

OPTIMIZATION OF CATALYST DISTRIBUTION IN THE CATALYTIC NAPHTHA REFORMER OF TEHRAN REFINERY

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Abstract

Catalytic reforming of naphtha is one of the most important processes in refineries in which gasoline with high octane number and aromatics such as benzene, toluene and xylene are produced. Simulation is normally used for optimization and prediction of operating parameters such as octane number, LHSV, input temperature to reactors and yield. In this paper, at first semi-regenerative catalytic reforming process of Tehran refinery was simulated by Hysys-Refinery Simulator. After validating the simulation, on the basis of experiments prepared by Design expert software, effect of catalyst distribution on the octane number of produced gasoline was studied whilst all other operating parameters were held constant. From the results, the best catalyst distribution in the reactors has been obtained.

The simulation result demonstrate that in the period of four months of plant data studied, the proposed distribution can increase the octane number and octane barrel values to 0,8 and 0,2 percent respectively whilst the total mass of the catalyst and operating conditions were keep constant.

Key words: Naphtha Catalytic Reforming; Octane Number; Optimization; Catalyst; Simulation; Hysys-Refinery

1. Introduction

The catalytic reforming of naphtha (HSRG) is the best method for producing high octane gasoline and aromatics in petroleum refineries and petrochemical industries respectively. The naphtha reformer is used to upgrade a significant portion of the crude oil from a low octane heavy naphtha that is unsuitable for motor gasoline into a high octane gasoline blending component.

The catalytic reforming process came into common usage in refineries in the late 1940s. The reforming of naphtha feed stocks over platinum catalysts was pioneered by Universal Oil Products (UOP), with the Platforming process introduced in 1947.

Industrial catalysts used in recent catalytic reforming units are consisted of gama alumina support and some metals, such as platinum, rhenium, germanium and iridium, less than one weight percent, and additive, such as chlorine to increase isomerization reactions. In the catalytic reforming process the seven types of reactions are taken place as the following:

1. Dehydrogenation
2. Isomerization
3. Cyclization
4. Aromatization
5. Hydrocracking
6. Hydrogenolysis
7. Coke Formation.

Some of these reactions are desired because of increasing octane number of gasoline and some of them are undesired because of decreasing it. For paraffins, increase of octane number is the result of increasing the number of branches, such as cyclization and aromatization. Therefore, normal paraffins conversion to isoparaffins, naphthenes and aromatics result in increasing octane number. On the other hand, coke formation and coke deposition, causing the deactivation of the catalyst, are undesired reactions.

There are three kinds of this process in use today: semi-regenerative, continuously catalyst regenerative (CCR) and cyclic. The semi-regenerative process is the oldest and consists of multiple fixed catalyst beds (usually three) in series ^[1,2,3].

Generally, the commercial semi-regenerative process is carried out in three or four fixed bed reactors in series with intermediate preheaters and it is operated adiabatically at temperatures

between 450 and 520°C, total pressure between 10 and 35 atm. and molar hydrogen-to-hydrocarbon ratios between 3 and 8.

In this paper, Investigation of catalyst distribution in the catalytic reforming reactors of Tehran refinery with semi-regenerative type was studied, and optimized distribution for high RON was determined.

2. Process Description

Prior to entering the catalytic reformer, HSRG undergoes hydrodesulphurization (HDS) reaction in the hydrotreatment unit using a Co-Mo/Al₂O₃ catalyst. The hydrotreated HSRG enters the reforming reactors that are of semi-regenerative types consisted of three radial flow fixed bed reactors connected in series.

As shown in figure 1, reformer feed is first preheated and then enters the first reactor where naphthenes are dehydrogenated to aromatics. The product stream from the first reactor after preheating enters the second reactor and similarly the product stream from the second reactor after preheating enters the third reactor. Overall reforming reactions occurring in the reactors are endothermic and therefore there is a preheater installed before each reactor.

The product stream from the third reactor enters a separator wherein a hydrogen rich gas stream is produced which is then is recycled and mixed with the first reactor fresh feed. The Catalyst distribution in reforming reactors of the Tehran refinery was shown in table 1

Table 1: Catalyst distribution in reforming reactors of the Tehran refinery

	First reactor	Second reactor	Third reactor
Catalyst weight (kg)	8 648	14 223	22 452
Catalyst distribution (wt%)	20	30	50

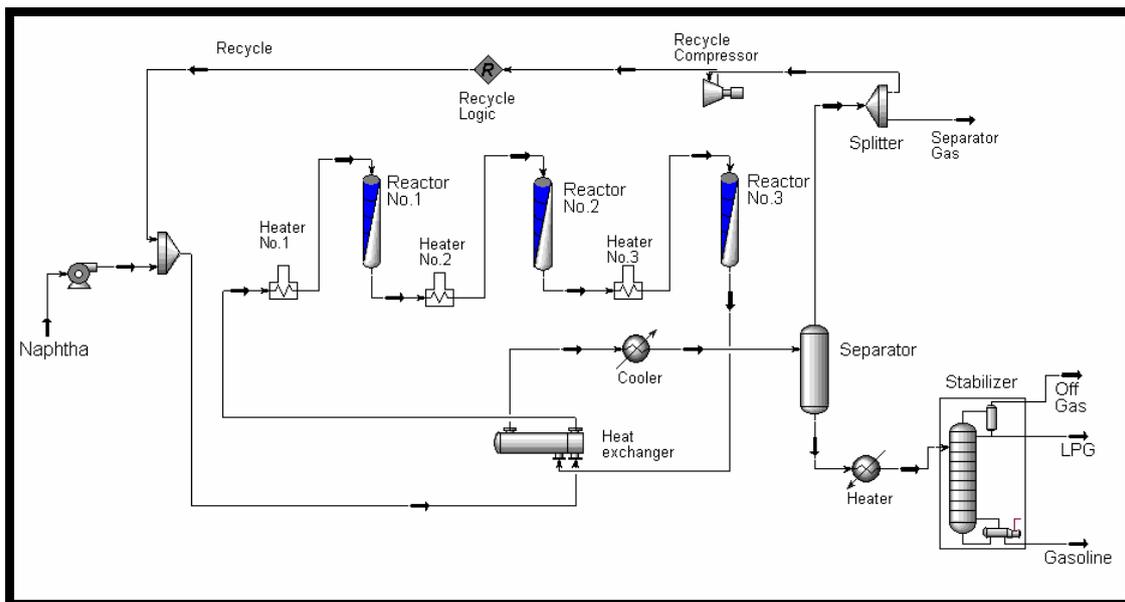


Fig.1: Block flow diagram of the catalytic reforming unit of the Tehran refinery

The liquid product stream from the separator is directed into the gasoline stabilizer unit where the LPG and gasoline streams are produced.

The normal operating conditions prevailing in the reforming unit of Tehran refinery are presented in table 2.

Table 2: Operating conditions in the catalytic reforming of Tehran refinery

	1 st reactor	2 nd reactor	3 rd reactor
Inlet temperature (°C)	497 - 515	497 - 515	497 - 515
Inlet and outlet pressure of recycle gas compressor (bar)		24,5 – 31	
Hydrogen / hydrocarbon ratio (mol/mol)		5 - 6	
LHSV (h ⁻¹)		1.6	
Yield (vol. %)		70 – 80	

3. Process Simulation

Catalytic reforming process is often modeled based on the two following factors:

1. The number of reactive species
2. The type of used kinetic model

Presence of many components as reactants or Intermediate products in the reactive mixture and presence of new reactions as a consequence, will extremely make a sophisticated situation for modeling the process. To decrease these complications, reactants in the mixture are classified in certain and limited groups, called Pseudo Components. The number of selected pseudo components in the mixture is a determinant factor resulted in designed models.

Obviously, the more the number of specified pseudo-components are, the higher the accuracy and management of the model will be. Arrhenius and Langmuir–Hinshelwood kinetics are used for Catalytic Reforming models. It should be noted that for all of the given models, the reactions are considered Pseudo homogen that some of them will be noted briefly.

Smith proposed the first kinetic model for catalytic reforming process in 1959 [4]. In this model the first model given for petroleum processes, the reactants mixture has been classified in 10 groups. Smith assumed that naphtha includes of three fundamental groups: paraffins, naphthens, and aromatics. Moreover, he introduced hydrogen, Ethane, propane, and butane into the system in addition to these groups. One year later in 1960, the other one was introduced by Krane and his colleagues [5]. In this model, feed was consisted of 20 pseudo components and hydrocarbons from 6 to 10 carbon atoms. Moreover, reaction network was contained of 53 reactions. Arrhenius kinetic model is used for above mentioned models. The other models are proposed by Zohrov, Heningsen, Kmak, and Marin [6,7,8,9]. Kmak used Langmuir kinetic model for catalytic reforming process for the first time in 1972 [8]. Marin and his colleagues developed that in 1983, as if it was consisted of naphtha from 5 to 10 carbon atoms and reaction network includes of 23 pseudo components [9]. In 1997, Froment model [10] was developed by Umesh Taskar so that it included of 35 pseudo components in the reaction network, and 36 reactions has been observed [11]. As a consequence of using Arrhenius kinetic, a well-known model has been proposed by Padmavathi [12] in 1997. At last, Krane model was modified by Ancheyta [13] in which naphtha contained 1:11 paraffinic, 6:11 naphthenic and aromatic hydrocarbons. Indeed, the reaction of cyclohexane formation from cyclopentane and paraffins isomeration is considered in this model unlike Krane model.

Hysys-Refinery, developed by Hyprotech and KBC companies, is a simulator which is capable to simulate an industrial scale of catalytic reforming unit [14]. This simulator can simulate the catalytic reforming units with three or four reactors. That enables to simulate reactors with different catalyst weights and different sizes [15]. In this research, Hysys-Refinery has been used to simulate and sensitivity analysis of catalytic reforming unit.

4. Validation of Simulator

After simulation of catalytic naphtha reforming by Hysys-Refinery which shown in figure 2, to evaluate the simulator, the operating data of Tehran refinery for four months gathered which has been presented in table 3.

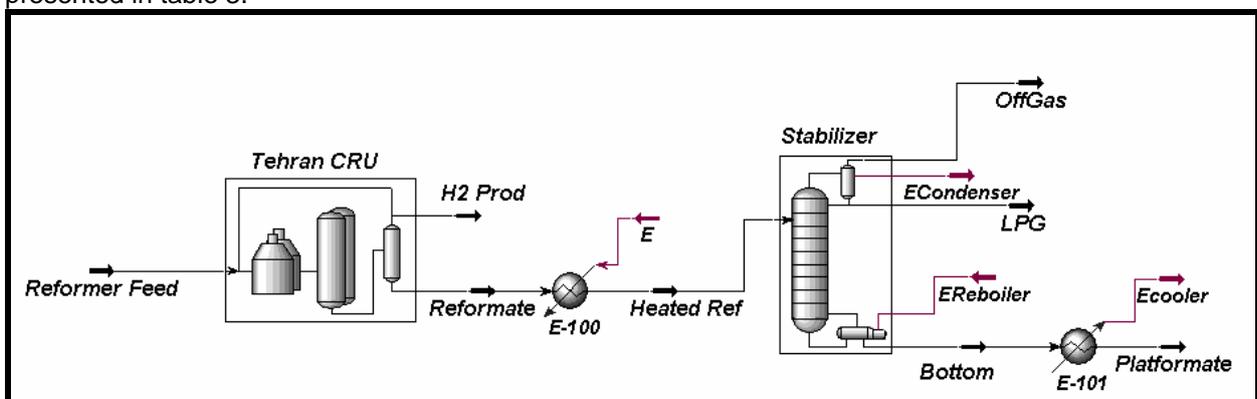


Fig.2:Simulation of catalytic naphtha reforming of Tehran refinery

Comparison of octane number (RON) and volume yield between actual data and simulation results were shown in figures 3 and 4. From them, the ability of Hysys-Refinery simulator to predict the desired outputs was confirmed.

Table 3: Catalytic reforming test runs of Tehran refinery

Variable	Unit	Test run 1	Test run 2	Test run 3	Test run 4
Date	---	December 2006	January 2007	February 2007	March 2007
Feed flow rate	m ³ / hr	95,29	95,94	97,65	97,67
Inlet temperature to 1 st Reactor	°C	499,44	499,44	501,11	500,56
Inlet temperature to 2 nd Reactor	°C	499,44	499,44	501,11	500,56
Inlet temperature to 3 rd Reactor	°C	498,89	499,44	501,11	500
Outlet temperature of 1 st Reactor	°C	436,66	437,77	437,22	437,23
Outlet temperature of 2 nd Reactor	°C	469,44	470	470	470,56
Outlet temperature of 3 rd Reactor	°C	489,89	488,88	492,78	491,11
C ₅₊ Yield	vol. %	78,3	76	76,55	77,63
RON	-	94,5	95	95,1	95,5

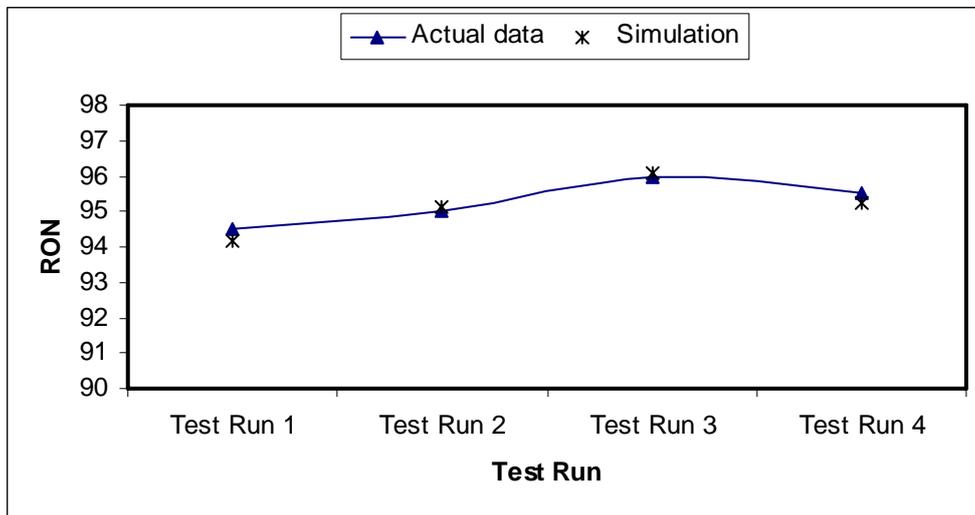


Fig.3: Comparison of RON between actual data and simulation

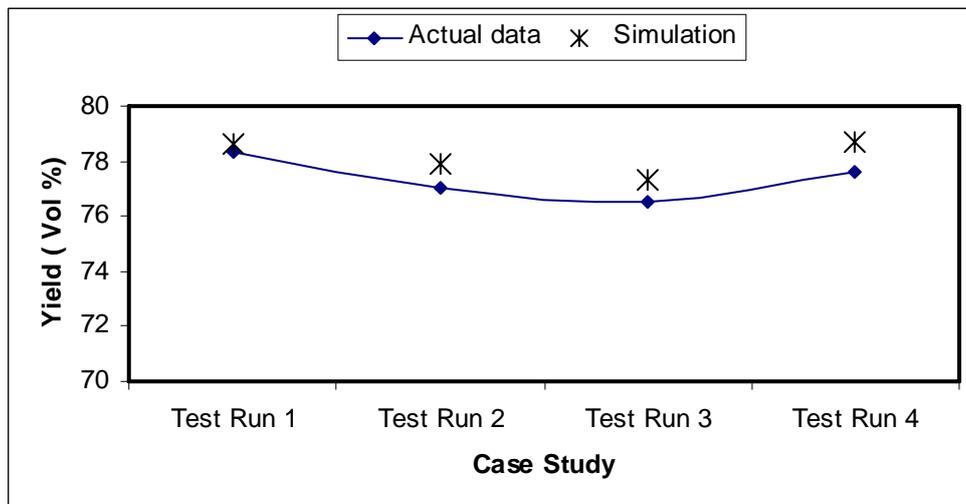


Fig.4: Comparison of yield between actual data and simulation

5. Optimizations of catalyst distribution

In modern experimental design techniques such as factorial design, fractional factorial design, D-optimal, response surface design [16], Packett-Burmann and Taguchi the most important parameters affecting the objective function are screened and their interaction is estimated. In this study a full factorial design incorporating the full interaction amongst the parameters was used to optimize the catalyst loading distribution in the reforming reactors. In the full factorial design the number of required experiments is n^k where k is number of parameters and n is number of parameter levels. The catalyst weights in the reactors at three levels were taken as the important parameters. As the reactor designs were preset and no change in the reactor specifications were attempted; therefore a ± 3 change in the catalyst loading in each reactor with respect to the design catalyst loading was permitted in the optimization study.

The designed catalyst loading for the reactors in Tehran refinery has been shown in fig.5 in which the 64 experiments obtained from the full fractional experimental design were included.

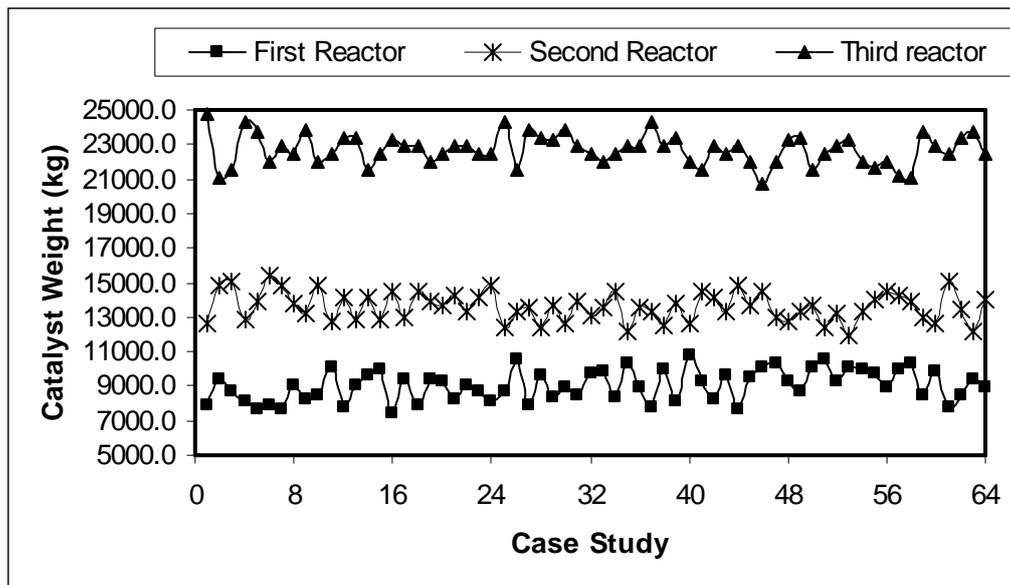


Fig.5: The designed catalyst loading for the reactors

6. Results

After designing the experiments, simulation was performed for all case studies. Then RON and Octane barrel were calculated for each case. The results have been presented in figures 6 and 7.

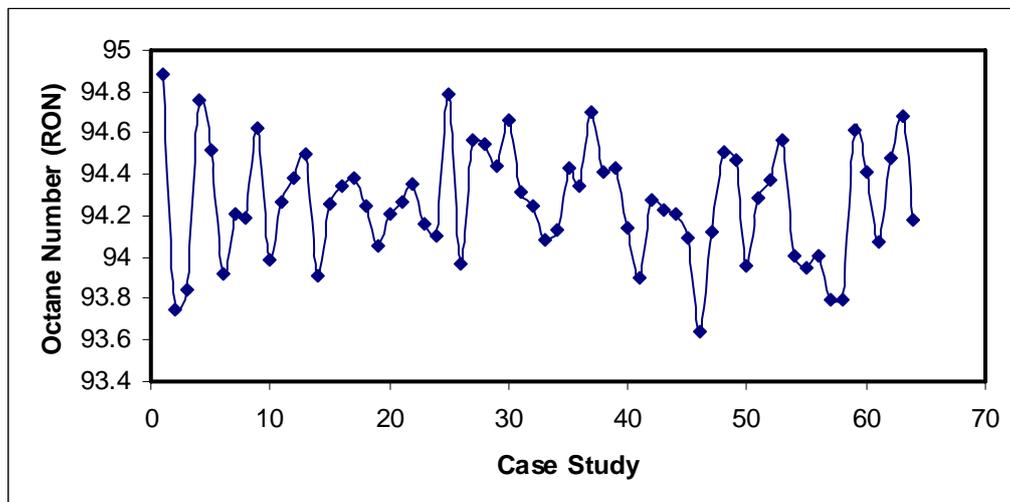


Fig.6: Octane Number calculated for designed experiments

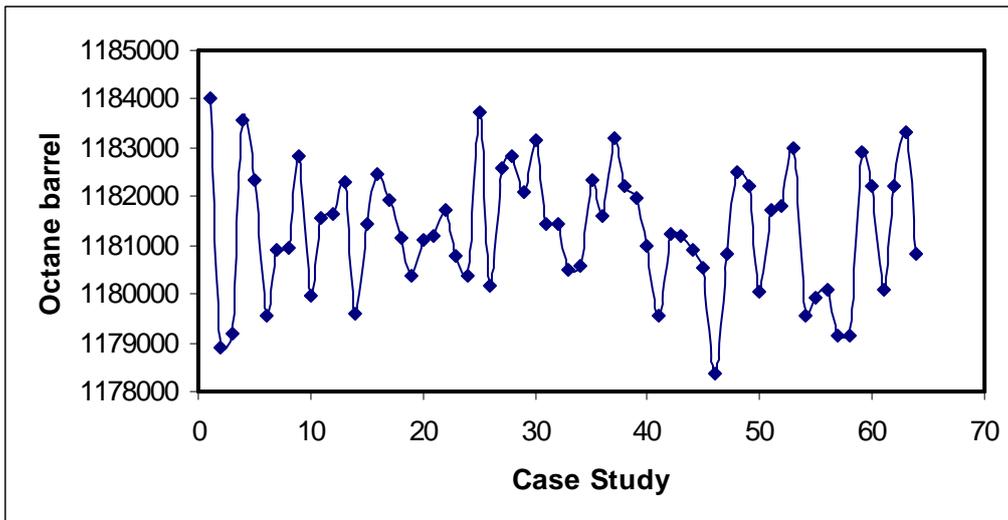


Fig.7: Octane Barrel calculated for designed experiments

From the mentioned figures, optimized catalyst distribution in reactors to meet the highest octane and octane barrel were concluded as table 4.

Table 4: Optimized catalyst distribution in the reforming of Tehran refinery

Variable	First Reactor	Second Reactor	Third Reactor
Catalyst distribution (wt%)	17,5	27,8	54,6
Catalyst weight (kg)	7 942,3	12 614,3	24 761,4

From Tables 1 and 4 it is obvious to optimize the catalyst in reactors the weight of catalyst in the first and second reactors should be decreased whereas it should be increased in the third reactor. In Tehran refinery, this revamp can be done by the techniques recommended by Axens^[17]. By them, the changes in catalyst weight in reactors can be manipulated in the range of $\pm 7\%$.

After optimizing the catalyst distribution, simulation was done again for actual data presented in figures 8 and 9.

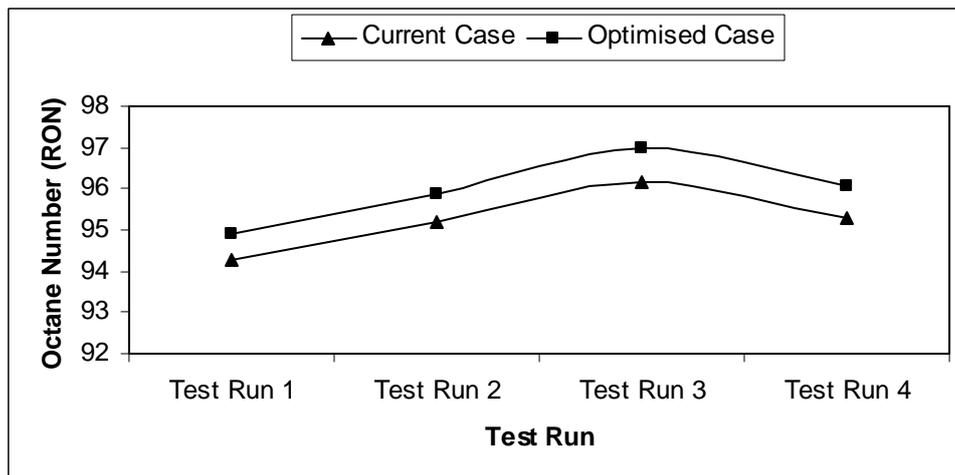


Fig.8: Comparison of RON between current and optimized catalyst distribution

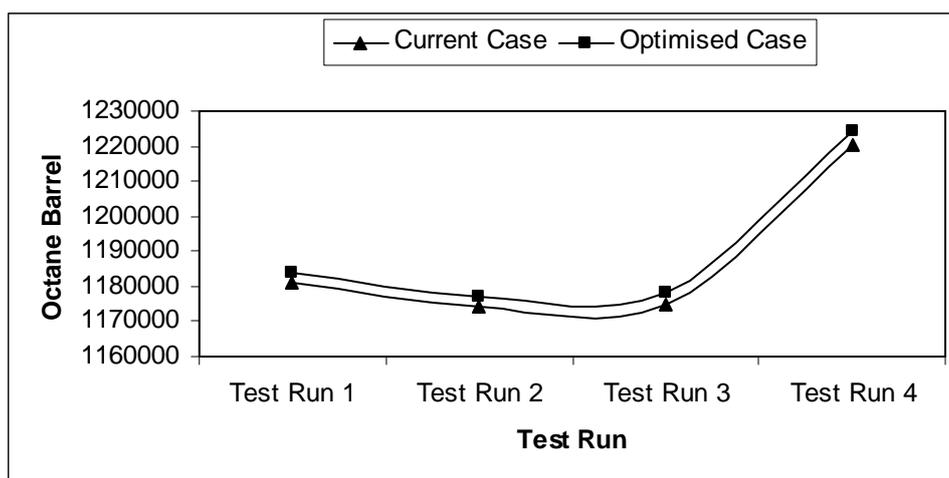


Fig.9: Comparison of Octane Barrel between current and optimized catalyst distribution

8. Discussion and conclusions

In this paper, the effect of catalyst distribution in reactors on the octane and octane barrel in the catalytic reforming unit of Tehran refinery were studied.

For this purpose, at first by using of pilot data, the kinetic of catalytic reforming reaction was determined and then the whole simulation was implemented in the house simulator as CRU-Sim. Comparison of CRU-Sim results with actual data proved the accuracy of simulation. After that, experimental design was performed to determine the catalyst distribution of catalyst. The resulted showed that the distribution of catalyst should be varied from 20, 30 and 50 percent to 17,5, 27,8 and 54,6 percent respectively.

Optimization of catalyst distribution in the Tehran refinery reformer has the following advantages:

1. By the mentioned method, the octane number of the gasoline product in the reforming unit can be increased up to one unit. Considering the fact that the furnace temperature should be increased at least 5F to meet the above added value in the current condition, the amount of energy as equal as 1000 kcal/hr will be saved in the reforming unit. This energy value is equal to 120,000 m³ natural fuel gas.

2. In a cycle, to meet the required product specification of Tehran refinery and deactivate the coking effect, the temperature of furnace should be increased from 497,8°C to 515,5°C in a period of 20 months. In this period, after optimizing the catalyst distribution, for every step from 497,8°C to higher value, temperature can be increased 5F lower as it mentioned before. Therefore, end of run temperature will be approximately met to 3 months later. It means that catalyst can be used 3 months more and it have considerable profit for Tehran refinery from the view of maintenance, procurement and preparation of catalyst.

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