SIMULATION, SENSITIVITY ANALYSIS AND OPTIMIZATION OF AN INDUSTRIAL CONTINUOUS CATALYTIC NAPHTHA REFORMING PROCESS

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Continuous catalytic regeneration (CCR) is a key process in petroleum refineries to produce high octane gasoline. In this article, a commercial scale CCR plant with the nominal capacity of 22000 bbl day^{-1} was simulated using Ref-sim module and Petro-sim simulator. The validity of this plant wide simulator was evaluated by actual test runs obtained during 6 months of operation. Simulation results showed that the AAD % of momentous output variables i.e. outlet temperature of reactors, product volume yield, product RON, H_2 purity of recycle gas and coke deposition on the catalyst against actual data were 0.5 %, 0.94 %, 1.098 %, 0.57 % and 0.347 %, respectively. Then, the optimal values for reactor temperatures, feed flow rate and recycle flow rate were determined using sensitivity analysis approach. After setting these decision variables on the proposed optimal values, the actual RON and volume yield of the CCR plant enhanced from 99.55 and 82.04 % to 99.67 and 82.4 %, respectively.

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Introduction

The main objective of the catalytic reforming process is to enhance the octane number of the feed, mainly heavy naphtha. The need to increase the antiknock quality of naphtha as a blending stock for motor fuels is the greatest single reason for installing catalytic reforming units.[1] A large number of reactions occur in catalytic reforming, such as dehydrogenation and dehydroisomerization of naphthenes to aromatics, dehydrogenation of paraffins to olefins, dehydrocyclization of paraffins and olefins to aromatics, isomerization or hydroisomerization to isoparaffins, isomerization of alkylcyclopentanes and substituted aromatics, and hydrocracking of paraffins and naphthenes to lower hydrocarbons.[2] Some of these reactions are desired because of increasing octane number of gasoline and also purity of the produced hydrogen, and some of them are undesired due to decreasing them. For instance, cyclization and aromatization reactions increase the octane number. They are thus favorite ones. In contrast, coke formation and coke deposition reactions cause the deactivation of the catalyst; consequently, they are undesired reactions.

From the view of the operation, there are three kinds of relevant catalytic reforming units: 1. Semi-regenerative; 2. Continuously catalyst regenerative (CCR), and 3. Cyclic[1, 2].

The CCR process consists of three or four adiabatic reactors in series with intermediate heaters.[2] Low octane hydrocarbons, such as paraffin's and naphthenes are converted to high octane aromatics, hydrogen and other light gases through this process.[3] In a CCR plant, the reforming reactions take place in a moving bed catalytic reactor from which the catalyst is withdrawn; then it is regenerated and recycled. The catalyst circulation and regeneration are performed on a continuous basis with full automatic control. Continuous regeneration eliminates the need of shutdown for regeneration of the earlier fixed bed reformers. Additionally, it minimizes the amount of catalyst in the unit, while allowing high gasoline yield and quality.[4,5] The variables that affect the efficiency of a CCR process are the volume flow of naphtha feed, reactor inlet temperature, hydrogen-to-oil molar ratio and temperature of the separator. [6]

In this research, after simulating a commercial CCR plant using Petro-sim simulator (KBC, 2009), the effect of process variables on the yield of reforming and RON of the product is discussed. Then, the optimal process variables were determined using the sensitivity analysis approach.

Process Description

A commercial CCR unit, called Platformer licensed by UOP cooperation with the nominal capacity of 22000 barrel per day was chosen as a case study. The block flow diagram of the process is shown in Fig. 1. The feed of the plant prior to entering reactors should undergo hydro desulphurization (HDS) reaction in the hydrotreatment unit. Then, the treated feed (Reformate) is passed through filters to remove any particulate matter which may deposit on the welded plates exchanger. The specifications of the feed are presented in Table 1. This feed is mixed with the recycle gas from the recycle compressor, and preheated against the fourth reactor effluent. Before entering to the catalytic reactors, it should be heated to reach the reaction temperature above 500°C. The reactors are radial flow types, so the feed flows through the catalyst bed from the outer circumference towards the center pipe. In the first reactor, the reactions are predominantly endothermic; therefore, the reactor effluent requires reheating in the first inter-heater to the required inlet temperature of second reactor. The reactions in the second reactor are less endothermic, but still require

reheating in other heater before entering the third reactor. The third reactor effluent is reheated in the third inter-heater before entering the fourth reactor. The effluent leaves the fourth reactor at approximately 468-486 °C (depending on position in the cycle) and 3.3 bar.

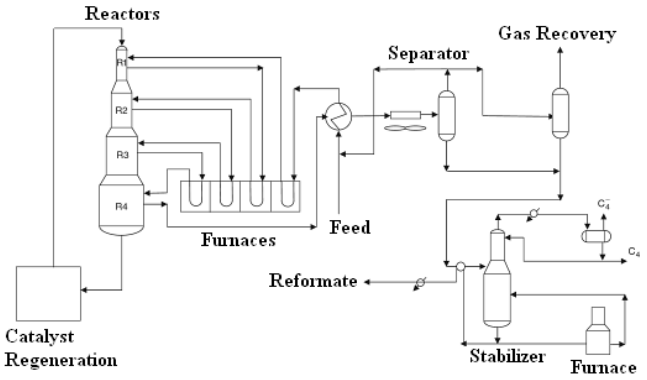

Figure 1. Block flow diagram of the continuous catalytic reforming unit [7]

In all reforming reactors the feed contacts with the reforming catalyst distributed approximately at the ratio of 15/20/25/40 %. In the continuous regeneration process the catalyst circulates continuously:

- In the reactors.
- From one reactor bottom to the top of the next one.
- From the last reactor to the regeneration unit for regeneration.
- From the regeneration unit, the regenerated catalyst returns to the first reactor.

In the regeneration unit, catalyst circulation is achieved either by gravity flow or by gas lift systems. In order to obtaining a good regeneration of the spent catalyst, operations such as coke burning, catalyst oxychlorination, catalyst calcinations, catalyst cooling and catalyst reduction must be carried out. Leaving fourth reactor, the effluent after heat exchange against reactor feed, is cooled by air and water exchange, respectively before entering the separator drum.

Table 1. Feed specifications of the CCR plant studied

Distillation Method (D86)		**Case1 Feb. 2011**	**Case2 April 2011**	**Case3 May 2011**	**Case4 July 2011**
IBP	° C	95	92	92	93
10 % vol	° C	107	104	104	104
30% vol	° C	112	111	109	111
50 % vol	° C	118	117	114	117
70 % vol	° C	126	127	125	125
90 % vol	° C	139	140	137	138
FBP	° C	161	164	161	159
PONA Analysis					
Naphthenes	vol %	33.2	33.8	33.8	-
Aromatics	vol %	12.2	12.4	11.8	-
Density	kgm^{-3}	746.5	745	745	744

A portion of the separated gas is compressed by a recycle gas compressor; then, it is recycled to the reactors. Finally, the liquid product leaving the separator is introduced to the gasoline stabilizer in which the LPG and light gases are separated from the gasoline to set the vapour pressure of the gasoline according to the market requirement. The distribution of catalyst between reforming reactors in the CCR plant studied in this work is shown in Table 2. Moreover, the normal operating conditions prevailing in this unit are presented in Table 3.

Table 2. Catalyst distribution in reforming reactors studied

Catalyst	**First Reactor**	**Second Reactor**	**Third Reactor**	**Fourth Reactor**
Weight (kg)	5880	6754	10545	18984
Distribution (wt %)	14	16	25	45

Table 3. Operating conditions in the CCR plant studied

Process variable	**Value**
Inlet temperature (°C)	500 - 515
Hydrogen/hydrocarbon ratio (mol mol^{-1})	3-7
LHSV (h^{-1})	1- 2
Yield (vol %)	70 - 85

Process Simulation

Catalytic reforming process is often modeled and simulated based on the: 1. Number of reactive species, and 2. Type of the used kinetic model.[8,9,10] Moreover, presence of many components as reactants or intermediate products in the reactive mixture makes a sophisticated situation for modeling and simulating 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 interested in designed models. Additionally, Arhenius and Langmuir–Hinshelwood kinetics are widely used for kinetic-based catalyst modeling and simulating of the catalytic naphtha reforming process[11,12]. Petro-sim simulator, developed by KBC, is capable to simulate industrial scale of catalytic reforming units.[13] This simulator can also simulate the catalytic reforming plants with three or four reactors; so, it enables us to simulate reactors with different catalyst weights and different sizes.[14,15] In this research, Petro-sim has been used to simulate and analysis of the CCR plant studied.

To simulate the catalytic naphtha reforming process using Petro-sim, external calibration in order to determining the kinetic parameters is essentially needed. For this unit, Ref-sim module is applied to provide these factors[15,16]. It should be mentioned that for generating these parameters i.e. frequency factors, activation energies and decay constants, actual test runs from the under study unit should be gathered. These parameters mainly consist of inlet and outlet reactor temperatures, catalyst weight, specification of feed and products, operating pressures, flow rates of makeup hydrogen, recycle rates and flow rates of all gaseous and

liquid products. After preparing test runs and running Ref-sim module, calibration factors are sent to the Petro-sim environment in order to simulating and optimizing the under study plant. The algorithm to tune and simulate CCR process studied in this research is shown in Fig. 2.

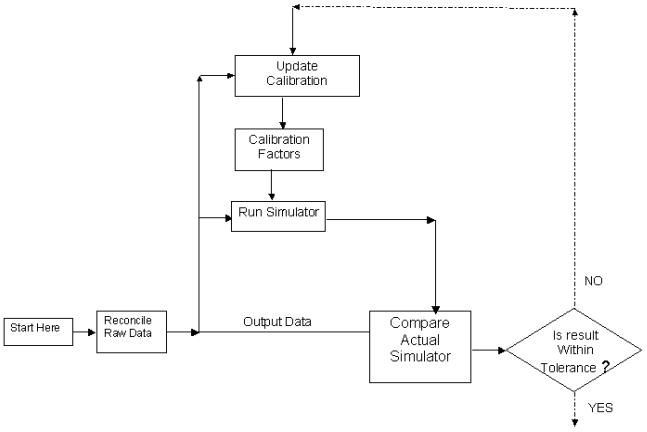

Figure 2. Algorithm of tuning and the CCR plant using Ref-sim module

Results and discussions

Actual test runs were gathered from the CCR unit described in the earlier sections. The data used for the calibration should be selected from the normal condition when no abnormalities, such as tower flooding, emergency depressurization and pump or compressor shut down were happen in the operation. Before using these data to estimate the tuning parameters, it was necessary to validate them. If a reasonable overall mass balance (±5%) cannot be calculated, the validity of test run was compromised. Additionally, from Table 1, it was found that the variation in feed specification was not considerable, and its effect on the yield and RON of the CCR plant can be ignored. The calibration parameters were then generated by Ref-sim module, and they were exported to the Petro-sim simulator to create the wide simulator of the CCR plant studied. The flow sheet of CCR wide simulator developed in Petro-sim environment is shown in Fig. 3. To evaluate and validate the simulation, the significant simulated variables i.e. outlet temperature of 1st, 2nd, 3rd, and 4th reactors, product volume yield, product RON, H_2 purity in recycle gas and coke deposition on the catalyst were compared against the actual data points.

Comparison of these momentous process variables for four data sets obtained during 6 months of study are shown in Tables 4 and 5. From these tables, it can be concluded that the average AAD % of the calculated outlet temperatures using the CCR simulator was less than 0.5 % for all data sets. In addition, the AAD % of simulation for yield, RON of product, H2 purity in recycle gas and coke deposition on catalyst were 0.94 %, 1.098 %, 0.57 % and 0.347 %, respectively.

From the AAD% of the simulation, the validity of wide simulator was confirmed during 6 months of operation; therefore, it is reliable to study the under study CCR plant.

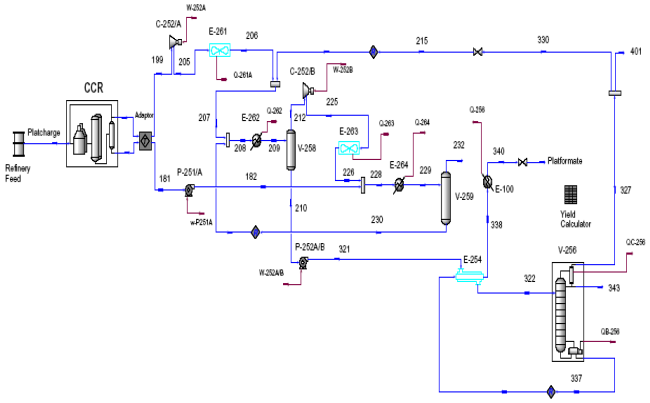

Figure 3. Wide simulation of CCR plant studied

After validating the CCR simulator, it was applied to sensitivity analysis of RON and yield of the produced gasoline. Fig. 4 and Fig. 5 show the sensitivities of RON and volume yield of the gasoline (or Reformate) to the temperature of reactors in the CCR plant studied.

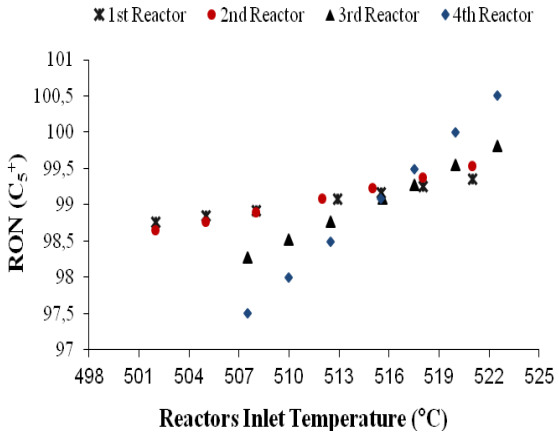

Figure 4. Effect of reactors inlet temperature on product RON

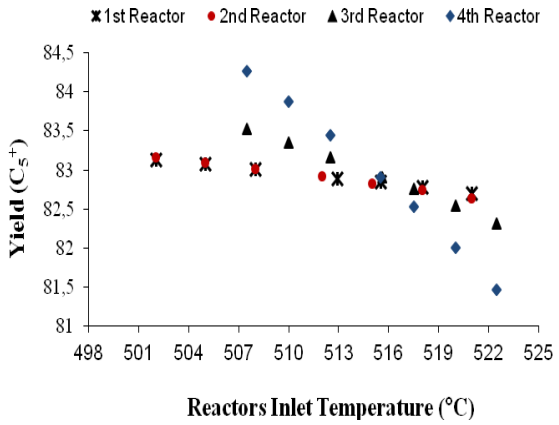

Figure 5. Effect of reactors inlet temperature on product volume yield

As observed in Figures 4 and 5, the RON of product was enhanced by increasing the temperature of reforming reactors. In contrast, the yield of the gasoline dropped by increasing the temperature.

Table 4. Comparison of outlet temperature of 1st to 4th reactors of the CCR plant studie

Variable	Unit	Test run 1		Test run 2		Test run 3		Test run 4		AAD %
		A	S	A	S	A	S	A	S	
1st reactor	° C	393.1	395.1	395.8	397.0	393	392	396.7	394.3	0.417
2nd reactor	° C	446.1	444.2	448.35	448.3	445.9	446.3	448.7	449.9	0.197
3rd reactor	° C	464.3	461.6	465.8	462.1	464.4	465.3	465.6	465.6	0.396
4th reactor	° C	480.8	476.65	480.9	475.8	479.9	479.7	480.9	479.6	0.558

A: Actual, S: Simulation, AAD: Absolute Average Deviation

Table 5. Comparison of product yield, product RON, hydrogen purity in recycle gas and coke on catalyst of the CCR plant studied

Variable	Unit	Test run 1		Test run 2		Test run 3		Test run 4		AAD%
		A	S	A	S	A	S	A	S	
Yield	vol %	84.48	83.8	81.59	81.76	81.5	82.29	81.69	82.51	0.94
RON	-	99.1	97.54	98.73	97.44	98.88	98.1	98.8	98.14	1.087
H_2 purity	mole %	89.27	89.49	88.48	88.87	88.3	88.95	88.37	89.13	0.57
Coke	wt %/	4.5	4.48	5.6	5.57	4.3	4.29	4.5	4.48	0.347

It may be supposed that the hydrocracking reactions are promoted more than the cyclization of paraffins, in consequence with increasing RON of the product, and also decreasing the volume yield. From Fig. 5, the optimum inlet temperature for all reactors is determined about 515 °C.

The effects of feed (heavy naphtha) and recycle flow rates on the RON and volume yield of gasoline are shown in Figw. 6 and 7. In these figures, for all cases, the left y-axis and (▲) points show the volume yield and the right y-axis and (●) points show the RON of the product.

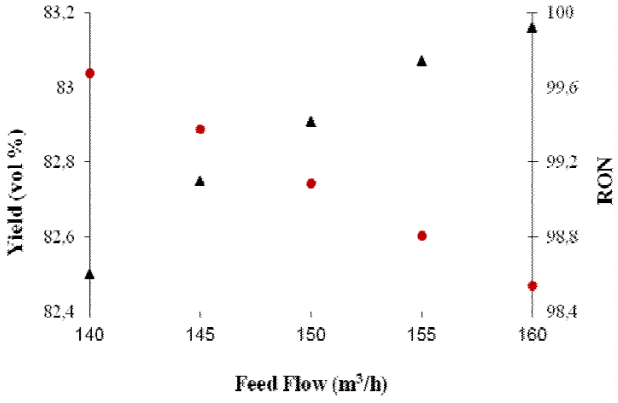

Figure 6. Effect of feed flow rate on product RON and volume yield

As illustrated by the (▲) points in Fig.6, by increasing the feed flow rate, the yield of the process (left y-axis) increases, but the right y-axis and (●) points show that increasing the feed flow rate drops the RON of the reformate. Since the inverse of the feed flow rate divided by the amount of catalyst is linked with the residence time of the reactor, it affects directly the kinetic of the reforming reactions. Decreasing the feed flow rate increases residence time in consequence with higher severity, hence it increases product RON, and decreases product yield. According to this figure, optimal feed flow rate of 148 $m^3 h^{-1}$ is determined. As illustrated by the (▲) points in Figs.7, increasing the recycle flow rate decreases the yield of the process (left y-axis), but the right y-axis and (●) points show that increasing this decision variable increases RON of the reformate. In fact, increasing the recycle flow rate elevates H_2 to hydrocarbon ratio; therefore, hydrocraking reactions are strongly promoted. Enhancing hydrocracking reactions in reforming reactors increases RON of product, and decreases product volume yield. According to this figure, optimal recycle flow rate of 45000 m^3 h^{-1} can be determined.

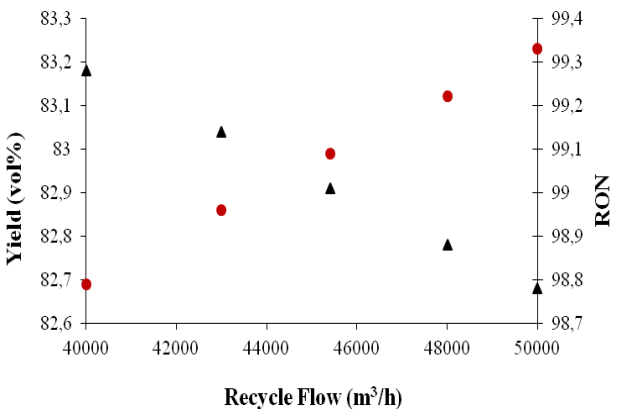

Figure 7. Effect of recycle flow rate on product RON and volume yield

Finally, to evaluate the optimal determined point for the CCR plant, reactor temperature of all reactors, feed flow rate and recycle flow rate were manipulated from 512.9°C, 150 $m^3 h^{-1}$ and 45400 $m^3 h^{-1}$ to the estimated optimal point i.e. 515°C, 148 $m^3 h^{-1}$ and 45000 $m^3 h^{-1}$, respectively. It was observed that the actual RON and volume yield of the CCR plant were enhanced from 99.55 and 82.04 % to 99.67 and 82.4 %, respectively.

Conclusion

In this work, a commercial scale continuous catalytic reformer, a key process for producing high octane gasoline, was simulated. Operating data was obtained from a commercial scale CCR plant for calibrating the simulator using Ref-sim module; then, the wide simulator of CCR unit was created in Petro-sim environment. Results showed that for four data sets gathered during 6 months of study, the average AAD % of the simulated outlet temperatures, volume yield, RON of product, H_2 purity and coke deposition on the catalyst against actual data were about 0.5 %, 0.94 %, 1.098 %, 0.57 % and 0.347 %, respectively.

After validating the simulation, sensitivity analysis showed that the RON of product increased by elevating the temperature of the reactors, but the yield of the gasoline dropped. Moreover, it was found that increasing the feed flow rate increased the yield of the process, but the RON of the gasoline decreased by increasing that. In contrast, increasing recycle flow rate increased the product RON, but it decreased the volume yield.

According to this analysis, the optimal inlet temperature for all reactors, feed and recycle flow rates were 515°C, 148 $m^3 h^{-1}$ and 45000 $m^3 h^{-1}$, respectively. After setting the process variables on these optimal values, it was observed that the actual volume yield and RON of gasoline increased to 99.67 and 82.4 %, respectively. Therefore the efficacy of the presented optimization approach was confirmed.

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