ABSTRACT

Catalytic processes are involved in different sectors that influence human life, world economy and environment. Different daily used products depend on catalytic processes: fuel, energy, plastics, cosmetics, pharmaceuticals products, etc. Considering the wide spread application of catalytic processes, and knowing that transport and environment are priority for some researches; this paper is focus on production of fuel (especially gasoline), that needs two important catalytic processes unit: Fluid catalytic cracking and catalytic reforming. Studies and development of design and modeling of fluid catalytic cracking and catalytic reforming were reviewed in this paper. At last, some paths were lighted in aim to pursue a design and modeling study further.

Keywords: Catalytic process, Fluid catalytic cracking (FCC), Catalytic reforming (CR), design, modeling, Gasoline.

INTRODUCTION

It has been many centuries since the catalyst technology was used in wide sectors. Firstly used in 1875 in production of sulfuric acid, catalyst usage have been developed in several fields such in production of nitric acid (1903), ammonia synthesis (1908-1914), catalytic cracking process (1935-1940) that change the energy evolution, catalytic hydrocarbon process (reforming in 1950) and hydrotreating (1960)(Guwahati, 2014).

With the propriety of not altered reversible of equilibrium of reactions, and to accelerate both forward and reverse reactions, the presence of catalyst can result in different product distribution. That is why we have operation such as decomposition some molecules and reforming of others. Gas and oil is one of the sector need the most such properties held by catalyst. In fact, in refining and petrochemical industries, presence of catalyst is a very important in reforming process for producing high octane gasoline, aromatic feedstock and hydrogen in petroleum (Hu, Su and Chu, 2002). And the process of catalytic cracking is used to convert higher-molecular-weight hydrocarbons to lighter.

As ensure by Sadeghbeigi (2012), amongst conversion processes cracking is the key unit used in modern refinery. The
primitive way used to crack petroleum crude oil was the thermal cracking was, but because increasing of gasoline production and the need of higher octane number, it has been replaced by catalytic cracking (Hug, 1998). More valuable products are obtained during fluid catalytic cracking of crude oil such as gasoline, olefin compounds having a (Han, Riggs and Chung, 2000; Barbosa, Lopes, Rosa, Mori and Martignoni, 2013).

Another process that is important for conversion of low-octane naphtha into high-octane without any change of carbon numbers in the molecule, is the catalytic reforming; it has high yield of aromatics production in petroleum-refining and petrochemical industries (Liang, Guo and Pan, 2005; Taskar, 1996). A couple of conversion reactions (dehydrogenation, dehydrocyclization, isomerization) occur in the process and there is also by-products such as hydrogen and lighter hydrocarbons. A good reforming feed must have high naphtene and aromatic hydrocarbon content.

To reach this paper goal investigation have been made on different methodologies used by researchers to design both unit FCC and CR. That includes the investigation on the data that must be provided to assist designer. Knowing that simulation has been developed and improved during the last decade in refining industry, survey of modeling method was done on some studies.

1. **PROCESS**

   - **FCCU process**

   Through FCC unit process, crude oil is mixed with a specific catalyst and then enters a fluidized bed reactor. About 45% of all gasoline contained in crude oil is extracted from FCC and ancillary units.

   The catalyst used is zeolite catalyst which behaves like a liquid when it is properly aerated by gas (air) (Sadeghbeigi, 2012). During feed residence time in the reactor, reactions take place on the surface of zeolite and long molecules are cracked into lighter molecules. During cracking of long molecules, carbon and other non-cracked organics components (hydrocarbon) get deposit over the catalyst causing its deactivation. To remove that from surface of catalyst, a stripping is done and produces spent catalyst which is taken to regenerator.

   In the generator the carbon is burned with air and the regenerated catalyst is then recirculated back into reactor beforehand mixing with fresh feed (Stephanopoulos, 1984).

   Reactor and regenerator therefore constitute the central nerve of FCCU. Beside reactor and regenerator there is the riser. Through the riser a preheated feed enter and react with regenerated catalyst. The feed is then vaporized and cracking as soon as the vapor contacts the catalyst. The process is represented in the figure below.

---

![Fluid Catalytic Cracking Process](image-url)

*Figure 1. Fluid catalytic cracking process (Farshi, Shayeigh, Burogerdi and Dehgan, 2011)*
CRU process

CRU is fed with Naphtha that passed through adequate hydrotreatment. During reforming, the feed passes over a slow-moving bimetallic catalyst bed in a series of adiabatic reactors in presence of hydrogen under low pressure and high temperature conditions. The catalyst is continuously circulated and regenerated in a Regenerator. The product obtained is then stabilized and routed for blending in specific vessels. Some quantity of hydrogen rich gases produced in reformer is recycled to reformer and the rest is sent to the naphtha hydrotreatment section or any unit that need hydrogen.

2. DESIGN OF CATALYTIC UNIT

Design projects have as goals to meet specific requirements and feasibility of a process by considering sustainability, economy, and environment impact of the system build. This study has considered only the technical part, which is determination of operating parameters. In the next sections, an accent will be put on variables that are base of each unit design.

Fluid Catalytic Cracking Unit

Different studies previously published (Arbel, Huang, Rinnard, Shinnar and Sarp, 1995; Grosdidier, Mason, Aitolhti, Heinnen and Vahamaki, 1993; Hovd and Skogested, 1993, Monge and Georgakis, 1987) have suggested several variables that influence FCC process. The following list is giving some of them:

- Measured variables: riser temperature, regenerator temperature, reactor pressure, reactor pressure, wet gas compressor, regenerator pressure, reactor stripper, total air flow through the regenerator, etc.
- Manipulated variables: total feed rate, preheat temperature, catalyst circulation rates, combustion air flow rate, stack gas flow rate, stack gas flow rate, etc.
- Disturbance: Variations in feed coking characteristics, feed temperature changes, fluctuations in reactor, pressure, etc.

Among those variables, the major operating variables influencing production of FCC are cracking temperature, catalyst/oil ratio, space velocity, catalyst type and activity. To these we can add the quality of the feed. Some of the previous terms are...
defined (Rao, 1990; Gary and Handwerk, 2001; Delhi, 2013):

- **Activity:** It is the ability to crack a gas oil or lower boiling fractions.
- **Catalyst/oil ratio:** 
  \[ \frac{C}{O} = \text{lb catalyst} / \text{lb feed} \]
- **Conversion:** 
  \[ 100 \times \left( \frac{\text{volume of feed}}{\text{volume of cycle stock}} \right) / \text{volume of feed} \]

- **Cycle stock:** Portion of catalytic-cracker effluent not converted to naphtha and lighter products
- **Efficiency:** conversion
- **Recycle ratio:** 
  \[ \frac{\text{volume recycle}}{\text{volume of fresh feed}} \]
- **Selectivity:** It is the ratio of yield of desirable products to the yield of undesirable products (coke and gas)
- **Space velocity:** It may be defined on either LHSV (volume) or a WHSV (weight) basis.
  \[ \text{LHSV} \left[ \text{hr}^{-1} \right] = \frac{\text{Liquid Hour Space Velocity in volume feed}}{\text{Volume catalyst}} \]
  \[ \text{WHSV} \left[ \text{hr}^{-1} \right] = \frac{\text{Weight Hour Space Velocity in lb feed}}{\text{lb catalyst}} \]

Catalyst design consists in calculation of weight and deactivation, and catalyst parameter and specifications as follows:

- **Mass of the catalyst at any given time is given as follows:**
  \[ m_{\text{cat}} = \rho_{\text{Cat}} V_{\text{cat}} \]
  Where: 
  \[ V_{\text{cat}} = t_c Q_{\text{cat}} \]
  \[ \rho_{\text{Cat}} : \text{Density of the catalyst} \]
  \[ V_{\text{cat}} : \text{Volume of the catalyst} \]
  \[ t_c : \text{Residence time} \]
  \[ Q_{\text{cat}} : \text{Flow rate of catalyst} \]
- **Catalyst deactivation:**
  \[ \alpha = \alpha_0 e^{-\frac{E}{RT}} \]
  Where:
  \[ \alpha_0 : \text{Catalyst deactivation coefficient at the entering temperature} \]
  \[ \alpha : \text{Catalyst deactivation coefficient at the exit temperature} \]

**Catalytic Reforming Unit**

To obtain RON (Research Octane Number), there are two types of reactions that take place during reforming: Desirable reaction (dehydrogenation, dehydrocyclization, isomerization) which gives to higher octane number and to higher purity hydrogen production and adverse (hydrocracking, coking, hydrogenolysis, hydroalkylation,...) reaction which decreases octane number and the purity of hydrogen (Delhi, 2013).

The quality and yield of reforming products are affected by following variables: reaction temperature, space velocity, reaction pressure, ratio \( \frac{H_2}{HC} \) and feed stock quality (Litke, 1985; Raseev 2003; Mohan, 2011). The temperature is the most important operating parameter of reforming process because by simply raising or lowering reactor inlet temperature, operators can raise or lower the ON. The higher is pressure, the higher is rates of hydrocracking reducing reformate yield. Lower \( \frac{H_2}{HC} \) ratio reduces energy costs for compressing and circulating hydrogen and favours naphthene dehydrogenations and dehydrocyclisation reactions (1.7 times from C8 to C4, 3.6 times from C4 to C2) (Delhi, 2013). \( \frac{H_2}{HC} \) ratio is given by the equation below:

\[ \frac{\text{hydrogen}}{\text{Hydrocarbon}} \text{ Ratio} = \frac{\text{Moles of } H_2 \text{ in Recycle Gas}}{\text{Moles of Hydrocarbons}} \]

In order to calculate the catalyst volume or weight in each reactor, space velocity is needed and can be obtained using space velocity:

- **Liquid hourly Space Velocity:**
  \[ \text{LHSV} \left( \text{hr}^{-1} \right) = \frac{\text{Volume of Reactor Charge}}{\text{Volume of Catalyst}} \]
- **Weight Hourly Space Velocity:**
  \[ \text{WHSV} \left( \text{hr}^{-1} \right) = \frac{\text{Weight of Reactor Charge}}{\text{Weight of Catalyst}} \]

Volume of each reactor can be obtained using relation propose by Fuente (2015), where \( \varepsilon \) is an industrial bed void fraction of 0.5 as stated by Korsten and Hoffman (1996):
\[ V_{\text{reactor}} (m^3) = \frac{v_{\text{catalyst}} (m^3)}{1-e} \]

3. MODELING OF CATALYTIC UNIT

As defined by Eykhoff (1974), a model is a representation of an essential aspect of an existing system (or designed) which represents knowledge of that system in usable form. It has objective to improve understanding of process and to optimize process design/operating conditions. FCCU and CRU are both process that depend on certain variables which can help to model according to the need.

Fluid Catalytic Cracking Unit

Many modeling work has been published, each different because of researcher focus. Some of the researches are represented in the table below:

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title</th>
<th>Outcome</th>
<th>Sample of equation used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pahwa and Gupta (2016)</td>
<td>CFD Modeling of FCC Riser Reactor</td>
<td>The riser is considered as the most important part of FCC process from a modeling point of view. Simulation uses Eulerian-Eulerian approach, gas and solid energy equations and four lump kinetic schemes.</td>
<td>Rate equation: ( R_{ij} = k_i C_i^n ) ( (31) ) Where, ( k_i ) is rate constant for ( r )th cracking reaction, ( C_i ) is concentration of ith species (kmol/m²).</td>
</tr>
<tr>
<td>Fadhil 2012</td>
<td>Modeling and simulation of FCC risers</td>
<td>The riser is considered as a plug flow reactor incorporating the four lumps model for kinetics of cracking reactions. Catalyst deactivation function is calculated based on linear Relationship between the catalyst coke content and its retention activity.</td>
<td>Concentration profile for gasoline lump: ( \frac{dY}{dz} = \frac{A_{gf} \rho_d}{m_y} [K_i Y_i - (K_i + K_j) Y_j] ) With ( K_j ): Constants of cracking reactions</td>
</tr>
<tr>
<td>Faray and Tsai (1987)</td>
<td>Simulation of Fluid Catalytic Cracking operation</td>
<td>Simplification of the complicated process variables and development of a computer model to simulate the operation of an FCC at different conditions, were both objectives of this study. The model provides a good base for troubleshooting and debottlenecking and may be useful in optimal control of the FCC.</td>
<td>The model used in the present work may be written in the following form: ( \frac{x}{1-x} = F \left( \frac{C_i^{0.5}}{\rho} \right) (\text{WSHV})^{-1} \exp(-\text{ERT}) ) With: ( n = 0.65 ) (decay exponent by the AMOCO model of Wallaston), ( E ): activation energy E, independent of temperature and catalyst hold-up. ( F ): function coefficient and may be computed from known design conditions.</td>
</tr>
<tr>
<td>Ahsan (2013)</td>
<td>Prediction of gasoline yield in a fluid catalytic cracking (FCC) riser</td>
<td>Granular Eulerian multiphase model with species transport are implemented and predicted in this study. The breaking of heavy hydrocarbon in the presence of catalyst is demonstrated. An approach proposed in this study shows good agreement with the experimental and numerical data.</td>
<td>Chemical reaction rate for gasoline lump: ( \frac{dY_1}{dt} = -(K_1+K_2)Y_1^2 \Phi = -K_0 Y_1^2 \Phi ) With ( K_i ): Constants of cracking reactions</td>
</tr>
</tbody>
</table>
| de Almeida (2016)         | Modeling of regenerator units in fluid catalytic cracking process    | In this study a model of FCC was developed, based on fluidized bed reactor, using gPROMS as modeling language. It has showed the necessity of combustion of hydrogen in the regenerator modeling and catalyst flow-rate and air flow-rate as manipulated variables for regenerator control. | The equation below describes the mass balance of the elements present in the coke, typically considered carbon and hydrogen: \( \frac{F_{in}}{MW_{c,k}} \Psi_k \left( x \right) \Phi_k \left( x \right) \rho_k \left( x \right) A_k \left( x \right) dz_k \)

Catalytic Reforming Unit

Catalytic reforming process has been topic of many investigations. Improvement of the process is reached either by studying the effectiveness of catalysts, or studying kinetics and deactivation, or designing more efficient reactors. There is confusion amongst some researchers who want to find collective information on catalytic reforming process due to fact that the number of articles published is so much (Rahimpour, Jafari and Iranshahi, 2013). From 1949 many studies mainly based
research on three important axes (Rahimpour, et al., 2013):

- For better operational conditions and higher yield, study of reactor configuration and operating mode;
- For better selectivity, stability and performance, study on invention and/or investigation of new catalysts;
- For better kinetic and less deactivation, study of catalytic reforming nature.

Studies on catalysts have shown that catalysts used for catalysts reforming need to a bifunctional which consists of a metal (mainly platinum) and an acid function. These functions promote reactions in the process such as hydrogenation, dehydrogenation, isomerization and cyclization (Benitez and Pieck, 2010; Benitez, Mazzieri, Especel, Epron, Vera, Marecot, 2007). Adequate balance is then needed in order to reach optimum production of the process. To be able to optimize such process improvement of stability and selectivity of catalyst is the key of good production, and should be coupled with reduction catalyst deactivation. Such target may be reached by modifying either the metal function or the acid function of the catalyst. Addition of a secondary or ternary metal component to platinum can modify metal function (Rahimpour, et al., 2013). Addition of components to the acid function, such as chloride, changes the strength and amount of support acid sites.

Kinetic modeling of catalytic reforming is a complex problem because of all the consideration that has to be taken: complexity of the feed (mixture of hydrocarbon) and multiplicity of reactions occurring (Marin and Froment, 1982; Marin, Froment, Lerou and De Backer, 1983). Thereby, came up “lumped” models, in which the large number of chemical components are classified to smaller set of kinetic lumps. Some steps of the evolution of lumped models throughout the time are retraced in the table below:

<table>
<thead>
<tr>
<th>References</th>
<th>Number of reactions</th>
<th>Number of lumped component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smith (1959)</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Jenkins and Stephens (1980)</td>
<td>78</td>
<td>31</td>
</tr>
<tr>
<td>Saxen, Das, Goyal and Kapoor (1994)</td>
<td>40</td>
<td>22</td>
</tr>
<tr>
<td>Padmavathi and Chaudhari (1997)</td>
<td>48</td>
<td>26</td>
</tr>
<tr>
<td>Hu, Su and Chu (2004)</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>WeiFeng, Hongye, Yongyou and Jian (2006)</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Hongjun, Mingliang, Huixin and Hongbo (2010)</td>
<td>52</td>
<td>27</td>
</tr>
<tr>
<td>Wang, L; Zhang Q; Q; Liang, C; (2012)</td>
<td>86</td>
<td>38</td>
</tr>
</tbody>
</table>

Studies on reactor configuration and operational mode have suggested different process and reactors. For a process point of view, categorization of catalytic reforming units is done according to the catalyst regeneration procedure. This categorization proposes three main groups of process (Rahimpour, et al., 2013; Bell, 2001):

- Semi-regenerative catalytic reformer (SRR): the most used around the worldwide;
- Cyclic catalytic reformer;
- Continuo us catalyst regeneration reformer (CCR).

Researchers have proposed various reactor configurations, each one having different advantages and disadvantages and all of them can be categorized according to the shape of the reactor and the entrance flow pattern of the feedstock as follow (Rahimpour, et al., 2013):

- Axial-flow tubular reactor;
- Radial-flow tubular reactor;
- Axial-flow spherical reactor;
- Radial-flow spherical reactor.

### 4. SUGGESTIONS

Due to the perpetual need of gasoline in the world and environmental issue that comes with, FCC and CR have to be improved. Although myriad of papers have been published on both topics, researcher still need investigate on the nature and heat production of reactions.
occurring during processes. That obviously influences yield and production of main product. For further studies design and modeling of catalytic process more tests and many comparisons are required to assess any reactor sized or model developed. Models are built with different assumptions that can be parameters to optimize. Further researches can also be focused on catalyst as it does not give of volume yield optimal yet. Finally, as crude oil has different components, to validate a model required a study of applicability with different composition of feed.

5. CONCLUSION

For production of gasoline with high octane number, cracking and reforming of petroleum cut are very important. Element that make possible such production is actually catalyst. Catalysts play a role key in favorite process of gas and oil industry.

Among parameters that are used to design FCC, variables that involve catalyst are the main elements that influence the design. It is then imperative to keep investigating on catalyst as well for design as for modeling. Literature review has shown that fluidized bed reactor is the suitable reactor for conversion of gas oils into gasoline. Design with optimization of configuration of this reactor is then very important. Design of FCC involves design of one facility unit (fractionner) as well. As FCC, design of CR unit involves design of facilities such as furnace, catalyst and reactors design.

This paper had the objective of investigating the established papers on catalytic process, especially FCC and CR. Afterward the obtained results shows that impressive number of studies in both field have been published and some of them were presented all along this paper. To rule off this paper some suggestions were given for further researches.

6. REFERENCES

- Faray, I. & Tsai, K.-Y., 1987. Simulation of Fluid Catalytic Cracking operation.. Department of chemical Engineering.

How to cite this article: Ngwanz MKD, Nkazi DB, Ngwanza HS et.al. Review of catalytic processes design and modeling: fluid catalytic cracking unit and catalytic reforming unit. International Journal of Research and Review. 2018; 5(11):136-143.