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Improvement in the Life of Catalyst in Continuous Catalytic Regeneration Process

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***Abstract*: Catalytic reforming process has been used to produce high octane gasoline since the 1940's. It is a major process in the petroleum product for gasoline blending and into high value aromatics for petrochemical processing. Catalytic reforming also provides valuable hydrogen for hydroprocessing units to produce clean fuels. In the reforming process, napthas rich in paraffins and napthenes are converted mainly to aromatic hydrocarbons by contacting with a platinum containing acidic catalyst at elevated temperatures and pressures. This paper will briefly review the ideas regarding to increase the octane number of reformate by implementing various possible outcomes of improving catalyst activity and also by varying the changes in parameters of the process.**

***Keywords*: Catalytic reforming, platforming , naptha, octane number ,paraffins**

1. Introduction

The catalytic reforming process has been a mainstay in most refineries throughout the world for many years. The original function of this process was to upgrade low octane number straight-run naphthas to higher octane motor fuel blending components by catalytically promoting specific groups of chemical reactions. Naphtha boiling range products from other processes (thermal cracking, coking, etc.) were soon being included in the charge to catalytic reforming units for octane improvement. The reforming application was logically and rather quickly expanded to include the production of specific aromatic hydrocarbons. High-purity benzene, toluene, and mixed xylenes were made available to the chemicals industry from petroleum fractions by the combination of reforming, reforming, aromatics extraction, and fractionation. Hydrogen, the "by-product" from the aromatic producing reactions, was found to be useful in supporting the operation of reformer feed preparation units as well as other hydrotreating units. The light hydrocarbon gases, byproducts of the cracking reactions, were generally added to refinery fuel gas systems. Butanes, other cracking by-products, were commonly used in adjusting vapor pressures of gasoline pools. Thus, most refiners and many petrochemicals manufacturers have found the catalytic reforming process an increasingly valuable tool. Hydrotreated naphtha from Naphtha hydrotreater is used as a feed for CCR Platforming unit. Reformate produced in CCR Platforming unit is sent to MS blending. LPG, Hydrogen, Make-up gas, Fuel gas are also produced in CCR Platforming unit. Catalytic reforming process, the Platforming process, has continually been improved to meet the changing needs of the industry. Combined efforts in the areas of catalyst and engineering development have increased the flexibility of the Platforming process to meet the current and anticipated future needs of the industry.has commercialized six series of bimetallic catalysts: the Platinum/Rhenium R-16 and R-18 series, the R-20 series, the R-30 series, the R-50 extruded series, the R-60 series catalyst, and most recently the R-130 series. These catalysts have been proven to give better activity, stability, and selectivity than the all-platinum catalysts. In many cases, they have allowed refiners to extend their Platforming operations to higher charge rates and higher product octane levels than would have otherwise been practical. Because of the increased sensitivity of these catalysts to feedstock contaminants and operational upsets, the refiner must now pay closer attention to the daily operation to realize their full benefits. More precautions need to be taken to ensure clean, continuous, upset-free operation. Even with these added requirements, refiners are realizing better Platforming operations than ever before. In 1971, a new Platforming unit started up which revolutionized the process. It was the first Continuous Catalyst Regeneration Platforming unit. Now extremely high severities are obtainable without frequent shutdowns due to catalyst deactivation. As of April 1996, there are 134 such units on stream representing over 318,000 m^3/day (2.0 million BPD) with many more in the design and construction stages. New unit sales are almost exclusively CCR Platforming Process Units. The Catalyst Regeneration Section of a UOP Platforming Unit gives refiners the flexibility to operate the reaction section at high-severity conditions. At high-severity conditions in the reaction section, reforming catalyst deactivates more rapidly because coke lays down on the catalyst at a faster rate. Without a Catalyst Regeneration Section, the reaction section would have to be shut down more often for regeneration to burn off this coke and to restore the catalyst's activity and selectivity. With a Catalyst Regeneration Section, however, the refiner is able to operate the Platforming reaction section without having to shut down for catalyst regeneration. This is done by regenerating the catalyst continuously in the Catalyst Regeneration Section while the Platforming reaction section continues to operate. The Catalyst Regeneration Section consists of a system of integrated equipment that is separate from, but still connected to, the reaction section. It performs two principal functions – catalyst circulation and catalyst regeneration – in a continuous circuit. First, spent catalyst from the last Platforming reactor is circulated to the Catalyst Regeneration Section. In the Catalyst Regeneration Section, the spent catalyst is regenerated in four steps: Coke Burning; Oxy chlorination – for dispersing the catalyst metals and adjusting the catalyst chloride content; Catalyst Drying; Reduction – for changing the catalyst metals to the reduced state. Finally, the regenerated catalyst is circulated back to the first Plat forming reactor. The logic and sequence of this circuit are controlled by the Catalyst Regeneration Control System.

2. Methodology

Various case studies and researches will be conducted to attain the proper reactions perform in CCR unit . Proper steps should be held to increase the efficiency of plant just in this case the catalyst utility will be monitored effectively. Other catalytic solutions should be implemented such as evaluating current catalyst performance to determine when a change out is warranted is a critical component to maintaining profitable operations in reforming units. Once a change out is justified, determining which catalyst features are able to provide the most profitable operations becomes important. Also the catalyst selectivity can be improved somewhat by reducing the chloride content of the reforming catalyst. This is because acid-catalyzed cracking reactions, which cause reduced selectivity, are minimized with low catalyst chloride levels. However there are limitations as to how far the catalyst chloride level can be dropped. Reforming unit operators who desire maximum yields of desired products should consider choosing a high selectivity catalyst for their next change out. The process variable favorable conditions such as temperature space velocity, reaction pressure, H2/HC ratio for different reforming reactions will be monitored. Also various calculations related to mass balances will be calculated to find out the overall mass loss and the heat balance of the equipment will be encountered for the heat loss

The four most important operating variables of the Burn Zone are:

- Catalyst circulation rate
- Burn zone oxygen content
- Spent catalyst coke content
- Burn zone gas rate.

These four operating variables are interrelated. That means, each has limits on its acceptable operating range that are set by the other three variables. The operator must select all four variables with one goal in mind: To ensure that essentially all coke burning occurs in the Burn Zone. If coke burning occurs below the Burn Zone, such as in either the Chlorination Zone or the Drying Zone, then there will be serious damage to both catalyst and equipment. There is a general operating guideline that helps the operator achieve this goal. It is called the General Operating Curve (Fig. 1). It shows how these four operating variables are interrelated to ensure that essentially all coke burning occurs in the Burn Zone. The operator should always operate the Regeneration Tower in accordance with the General Operating Curve.

A. *Catalyst circulation rate*

The operator controls the catalyst circulation rate using the Catalyst Flow Set in the Catalyst Regeneration Control System (CRCS). This set point sets the regenerated catalyst lift rate that in turn sets the catalyst circulation rate for the entire system. The recommended operating range for the catalyst circulation rate is 25-100% of design. The catalyst circulation rate should not be operated above 100% of design. There are limits on the acceptable operating range of the catalyst circulation rate. These limits are set by the Burn Zone oxygen content, the spent catalyst coke content, and the Burn Zone gas rate.

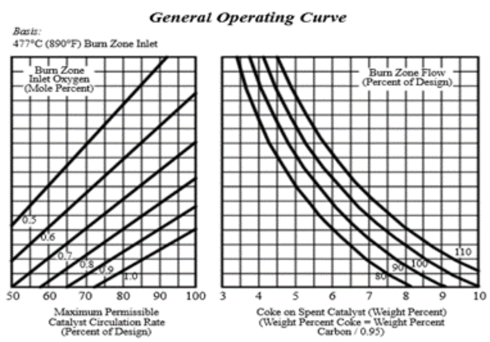

Fig. 1. General Operating Curve

The maximum permissible catalyst circulation rate is determined using the General Operating Curve as shown in the following

Maximum Permissible Catalyst Circulation Rate
If the current Regeneration Section operations is:
Spent catalyst coke content 5 wt-%
Burn Zone flow 90% of design
Burn Zone inlet oxygen 0.6 mole-%

From Fig. 1:

Maximum permissible catalyst rate 82% of design Using the General Operating Curve, start at 5 wt-% on the coke axis. Move vertically to the 90% Burn Zone flow curve. Move horizontally to the left to the 0.6% oxygen line. Then move vertically down to the circulation rate axis. Read 82% of design. As a result, if the actual catalyst circulation rate is greater than 82% of design, then it should be reduced. If the actual rate is less than 82% of design, then it can be increased gradually if desired. Certain combinations of values for spent catalyst coke, Burn Zone gas flow, and Burn Zone oxygen may give a maximum permissible catalyst circulation rate from Fig. 1 that is greater than 100% of design. However, for various technical reasons, the catalyst circulation rate should not be increased above 100% of design. When a catalyst rate is obtained from Figure 4.1 that is greater than 100% of design, it is usually because the chosen value of the Burn Zone inlet oxygen content is too high for the spent catalyst coke level. In the interest of minimizing the oxygen concentration without sacrificing complete combustion in the Burn Zone, the oxygen content should be reduced in accordance with the General Operating Curve. However, the Burn Zone inlet oxygen content should NOT be operated outside the range of 0.5-1.0 mole percent.

Computation

The operator computes the catalyst circulation rate using two methods: by the cycling of the Lock Hopper and by the combustion air usage.

Lock Hopper

To compute the catalyst circulation rate by the Lock Hopper, use the final calibration of the Lock Hopper Zone size.

$$CCR = \frac{(\text{number of L.H. cycles}) \times (\text{L.H. Zone size, wt})}{(\text{time, hrs})}$$

Combustion Air Usage

To compute the catalyst circulation rate by air usage, use the following

CCR(kg/hr)= (0.488)X(100/X-1) X AT X (0.21-Y)

B. *Burn zone oxygen*

The operator controls the Burn Zone oxygen content using the oxygen analyzer. During normal operation, the oxygen analyzer controls how much excess air is vented from the Regeneration Tower: as less excess air is vented, more enters the Burn Zone, and the oxygen content becomes higher. The recommended range for the Burn Zone oxygen is 0.5-1.0 mole-% oxygen. Higher oxygen causes higher burn temperatures that could cause damage to the catalyst, primarily in the form of surface area loss. Lower oxygen causes slower coke burning that might not finish completely in the Burn Zone. If coke burning occurs in the Chlorination Zone, extremely high temperatures will occur that will cause serious damage to catalyst (i.e., alumina phase change) and equipment in the Chlorination Zone. In order to minimize the negative effects of high temperature burning on catalyst performance, it is recommended that the Burn Zone oxygen be minimized, provided that coke burning is completed in the Burn Zone. Minimum Allowable Burn Zone Inlet Oxygen Content. If the current Regeneration Section operation is:

- Spent catalyst coke content
- 5.5 wt-% Burn Zone flow.
- 110% of design Catalyst circulation rate.
- 90% of design

C. *Spent catalyst coke: Principle*

The operating conditions in the reaction section control the coke on the spent catalyst from the last Plat forming reactor. The coke content is a function of charge rate, product octane, charge quality, reactor pressure, recycle rate, and catalyst circulation rate. The recommended operating range for the spent catalyst coke is 3-7 wt-% coke. Within this range, catalyst performance and catalyst life are optimum.

D. *Computation*

Combustion Air Usage

To compute the coke content by air usage

X= 100/1+CCR (kg/hr)/0.488 x At x (0.21-Y)

Where X = spent catalyst coke

CCR = catalyst circulation Rate ,kg/hr

Y = Burn zone inlet oxygen concentration,mole fraction

At= Total Combustion air,Nm /hr

If the current Regeneration section operation

Total combustion air = 670 Nm^3hr

Catalyst circulation rate = 1362 kg/hr

From graph

Spent Catalyst coke = 4.7 wt%

- Following are the inputs which should be taken by the chemical engineers
- Use of High Promoter base Catalyst
- Removing the metal content from the feed to protect the catalyst
- Chocking can be avoided by using nitrogen flush method
- Proper process parameter handling by operator such as temp , pressure
- Sulfur Contents in the feed should be examined periodically

3. Conclusion

From the project analysis and survey it can be concluded that the life of catalyst can be increase by maintaining the following inputs and controlling the catalyst circulation rate. From the survey, using of micro induced method to regenerate platinum is the best advanced remedy for increasing the life of catalyst. The computation of catalyst circulation rate enables the catalyst life if it is circulated within the range

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