Original Article: Energy Optimization in Furnaces and Using Packinox Conversion to Reduce Benzene Production in OCT Units

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ABSTRACT

Naphtha catalytic conversion is one of the key processes in refineries. Naphtha is a section of crude oil that its boiling point is in the range of 40- 185 °C and constitutes 17-25% oil mass percentage. These values can be slightly changed depending on the conditions of each refinery. The reforming reactions on the platinum-containing catalyst are advanced to produce aromatics and hydrogen and are enhanced by the formation of branched and cyclic octane number gasoline for use in cars. In this paper, the independent variables, modifiable system variables to maximize the objective function, reactors input temperature and intensity of return hydrogen gas flow are investigated. The results show increasing the furnace temperature, adjusting the furnace damper, increasing the intensity of the return hydrogen gas flow rate, and using a plate conversion can reduce the amount of benzene in the gasoline and unauthorized carbon compounds. It dropped 0.4 %, which is very important for the environment. Also, by performing the calibration process, the error rate can reduce less than 3%, indicating the matching of unit data with the results is achieved.

Introduction

The formation of coke on the surface of the catalyst as a by-product reduces catalyst activity and reduces the quality of the product produced [1-4]. Changes in operating conditions such as temperature can partially offset the drop in activity, but increasing temperature will accelerate the formation of coke, and eventually, after reaching the upper limit set by the catalyst manufacturer, the catalyst must be resuscitated or replaced. To this end, three types of catalytic conversion processes have been developed based on the type of recovery process and operating conditions [5-7].

The first catalytic conversion unit was a periodic resuscitation unit that, after a period of unit activity, had to be shut down and the

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catalyst restored. These processes work at high operating pressures, which require special alloys in the reactor building. In order to prevent the unit from being stopped during the catalyst recovery, a revival process has been introduced that allows for lower pressures and requires catalyst recovery without the need to remove the unit. Today, with the advances in catalytic conversion units of continuous resuscitation as well as operating at low pressures, it has been possible to maintain catalyst activity due to its continuous resuscitation over time [8-10]. The catalytic conversion unit generally consists of three fixed bed reactors in series and the process is in periodic regeneration. For the reforming reactions, 20% of the catalysts were loaded in the first reactor, 30% in the second reactor and 50% in the third reactor. In this process, their activity decreases over time with the formation of coke on the reactor catalyst surface. In these conditions, by increasing the input temperature to the reactors, the quality of the gasoline product (octane number) can be controlled at a desirable level over time, albeit with a decrease in the quantity of product produced. After some time in the process of being in service, the conversion unit is out of service and the process of catalyst recovery is performed [11-13]. Benzene in gasoline in our country is about 3%. Benzene is produced in refineries during the catalytic conversion process of the fixed bed and in petrochemical complexes in the catalytic conversion process of the mobile bed. Majidian et al., reported the separation of benzene from gasoline using a reactive distillation reaction with benzene hydrogenation [14]. Samimi et al., (2019) investigated the feasibility of increasing feed in NHT mod units [15-17]. The results of the study indicated that by increasing the feed rate and raising the reactor temperature, the octane number can be fixed and, in some cases, increased. This will, of course, reduce the useful life of the catalyst. This paper addressed important results for feed increment with respect to unit reactor temperature analysis. Generally, by removing all six-carbon compounds from the catalytic conversion unit input feed and examining the operating conditions, i.e., temperature and pressure, the six-carbon compounds can be separated from the feed into the catalytic conversion unit and sent to the isomerization unit in addition to branching compounds Paraffin. The increased octane number also saturated the existing benzene [18]. In this study, the independent variables of the Octanizer unit, which are modifiable system variables to maximize the objective function, included the reactors input temperature and the intensity of the return hydrogen gas flow were optimized [19-21]. In order to determine the system parameters, the feed and product experimental values and specifications should be known and the objective function defined on the product quantity and specifications. By changing the reaction parameters, the calculated values of the output materials will also change [22].

Calibration Performing

If there is a discrepancy between the calculated and laboratory values, the parameters must be changed. The software changes the parameters of the system's reaction to such a degree that this difference becomes negligible, this type is called calibration calculation [23].

In other words, to determine the optimal values of the reactions in such a way that the difference between the calculated values based on those parameters and the experimental values reaches the minimum value.

Therefore, the simulation uses the parameters of the reaction corresponding to the actual system. Ref-Sim is a generic model for calibrating the catalytic conversion process that creates parameters that match the actual process condition. Because in order to simulate a high-precision catalytic conversion process, the kinetic parameters are required which have been obtained by the actual conditions of the system [24].

The parameters made by Ref-Sim calibration are catalyst activity constant, constant decrease in catalyst activity, relative reaction

rates, temperature coefficients of reactions, relative speed of reactions, equilibrium separation factors, pressure drop [25]. factors, product characterization factors, and gas flow [26].

Plate Heat Exchangers were first used in the 1980s to revamp large-scale catalytic converters. In the process, batches of shell and tube converters (Shell & Tube) were replaced by a bundle of plates inside a shell. This type of converter will find industry standard state for catalytic converters and aromatic production units and hydrogen purification units [27].

Replacing a batch of shell and tube converters with a single high-efficiency plate converter can reduce the heat load of the furnace and air conditioner by half [28]. This reduction directly reduces energy costs and fixed investment. In addition, the simple mechanical design of the plate transducers as well as the reduction of pressure drop in smaller furnaces, due to the high thermal efficiency of these transducers, cause the overall operating circuit pressure drop to be reduced and consequently the energy consumption in the furnace is reduced [29].

The gas compressor is also reduced by about 20% to 40%. Also, the cost of not servicing the unit is reduced to a minimal extent due to the repair work being done on the shell and tube converters, especially to clean the converters. This is due to less fouling in the plate transducers due to the uniformity of the turbulence intensity within the transducer. The bundle is made of thin sheets of S.S. These plates, which have been crushed underwater, are welded together and welded together half [30].

Process Operational Variables

Independent variables, which are modifiable system variables to maximize the objective function, include the input temperature to the reactors and the intensity of the return hydrogen gas flow. Reactor input temperature and hydrogen production rate are the most important factors affecting the octane number and product yield, and together with the hydrogen to hydrocarbon ratio have the greatest effect on chemical reactions [32-35], and also coke formation on the catalyst surface. Inhibitors are selected in the operating conditions of the conversion process and include:

Reactors input temperature: (470-530 °C)

The highest operating temperature of the conversion unit is considered to be 525 °C. In the temperatures lower than 480 °C, no favorable reactions occur [31].

Hydrogen to hydrocarbon ratio: (2/5-4)

At H2/HC ratios below 2, the coke formation rate on the catalyst surface increases sharply and the unit operation period decreases, so the catalyst should be in service, resuscitated, or replaced after a short period of time. The upper limit of the hydrogen to hydrocarbon ratio is also determined based on the compressor capacity of the return gas flow [32].

Also, the lowest allowed octane number is 92. Practical suggestions are made to increase the efficiency of the furnace and reduce its pollution. Catalytic conversion units also have the ability to work up to 535 °C, but at these temperatures, the coke surface on the catalyst surface can be greatly increased, and at higher temperatures it is possible to break down the catalyst and even deform it [33].

The compound of input gas to torch

The compound of feed input to furnace includes:

- ➢ Naphtha feed and hydrogen gas mixture;
- ➢ input and output temperature and pressure of furnace;
- ➢ environment temperature;
- ➢ air relative humidity;
- ➢ products from combustion and furnace chimney output; and,
- ➢ excess air percentage used.

Energy Optimization of OCT Unit Furnaces

Gathering the refinery operational information and necessary studies followed the energy-optimization patterns in the furnaces, following by performing manual calculations and obtaining the reaction equation in the furnace. It seems that comparing the information obtained from the reaction equation and the information as shown by the refinery is practical. In Tables 1, 2 and 3, the composition of natural gas and molar percentage compressibility coefficient, composition of combustion gases and thermodynamic properties of natural gas are shown [34].

Table 1. Composition of natural gas and molar percentage compressibility coefficient

Composition	N_2	CO_2	CH_4	C_2H_6	C_3H_8
Percentage	3/47	1/9	88/02	2/2	**1/02**
Composition	$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$i\text{-}C_5H_{10}$	$n\text{-}C_5H_{10}$	C_6H_{14}
Percentage	0/1	0/22	2/2	0/5	**0/37**

Table 2. Composition of combustion gases

Composition of combustion	CO_2	H_2O	O_2	N_2
Percentage	7	11.94	8	**73.06**
Composition of combustion	S_{0x}	CO	N_{0x}	
Percentage	14.4 ppm	105.22 ppm	39.24 ppm	

Table 3. Thermodynamic properties of natural gas

LHV	55 mj/kg
Molecular weight	**19.34 Kg/kmol**
Temperature	**33℃**
Δh Enthalpy changes	**-78091/ 75 Kj/kmol**
pDensity (kg/m³)	**0.662**

By combustion reaction according to the sampling carried out by the refinery the combustion products are as follows: The refinery reportedly reacted with 55% of the excess air.

(1) (*Fuel gasses*) + *Air* → CO_2 + H_2O + N_2 + O_2 + *gasses (ppm)*

Furnace combustion reaction equation

By balancing the reaction equation and considering complete combustion with 55% excess air and 17% relative humidity, we will have a temperature of 37 ° C:

(2) $100(fuel\ gasses) + 199.57 + 1.55 (O_2 + 3.76$

$N_2) + 15.8\ H_2O$

$→ 104.11\ CO_2 + 210.72\ H_2O + 1168.28\ N_2 +$

$109.760\ O_2$

In Tables 4 and 5 the, combustion air composition and enthalpy changes and compressibility coefficient and calculation of combustion air enthalpy at 35 °C are presented. Based on the available data, the furnace operates with 67% of the excess combustion air, which is extremely undesirable. Because it increases fuel consumption and reduces adiabatic flame temperature. Therefore, the furnace combustion equation for different amounts of excess air was investigated, the results of which are presented in Tables 5 and 6.

Table 4. Combustion air composition and enthalpy changes and compressibility coefficient

Composition	Percentage	$h°_f$	$h_{25°c}$	$h_{218.61°c}$	$h\ ^{kj}/_{kmol}\ \Delta$
CO_2	7.08	-395320	9364	17310.5	**-417373.15**
N_2	75.01	0	8669	14337.1	**5768.9**
O_2	6.88	0	8682	14514.6	**5732.16**
H_2O	11.03	-24820	9904	16538.8	**-275185.12**

Table 5. Calculation of combustion air enthalpy at 35 °C

Composition	Normal percentage	$h°_f$	298K $h_{25°c}$	310.15K $h_{37°c}$	$h\ ^{kj}/_{kmol}\ \Delta$
O_2	19.33	0	8682	9030	**378**
N_2	72.68	0	8669	9014	**375**
H_2O	0.286	241820	9904	10302	**-271427**

Table 6. Comparison of excess air percentage and adiabatic flame temperature

Excess air percentage	Oxygen percentage	adiabatic flame temperature
67%	8.8	**1713.51**
55%	6.91	**1758.85**
40%	5.61	**1912.94**
20%	3.98	**2103.15**
15%	2.98	**2160.11**

Several approaches have been recommended to increase the efficiency of industrial furnaces. Among the methods mentioned in the introduction section are the furnace conditions and abilities and the characteristics and climatic conditions of the extra combustion control area. Whereby we will get the following results:

➢ Significant reduction in fuel consumption of the furnace;
➢ reducing environmental pollutants due to proper combustion;
➢ reducing excess air intake for combustion;
➢ increasing the combustion speed;
➢ preventing incomplete combustion; and,
➢ using more flame temperature.

Results

The diagram below shows that as the excess combustion air decreases, the adiabatic flame temperature increases. The percentage of excess air consumes the fuel to heat the combustion air until it reaches the ignition temperature. It is associated with increased fuel consumption, which reduces the temperature of the adiabatic flame. Therefore, by reducing the excess combustion air from 67% to 15%, the adiabatic flame temperature can be increased to 29.06%. By reducing the percentage of excess combustion air, the AF value also decreases sharply [35].

The decrease in AF indicates that the amount of fuel consumed can be reduced and the more air is reduced, the higher the adiabatic flame temperature, and the less fuel is required for the furnace. By reducing the excess air from 67% to 19%, the AF value is reduced to 38.98%. The current fuel consumption of .08 tons / h is calculated to be 59% of the excess air, which, if controlled by the excess air by damper adjustment, will increase the excess air to 9% which is suitable for natural gas; one can therefore save a significant amount on fuel [36].

Analysis of Results

The temperature diagram and concentration changes of the main compounds of the reaction medium, including aromatics, paraffin's and naphthenes, are plotted. The severe temperature drop occurring at the input of the first reactor indicates the rapid conduction of dehydrogenation reactions that are the fastest and most endothermic reactions among the reforming reactions.

Most residues in the second reactor are dehydrogenated and a temperature drop of 19 degrees Celsius is created in the reactor. In the third reactor, the reaction of ring formation on paraffin's and the formation of naphthenic compounds is relatively endothermic followed by the dehydrogenation reaction of naphthenes to form aromatics.

The sum of these reactions results in a low temperature drop in the final reactor, and due to the relatively exothermic hydrocracking reactions, the temperature drop in this reactor is very low and is as low as 7 degrees Celsius. The most important reaction in the first reactor bed is the dehydrogenation reaction of the non-reactants. Therefore, in this reactor, the concentration of non-slopes decreases steeply and the concentration of aromatic compounds increases.

At the bottom of the bed, due to the low activation energy of the reactions, the reaction rate is very low, so adding a catalyst to the first reactor will not result in a higher conversion rate.

The residues left in the second reactor are converted into aromatic compounds. These reactions occur at the beginning of the second substrate and will result in severe temperature drop. The isomerization reactions of paraffin are carried out in the first and second substrates. In the final reactor, the paraffin ring formation reaction is carried out simultaneously with the hydrocracking reactions of these compounds. In the first reactor these compounds were removed unchanged.

The speed of the two reactions is approximately the same, and the concentration of paraffin in this reactor drops very little. Thus, with the formation of the ring, a greater number of aromatics is produced. In this reactor, the aromatics concentration diagram is decreasing, which is the result of most of the hydrocracking reactions. Hydrocracking reactions in the second and third reactors are due to high temperature and sufficient amount of hydrogen to form light compounds [36-38].

In Table 3, the N / H value was calculated by maximizing the operating profit at constant input temperature to the reactors. Also, as the input temperature to the reactors increases, the amount of benefit increases (Table 7).

Table 7. Change of operational variables to the optimal value of ratio

Temperature (°C)	H2/HC	Octane number	Mass Efficiency of Reformate (wt %)	Profit ($/hr)
490	7.724	89.03	78.5	5979.6
492	6.307	89.58	78.64	6080.4
494	4.291	89	78.41	6141.6
496	3.69	89.93	78.22	6213.6
498	3.551	89.99	77.05	6303.6
500	3.432	92.57	75.46	6390
502	3.209	92.25	73.76	6458.4
504	3.089	93.21	71.87	6526.8

The amount of coke deposited on the catalysts strongly depends on the reaction conditions and especially the ambient temperature. Therefore, in the final reactor, due to the higher average bed temperature, the highest amount of coke is formed [39].

The slope of these graphs has been decreasing over time because of the coke formation on the catalyst surface, the reaction

rate of coke formation is reduced as with other reactions. In Table 8 the critical conditions of target refinery catalytic conversion process performance are displayed. It should be noted that the accumulation of coke on the surface of the catalysts decreases the catalyst activity over time and limits the rate of progression of the desired reactions.

Table 8. Critical Conditions of Target Refinery Catalytic Conversion Process Performance

Fourth reactor	Third reactor	Second reactor	First reactor	Variable
525	525	525	525	Input temperature (Degree Celsius)
21-35.5				(Input and output pressure) Circulating gas compressor (bar)
3.25				Hydrogen to hydrocarbon ratio (mol/mol)
2.22				Space speed (hour $^{-1}$)
79.89				Portion (volume)

Investigation of input temperature changes to catalytic conversion unit reactors on benzene rate

According to the result, inlet temperature changes of catalytic converters and volume benzene volume and octane number has a straight relationship with together. Due to the importance of the reactor input temperature in the catalytic conversion process, sensitivity analysis was performed to change the input temperature to the reactors on the amount of benzene produced. The lower the temperature, the lower the production of benzene, but in the catalytic conversion process the temperature cannot be lowered to the desired level, as gasoline octane number and the yield of product will change. Therefore, in order to determine the reactors optimum temperature, the effect of temperature on these two variables was investigated, considering the optimum input temperature of the catalytic conversion in the range of 521-500 °C.

Investigation of input pressure changes to catalytic converter unit reactors on benzene rate

The amount of pressure in the catalytic conversion process is usually in the range of 25-32 bar, if the pressure is lowered the coke will increase, and if the pressure is higher, the hydrocracking reaction will increase, resulting in a yield or product yield. As it is known, the pressure is in the range of 29-33 bar. As can be seen, changes in operating temperature and pressure have little effect on reducing the amount of benzene and approximately 0.7 - 0.9 % of benzene reduction is observed.

The use of the stripping tower to separate the six-carbon compounds into the catalytic conversion unit

In addition to producing gasoline in the catalytic conversion unit, we use the isomerization unit that produces high-quality gasoline. In addition to benzene, we had to separate the six carbon compounds from the feed into the catalytic conversion unit by a stripping tower and sent it into the isomerization unit for the addition of branching paraffin compounds to benzene saturation. The characteristics of the stripping tower used to separate the six-carbon compound from the catalytic conversion unit feed are presented in Table 9.

Table 9. Characteristics of the separator tower used to separate the six-carbon compound from the catalytic conversion unit feed

The characteristics of tower	
Trays number	**36**
Feed tray	**15**
Type of condenser	**Complete**
Pressure of condenser (bar)	**5.0**
Pressure of Reboiler	**6.5**
Temperature of Reboiler	**190**
Temperature of condenser	**121**
Benzene molar component at the bottom of the tower	**0.2**
Benzene molar component at the top of the tower	**0.2**
Returned molar component	**9.6**

The amount of benzene in the gasoline product is also reduced by reducing the six-carbon compounds in the feed to the catalytic conversion unit. As is evident, by reducing the six-carbon compounds in the feed to the catalytic conversion unit, the amount of benzene in the gasoline product is reduced to zero. As it is known, by reducing the number of hexavalent compounds, in addition to the reduction of benzene in the gasoline product, the octane number and efficiency are also increased, so that all six-carbon compounds can be eliminated.

It is also found that the lower the reactors input temperature, the lower benzene is further reduced but will lose performance due to the catalytic conversion process, and the gasoline octane number will drop sharply, which is unacceptable, so the optimum input temperature of the catalytic converters in this state was chosen in the range of 530-500 °C. By examining the input pressure of the catalytic conversion, it was found that with increasing pressure, the amount of benzene decreased but increased in response to the hydrocracking reaction, resulting in a lower yield or product yield, hence appropriate pressure was selected in the range of 28–31 bar. In addition to investigating the operating conditions, according to the sources, either six-carbon compounds could be separated from the feed to the catalytic conversion unit and sent to the isomerization unit.

In addition to branching off paraffinic compounds and increasing the octane number,

it also saturated existing benzene and eventually produced high quality gasoline. An stripping tower was used to separate all the six-carbon compounds from the input feed into the catalytic conversion unit so that the amount of benzene in the gasoline output from the catalytic conversion unit was reduced by 2.5% to 0.5% without any change in the octane number and process efficiency, and, as explained, it was reduced by reducing the amount of six-carbon compounds in addition to reducing the benzene in the gasoline product

Conclusion

In this study, according to the results, the effect of temperature on the octane number in the end reactors is higher than the first reactor due to the higher average temperature of the catalyst substrate, which will result in a higher coke content on the surface of these catalysts. Also, as the temperature increases, the optimum profit margin increases. The slope of the optimum temperature – profit diagram decreased with increasing operating temperature due to a decrease in the volumetric efficiency of the reformer coupled with an increase in the octane number. As reactors input temperature decreases, the amount of hydrogen required for the reforming reactions increases.

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