

CATALYST REGENERATION TECHNIQUES IN NAPHTHA REFORMING: SHORT REVIEW

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Catalytic reforming is an important intermediate in the processing of crude (naphtha in particular) to obtain gasoline. The catalyst used in the process (platinum) is quite expensive and may negatively impact the business if not used judiciously. The aforesaid not only refers to the reduction in loss of the catalyst per unit of gasoline produced but also to the manufacturing of an environmentally friendlier product alongside which is the need of the planet and also a necessity to meet the increasingly strict government norms. In order to meet the above requirements, various refineries around the world use various well-known conventional methods which depend on the quality and quantity of crude manufactured by them.

This paper focuses on highlighting recent advancements in methods of catalytic regeneration (CR) in the reforming unit of petroleum industries to produce high octane gasoline, without any major replacements in their existing setup. Research papers formulated by the application of methodologies involving non-linear models and real-time refinery data have only been considered to avoid any deviations/errors in practical applications. In-depth analysis of these papers has led to the origin of some ideas which have been included as suggestions and can be considered as subjects of further research. In all, the objective of the paper is to serve as a reference for researchers and engineers working on devising optimum methods to improve the regeneration of reforming catalysts.

Keywords: heterogeneous catalysis, regeneration, naphtha reforming, catalyst reactivation, non-linear modelling

1. INTRODUCTION

The need for catalyst regeneration arises due to its consumption in the reforming process. Therefore, to understand the various intricacies of regeneration it is important to have a brief knowledge of catalytic reforming. Desulphurized naphtha can be reformed in several ways, viz. by thermal reforming, steam reforming and catalytic reforming. The former two being outdated due to the consistent requirement of larger amounts of energy as compared to the catalytic method. Catalytic reforming comprises four major reactions (Krane et al., 1959):

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- dehydrogenation of naphthenes to aromatics,
- dehydrocyclization of paraffins to aromatics,
- isomerization of naphthenes,
- hydrocracking.

Along with these, there are several other reactions of less importance. The first reaction is very endothermic and requires that after every catalyst bed the intermediate streams should be heated. It is quite important to notice that the heat requirement is lower than in other known methods (Bartholomew, 2001). The formation of considerable amounts of hydrogen in this reaction directs it towards two uses. Some of it is recycled back into the reactor to sustain reactor pressure and reduce the formation of coke. The remainder of it is used in hydrotreatment and other processes. All the reactions are desirable, except for the hydrocracking at this stage. The reason being increased light ends in the final reformat because cracking has already been performed at an earlier stage. Based on the mechanism used, reforming can be classified into two types, which are Fixed Bed Type and Moving Bed Type (Ciapetta and Wallace, 1972).

2. CATALYTIC REGENERATION TECHNIQUES

The reforming mechanisms typically use platinum catalysts combined with one or two other metals namely Ir, Sn, Al or their oxides such as Al_2O_3 as support bases (D'Ippolito et al., 2008). The catalyst is formed after blending the above individual components in a unique ratio as per the setup requirement after studying the variation in their properties upon combination. Active sites occur inside the pores on the freshly chlorinated catalyst surface which is usually present in the form of small pellets in the reactor to maximize surface area.

The pores are blocked by coke and other impurities, which leads to a reduction in sites that are active over time and the catalyst surface is said to be deactivated. Thus, an optimum pressure of hydrogen in the reformer is necessary as it hinders coke deposition on the catalyst (Argyle and Bartholomew, 2015). Yet, this can only prolong the activated time period of the catalyst and at some point, it becomes necessary to regenerate the catalyst.

Three major regeneration techniques applied to the fixed and moving bed type mechanisms are (Babaqi et al., 2016):

- semi catalytic regeneration (SCR),
- cyclic catalytic regeneration (CCR),
- continuous catalytic regeneration (CoCR).

2.1. Semi catalytic regeneration

This is one of the foremost methods of regeneration to be used in the industry. Here, platcharge is the naphtha obtained by hydrodesulphurization of naphtha in the hydrotreatment unit. It is then pre-heated in furnace H-1 and subsequently reformed in fixed bed reactor R-1 where the four major reactions occur. The same is repeated in the next two sets of furnaces and reactors to increase residence time and thus, LHSV ranges from $1\text{--}2\text{ h}^{-1}$. V-1 is the flash drum, where hydrogen is separated from the reformat to further separate it into LPG and gasoline in the stabilizer. The mass of catalyst in the reactors increases and mass distribution rises from 20–30–50% successively. Hydrogen to hydrocarbon ratio ranges from 3–7 and yield volume is 70–85% (Mohaddecy and Sadighi, 2014).

The shutdown period for in-situ regeneration of the catalyst in this process ranges somewhere between six months to two years. In this kind of regeneration, the feed to the reformer is stopped and the catalyst is

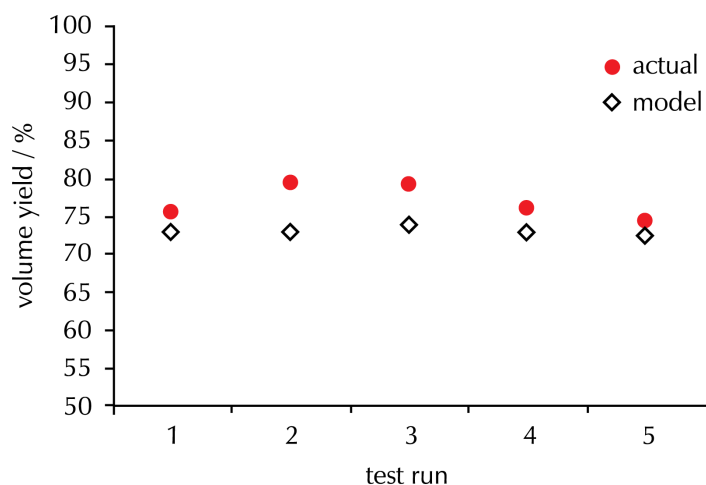


Fig. 1. Simulated volume yield of gasoline against actual values.
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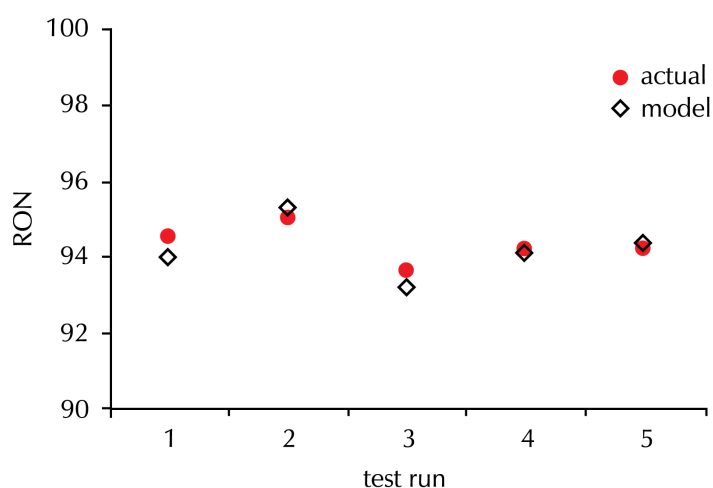


Fig. 2. Simulated RON of product against actual values.
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not moved. Hydrogen gas is recycled at this time, to remove any hydrocarbon residue left. With advent in importance of hydrogen as a source of energy and also due to its reducing nature, implication of an external supply of nitrogen is common in many semi-regenerative facilities. This ensures purity of hydrogen obtained and also guarantees safety and the uniformity required in heating the catalyst, so that the coke deposits burn off uniformly (Yusuf et al., 2019). Besides physical removal, coke can also be removed by oxidizing it in a controlled manner. Currently, this process is incorporated in the physical removal by using hydrogen/nitrogen (discussed earlier). This is necessary because in spite of the catalyst purge, considerable amount of carbon remains. For oxidation, the air is used as the source for oxygen, which is maintained between 0.5–2.0% in nitrogen/hydrogen stream. The temperature must rise gradually at 50–100 °F per hour and achieve a final temperature of 750 °F. The temperature must not exceed 850 °F to prevent sintering of the catalyst crystallites and maintain optimum reaction conditions for decoking. Here, coke is removed in a series of steps till none of it remains. These steps may coincide with jumps in oxygen concentration or temperature (Rahimpour et al., 2013).

Yet, carbon is not the only hurdle in achieving the activated catalyst. Removing the coke sintering is unavoidable, even when the reactions occur in a controlled manner. Thus, continuously adding organic chloride to the semi-regenerative fixed bed units can reduce the agglomeration of metal from the spent

catalyst (fixed bed). High chloride concentrations in the effluent gas from the previous reactor needs to be neutralized. This is necessary to prevent corrosion and fouling of the reformer interior and is done by an alkaline caustic solution which is circulated continuously. The targeted chloride content ranges between 0.9–1.1 wt%. Sintering causes the diameter of the metal crystallites to increase and thus the activity of the catalyst decreases (Ren et al., 2002). However, sintering can be reversed to some extent which can reduce the crystallite diameter to an extent that it has sufficient enough activity. This can be done under a full-air atmosphere by adding chlorine at a temperature of 932 °F to the reactor. The sub-process is also known as rejuvenation and results in many days of downtime for the semi-regenerative reactor. Nitrogen is purged through the catalyst bed in order to provide it with an intermediate stage to move from the reduction phase to the oxidizing phase. The second advantage of purging nitrogen is that it also dries the catalyst of the water generated in metal reduction reactions (Elfghi, 2016).

Periodic draining of low points in the regeneration circuit and nitrogen purge help reduce the water in the reduction zone which is crucial for optimized reduction of catalyst (Elfghi, 2016). This reduction is accomplished by using electrolytic hydrogen of high purity or by using the recycled gas from the reformer. The balance between the concentration of hydrogen in the reduction gas and the reactor temperature is crucial in the determination of residence time for the gas and thus economic feasibility of the operation. This is because high-temperature results in undesired hydrocracking of the hydrocarbons in the recycle gas hampering the reduction. Multiple studies suggest that a temperature ranging between 600–900 °F is optimum for the process to obtain high purity hydrogen, in an economically feasible manner. Hyperactive sites on platinum/rhenium catalyst require tempering. This is usually done by sulfiding the catalyst which is in accordance with the amount of rhenium present in it. 0.05 to 0.06 wt% of sulfur is recommended for balanced equimolar Pt/Rh catalyst (McClung and Oyekan, 1988).

2.2. Cyclic catalytic regeneration

This method is preferably used when the naphtha feed quality is very poor, which also decides the regeneration interval for this process and it ranges from a few weeks to a few months. Despite the feed quality being poor, it can return a reformat with an octane rating of 95–108. To add to its merit, it also produces a higher yield of hydrogen gas and retains the catalyst at a higher activity with time. The excellent yield of hydrogen also leads to less pressure requirement and thus external pressure of 3.5 bar is sufficient for operation (Szczygieł, 2011). Kinetic model is used, comprising reactions lumped in groups which are interconnected to form a network. There are 27 lumps in all in the network including hydrogen, of which dehydrogenation and isomerization reactions are considered as reversible reactions. The only irreversible reactions in the model are those of hydrocarbon cracking. The first-order reaction kinetic model given below summarizes the change in rates of various reactions of pseudo-homogenous nature (McClung and Oyekan, 1988). Generally, two kinds of dispersion effects (i.e. radial and axial) are encountered in such systems, but a reduced amount of operating pressure leads to normalized reformer conditions, thus producing negligible dispersion. Catalysts and feedstock interact in a pattern that can be considered similar to that in a general plug flow reactor.

Treanor's method is used for solving the ordinary differential equations (Hongjun et al., 2010). Free energy and heat of formation are the two major thermodynamic properties of the lumps for which the arithmetic average of the pure chemical components in the lumps is computed. At the inlet of the first reactor, a distinct drop in temperature is observed which becomes less distinct in the subsequent reactors. Instantaneous occurrence of the most endothermic reaction i.e. dehydrogenation of naphthenes takes place, which also have the property of occurring at the fastest rate, hence the sharper drop. Thus, the reaction mixture needs to be reheated (Hongjun et al., 2010).

Two dimensional coke distribution on the catalyst surface is also very helpful in terms of prospects for future research. Amounts of formation of methylethylbenzene, propylbenzene trimethylbenzene, ethylbenzene, benzene, toluene and xylene are also accurately predicted. In the cyclic regenerative reformers, safety is one of the primary concerns. This is because when such a reformer is operated, hydrocarbon/air explosion may constrain the operators sometimes to help in conduction of dispersion of metals. The conditions must be less than those required under optimal oxychlorination conditions. Typically, the concentration of oxygen in the chlorinating gas is less than 2.5 vol% (Schorfheide and Schweizer, 1993). Also, in such a reformer reduced catalysts are not sulphided as it is operated using monometallic platinum catalysts. This is because sometimes it is experienced that over hyperactive metal sites, excessive hydrogenolysis occurs when the regenerated reactor is brought into the naphtha-reforming processing loop (Arani et al., 2009). In continuous reformers Pt/Sn catalysts are used unlike the cyclic process in the process, which enables catalyst to be regenerated without sulfiding.

2.3. Continuous catalytic regeneration

Catalyst deactivation can have a considerable impact on the industrial operating cycle of the reformer. Thus, the deactivation kinetics of the catalyst have been therefore given prime importance in the modeling of the reforming process. Deactivation model of the catalyst should accurately predict performance of the reactor over multiple reactor pressures and temperatures and thus the formation rates of coke. Simulations of a defined catalyst deactivation factor can thus predict the effect of catalyst deactivation on reactor performance (Sa'idi et al., 2011).

For model validation and parameter estimation, the function required is given below in the minimized form and can also be referred to as the objective function, which is introduced for the purpose of estimating the parameters and validating the model. *GA 5 algorithm* is used to optimize the process (Mills et al., 1953). Only a fixed amount of catalyst is regenerated at a time, which is determined by the catalyst circulation rate. Hydrogen purge of the spent catalyst is conducted, which flows to a catalyst collector from the last reactor. This catalyst is then transferred through a disengaging hopper to numerous vessels, piping and valves to the regenerator tower. However, catalyst fines should be substantially reduced before finally transferring the catalyst to the regenerator (Samimi et al., 2020).

Coke burning temperatures for this kind of reformer are usually between 750–1050 °F. At higher temperatures, there are chances of rapid loss in surface area due to alumina phase transitions. Such transitions can also occur readily in the core of the catalyst. The reason being, temperatures there are 200–300 °F higher than those in the bulk. Heat-up is controlled as it may damage the reactor internals and also the catalyst (Ren et al., 2002). Also, the oxygen concentration in the nitrogen stream is between 0.3–1.0%. Spent catalyst treatment in the continuous method follows the same preliminary procedure as the semi-regenerative method. The temperature ranges between 950 °F and 1100 °F. Also, oxygen concentration (0.8–1.3 wt%) and air flow is regulated to ensure controlled combustion of the coke on the catalyst surface. An exclusive characteristic of this process is the use of screens to contain the catalyst (Jess et al., 1999).

They are used on the outer and inner surface to control the flow of catalyst in the regenerator annuli and the reactors. These screens usually get plugged with catalyst fines and lead to incomplete burning of coke, along with catalyst damage. Yet, these screens can be cleaned and the regenerator can be restarted, without hindering reformat and hydrogen production. A specially formulated regenerator metallurgy can withstand the oxidation/chlorination of the catalyst with high oxygen and high chloride content (Pashikanti and Liu, 2011). The partial pressure of oxygen in the oxychlorination zones is usually less than 10 psi in atmospheric CoCR units.

3. REGENERATION AND PHYSICAL PROPERTIES OF THE CATALYST

Several catalyst properties influence the activity of the reforming catalyst and thus its performance. Properties such as surface area stability, attrition, crush strength and metal redispersion have been found to have a dominating effect on the efficiency of the catalyst. Thus, restoring these properties to the desired level is the key objective of catalyst regeneration.

The surface area of the catalyst material is quite large and ranges from 110 to 200 m²/g. This is the reason that despite the extraordinary care taken to have an even surface, mild sintering occurs at some parts due to the presence of small amounts of foreign ions and impurities and leads to difficulty in coke removal and thus increase in regeneration cycles over time (Said-Aizpuru et al., 2020). Also, the loss of small amounts of surface area and pore volume with each regeneration cycle is unavoidable. The loss of surface area for a catalyst bed during 4 years of its use is observed. It is found that the rate of loss in the area is higher in the beginning as compared to the later cycles. On a continuous basis, the catalyst is transported from the reactor to the regenerator where, before being replaced by a fresh material it undergoes 200–300 regeneration cycles. To withstand the various compressive and shear stresses during the movement throughout its lifecycle, it is necessary that the material is resistant to attrition. These stresses are compounded along with high-temperature reduction and oxidation cycles during the regeneration process which the catalyst has to bear (Ramage et al., 1980). This also gives a reason why a catalyst should have high attrition resistance. Crush strength of the catalyst provides measurements that can help in the identification of weak points of the catalyst. Crush strength is measured in pounds per sphere and catalyst pills possessing a strength of more than 2.5 lb/sphere have a fairly lesser chance to fracture. Rotating drum test is used to determine crush strength in which both, catalyst-wall and catalyst-catalyst interactions are taken into consideration (Antos and Aitani, 2004).

4. CONCLUSION

A comparison of various types of catalytic reforming processes based on the time interval required to reactivate/regenerate the catalyst was made so that new opportunities for process improvement as a future study could be considered. Higher octane reformates with poorer quality of feed were processed by CoCR with greater efficiency as compared to SCR and CCR. To add to its merit, the continuous generation of hydrogen gas in this process as a by-product under higher catalyst activity at an optimum temperature of the reactor increases its efficiency innately, without external support (Lee and Yoo, 2014). Thus, opportunities for further improvement and research are shown by CoCR as compared to SCR and CCR.

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