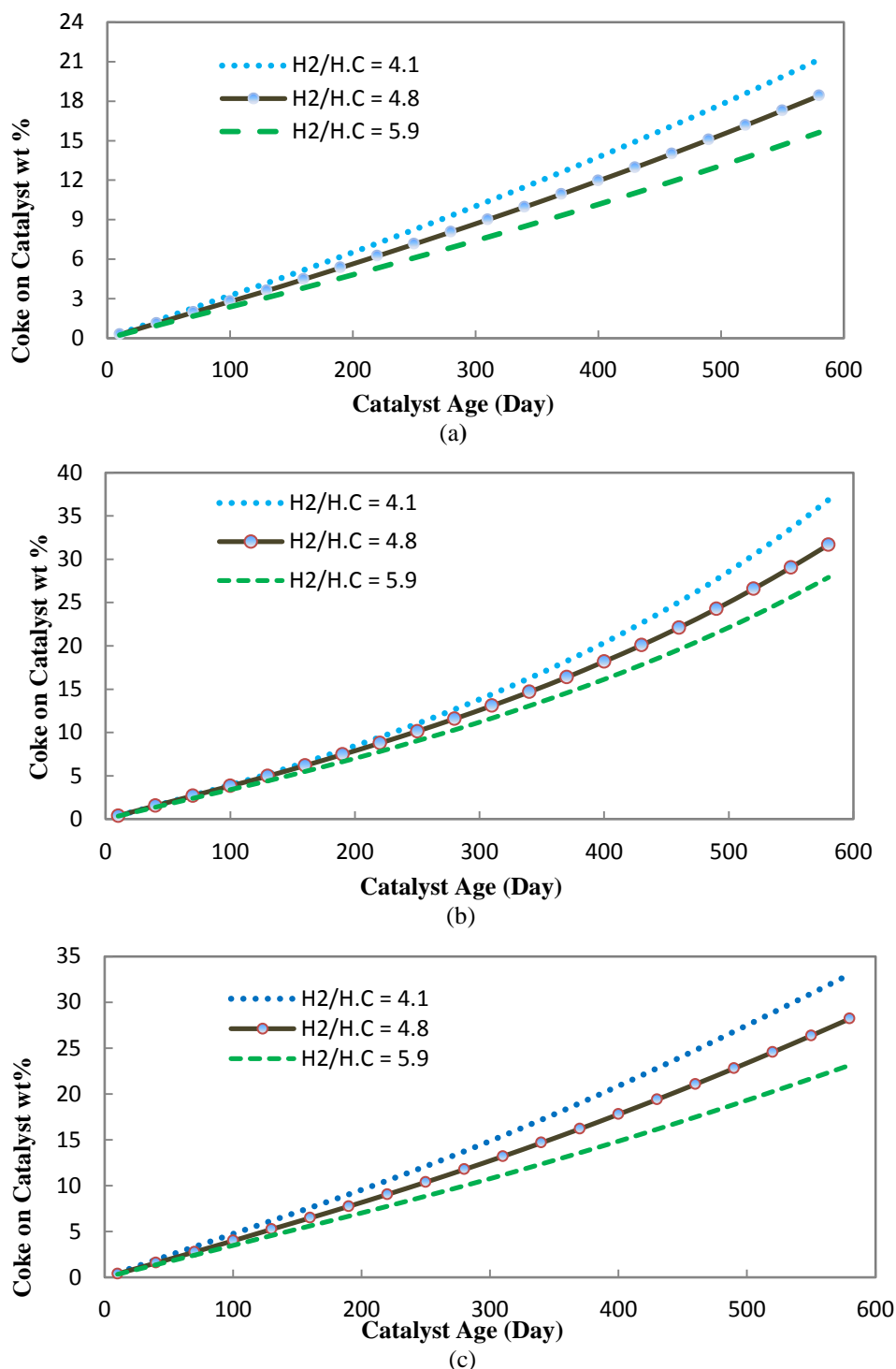


Figure 6. Effect of H_2/HC on coke deposition (a) reactor No. 1, (b) reactor No. 2, (c) reactor No. 3.

3.5. Optimization

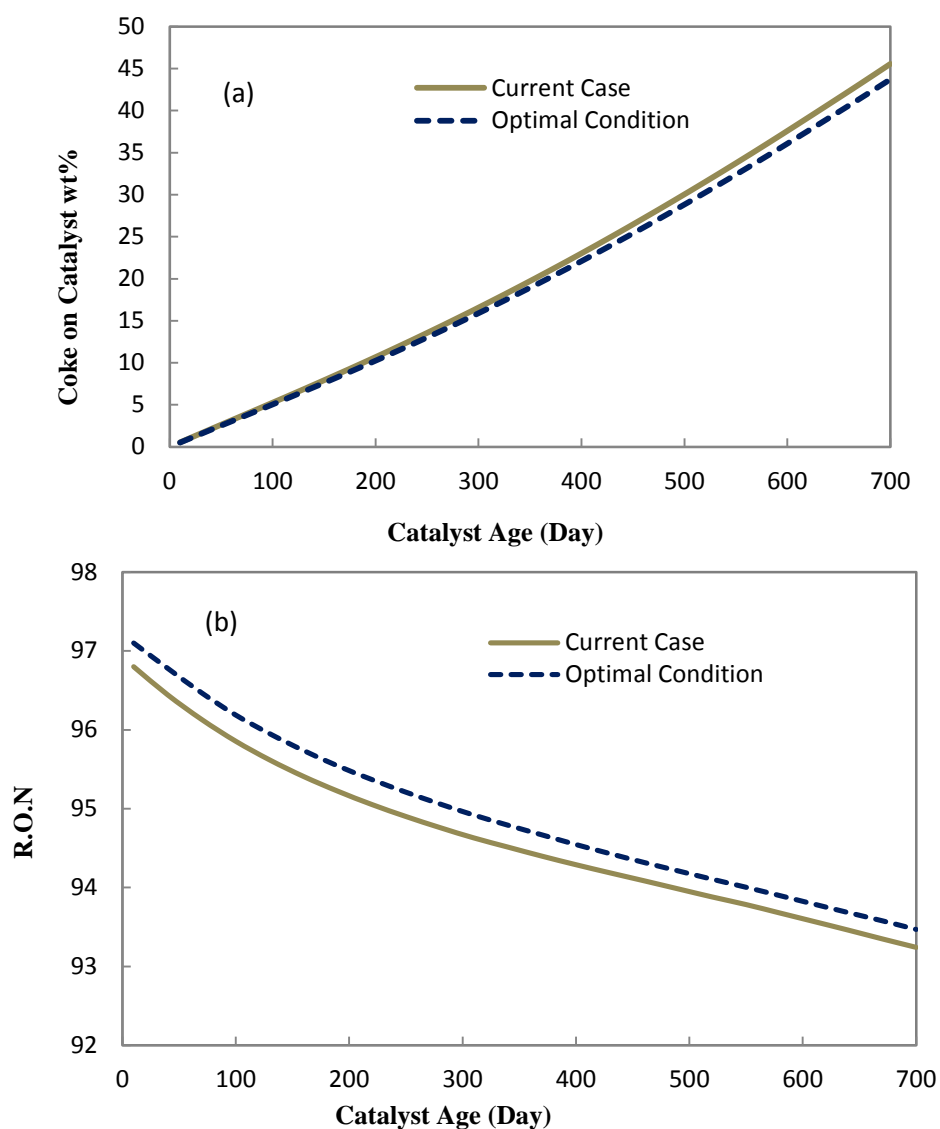
According to the previous sections, the important variables, which affect the naphtha reforming process, are the average inlet temperature of the reactors, operating pressure, and hydrogen to hydrocarbon ratio. As mentioned previously, the objective of the process is to find maximum values of octane number, yield and hydrogen production as well as the minimum value of coke formation. In this part of study, the optimum condition of the process is estimated using genetic algorithm optimization method as an efficient optimization method. After many attempts, the optimal values of decision variables were

found and compared with the current status of the process in Table 4.

The obtained optimal values of octane number, yield and coke formation for a two-year period are compared with the current status in Fig. 7. By applying the optimal condition, the octane number and yield are improved by 0.3 % and 1.23 %, respectively, and the coke formation is decreased by 2.1 %.

Table 4
Comparison between optimal and current cases.

Comparison	Pressure (kPa)	WAIT (K)	H ₂ /HC
Optimal Value	29	773-782.3	5
Current Value	30	777-785	4.8



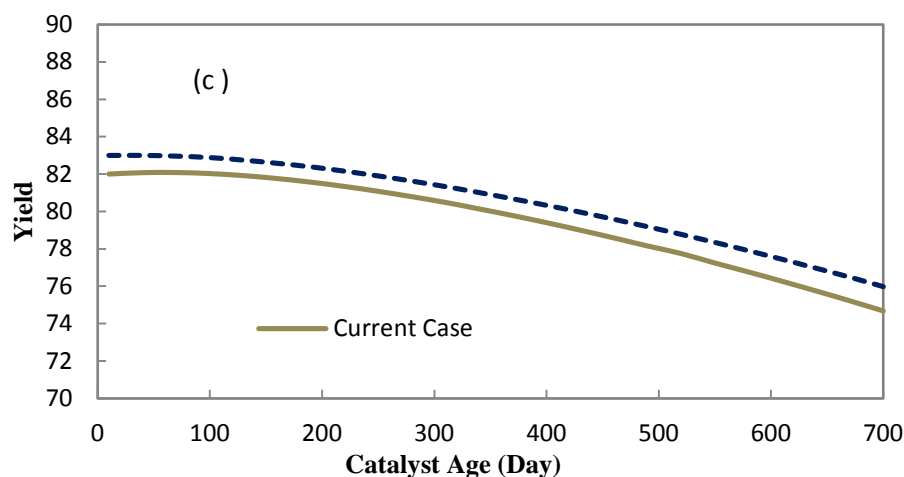


Figure 7. A comparison between optimal and current cases: (a) coke on catalyst versus catalyst age (b) research octane number versus catalyst age, and (c) reformate yield versus catalyst age.

4. Conclusions

In this study, optimization of catalytic naphtha reforming unit is successfully performed using the genetic algorithm. The objective of the optimization is to find maximum values of octane number and yield and minimum value of coke deposition. Optimization results show that, in optimal condition, the octane number and yield are improved significantly. Furthermore, the time period of the process can be increased due to less coke formation.

By applying the optimal condition, the octane number and yield are improved by 0.3 % and 1.23 %, respectively, and the coke formation is decreased by 2.1 %.

Acknowledgements

The author is grateful to the Shiraz University of Technology for supporting this work.

Nomenclature

A	area [m ²].
d	reactor diameter [m].
d _b	bed diameter [mm].
dis	catalyst distribution [wt %].
d _p	particle diameter [mm].
H	height [m].
H ₂	hydrogen [kmol/h].

k _{f1}	forward rate constant for reaction (8) [kmol h ⁻¹ kg cat ⁻¹ MPa ⁻¹].
k _{f2}	forward rate constant for reaction (9) [kmol h ⁻¹ kg cat ⁻¹ MPa ⁻²].
k _{f3}	forward rate constant for reaction (10) [kmol h ⁻¹ kg cat ⁻¹ MPa ⁻²].
k _{f4}	forward rate constant for reaction (11) [kmol h ⁻¹ kg cat ⁻¹ MPa ⁻²].
k _{e1}	equilibrium constant [Mpa ³].
k _{e2}	equilibrium constant [Mpa ³].
L _D	loading density [kg/l].
P	total pressure [kPa].
P _i	partial pressure of i th component [kPa].
P _V	total pore volume [cm ³ gr ⁻¹].
S _a	surface area [m ² gr ⁻¹].
T	temperature of gas phase [°K].
V	volume [m ³].
W	weight [kg].

Greek letters

ε	void fraction of catalyst bed.
ρ _b	catalyst bulk density [kg m ⁻³].
ΔH	heat of reaction [kJ kmol ⁻¹ H ₂].

Subscription

a	aromatic.
h	hydrogen.
n	naphthene.
p	paraffin.

Abbreviations

IBP	initial boiling point [°C].
FBP	final boiling point [°C].
LHSV	liquid hourly space velocity (reactant liquid flow rate/reactor volume).
N7	a naphthenic compound with 7 carbon atoms.
N8	a naphthenic compound with 8 carbon atoms.
N9	a naphthenic compound with 9 carbon atoms.
N10	a naphthenic compound with 10 carbon atoms.
MCP	Methylcyclopentane.
RON	research octane number.
TBP	true boiling point.
WAIT	weighted average inlet temperature [°C].
Pt	Platinum.
Re	Rhenium.

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