Optimization of Hydrogen Production from Nigerian Crude Oil Samples Through Continuous Catalyst Regeneration (CCR) Reforming Process Using Aspen Hysys

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To cite this article: Ipeghan Jonathan Otaraku, Ishioma Laurene Egun. Optimization of Hydrogen Production from Nigerian Crude Oil Samples Through Continuous Catalyst Regeneration (CCR) Reforming Process Using Aspen Hysys. American Journal of Applied Chemistry. Vol. 5, No. 5, 2017, pp. 69-72. doi: 10.11648/j.ajac.20170505.11

Received: May 25, 2017; Accepted: August 21, 2017; Published: September 21, 2017

Abstract: The aim of this paper is to increase the level of hydrogen produced in the refinery from heavy treated Naphtha of Nigerian crude oil during catalytic reforming process. An existing continuous catalyst regeneration catalytic reforming process plant with four beds reactor was simulated using Aspen Hysys while treated heavy Napthene from Bonga Crude and Bonny Crude were used as feed for the process. The temperature of reactors for the process was varied between 430 – 540°C and the outlet concentrations of hydrogen (Vol.%) produced was recorded. It was observed that an increase in temperature lead to an increase in the concentration of hydrogen produced as the volume of hydrogen at 430°C was 23.46% volume while at 540°C it was 51.38% volume showing a significant increase in the aromatic yield level. The results also showed that the naphthene content of feed affects the volume of hydrogen produced which made Bonga crude a better source for hydrogen when compared with Bonny crude.

Keywords: Hydrogen Yield, Bonga Crude, Bonny Crude, Catalytic Reforming, Naphthene, Temperature

1. Introduction

In a country like Nigeria, the need to increase the availability of Hydrogen (H$_2$) cannot be underestimated as it is one of the gases needed in various aspects of life. Large quantities of are needed in the petroleum and chemical industries. The largest application of H$_2$ is for the processing ("upgrading") of fossil fuels, and in the production of ammonia [1]. Hydrogen production through steam reforming of biomass-derived compounds has shown that it is an economically feasible and environmental way to efficiently use renewable energy resources. The search for more efficient strategies to produce hydrogen from bio-derived aqueous phases as an environmentally friendly strategy to power diverse energy needs is still on [2].

Currently the level of hydrogen produced is not enough to meet the industry need, therefore there is need to optimize the production from the most predominant industry process which is the catalytic reforming process. For small scale hydrogen plants, air-blown catalytic partial oxidation coupled with membrane separation may be a preferred route [3]. There is a growing need for hydrogen. Hydrogen will play a key role in the manufacture of better transportation fuels. It may also play a role in the introduction of a “hydrogen economy”. The conversion of hydrocarbons is the most economic route to hydrogen [4].

2. The Process

Catalytic reforming is a process for producing high octane gasoline blending component as main products with hydrogen and liquefied petroleum gas as by-products from heavy naphthene [5]. Catalytic reforming is a vital in the refinery processes, because it leads to the production of high-octane components and hydrogen which is highly demanded in other refinery units like hydrotreaters [6]. The significance of this industrial process has made researchers to investigate different aspects of catalytic reforming process intensively...
Most naphtha reforming processes usually take place in three or four fixed bed reactors which operate adiabatically at temperatures between 450 and 520°C, total pressures between 10 and 35 bar, and molar hydrogen-to-hydrocarbon ratios between 3 and 8 [7]. “Figure 1” below shows the process flow diagram of the catalytic reforming process.

The advantages of Continuous Catalytic Reforming process include: Production of higher octane reformate despite feed quality, long time working of the process to increase hydrogen produced, using catalyst with higher selectivity and yield, low recycle ratio and the low pressure involved during operation with high yield of hydrogen [8].

The feed for the catalytic reformer is usually heavy treated Naphthene. For this work, heavy treated Naphthene from Bonga Aromatic and Forcados were chosen.

Bonga Aromatic crude is a medium gravity, low sulphur, naphthenic crude. It is similar in quality and yield pattern to Forcados, though slightly heavier [9].

Bonny Light: Bonny light is a high quality of Nigerian crude oil with high American Petroleum Institute (API) gravity (low specific gravity). It is mainly gotten in the Niger Delta region of Nigeria and it is named after the city of Bonny in Rivers State [10].

2.1. The Simulation

The catalytic reformer was modeled in a steady state mode using catalytic reformer template of ASPEN Hysys 7.2. In setting up the model, the fluid property package was chosen to be Peng-Robinson and the reactors configured as 4 beds.

Figure 2 is the catalytic reformer template configured with four bed reactors for the reforming process in the Hysys environment.

The feed and other input values used for modeling the catalytic reformer are given in Table 1 below

| Sample 1: Bonga Crude | Sample 2: Bonny light Crude |
Table 1. Bonga Crude Assay [9].

| Crude          | Heavy Naphtha |
|----------------|--------------|
| Density at 15°C: 879.5 kg/m³ | Density at 15°C: 761 kg/m³ |
| Nitrogen ppm: 1219.9     | Cut°C 80-160     |
| Sulphur wt%: 0.24863     | Yield 13.97 Vol.% |
| API 29.4              | Naphthene 60.59 Vol.% |
|                      | Paraffin 25.53 Vol.%  |
|                      | Aromatics 13.88 Vol.%  |

Table 2. Bonny Light Crude Assay [10].

| Crude          | Heavy Naphtha |
|----------------|--------------|
| Density at 15°C: 854.8 kg/m³ | Density at 15°C: 780.0 kg/m³ |
| Nitrogen wt%: 0.220     | Cut 80-160°C     |
| Sulphur m/m%: 0.16      | Yield 18.72 Vol.% |
| API 34               | Naphthene 50.6 Vol.% |
|                      | Paraffin 33.7 Vol.%  |
|                      | Aromatics 15.7 Vol.%  |

2.2. Kinetic Model

The kinetic model used in the catalytic reformer template was that of Smith’s which considers the following reaction:
- Dehydrogenation of naphthenes to aromatics,
- Dehydrocyclization of paraffins to naphthenes,
- Hydrocracking of naphthenes to light ends and Hydrocracking of paraffins to light ends.

The kinetics, as described in [11], is written as:

\[ N \leftrightarrow A + 3H_2 \]  \hspace{1cm} (1)
\[ P \leftrightarrow N + H_2 \] \hspace{1cm} (2)
\[ N + 2H_2 \leftrightarrow 2G \] \hspace{1cm} (3)
\[ P + H_2 \leftrightarrow 2G \] \hspace{1cm} (4)

Where N, A, G, H and P; are Naphthenes, Aromatics, Gases, Hydrogen and Paraffin respectively.

The Arrhenius type of rate expression is assumed for the reactions to occur:

\[ k_f = k_0 e^{(-\frac{E_f}{RT})} \]  \hspace{1cm} (5)

The activation energy E is dependent on the catalyst and \( k_0 \) is dependent on the molarity of the reaction R is the universal gas constant [11]. Dehydrogenation reaction which is endothermic dominates the entire reactions thereby causing significant change in the temperature of the reactant [12]. To maximize the production level of hydrogen “(1)” and “(2)” should be optimized (dehydrogenation of naphthenes and the dehydrocyclization of paraffins produce hydrogen).

3. Results and Discussion

The result obtained from the simulation is shown below:

Table 3. Total Hydrogen Yield Results.

| Temperature | Samples (Vol.%) | Sample 1 | Sample 2 |
|-------------|-----------------|----------|----------|
| 4.3         | 0.6             | 0.46     |
| 4.4         | 0.77            | 0.61     |
| 4.5         | 0.94            | 0.76     |
| 4.6         | 1.12            | 0.93     |
| 4.7         | 1.32            | 1.10     |
| 4.8         | 1.53            | 1.29     |
| 4.9         | 1.74            | 1.47     |
| 5.0         | 1.97            | 1.66     |
| 5.1         | 2.03            | 1.85     |
| 5.2         | 2.17            | 1.97     |
| 5.3         | 2.32            | 2.10     |
| 5.4         | 2.47            | 2.24     |

The volume of hydrogen yield of the samples at various temperature changes for the reactor is shown in Table 3 above. As the temperature increases, the volume of hydrogen produced increases. From the simulation result, it is seen that at higher temperature there is increase in the hydrogen yield which is good for other refinery units.

From Figure 3 above, it is seen that the curves are linear; showing that as the temperature increases the hydrogen yield increases, showing a linear relationship between temperature and hydrogen yield. Therefore to increase the level of hydrogen produced in an existing refinery, the temperature of the catalytic reforming process will be increased.

From the table above it is seen that sample 1 gave a higher level of hydrogen yield when compared to sample 2. The
temperature increase leads to higher yields of hydrogen and less amount of light carbons in agreement with literature [13]. Also, the significant difference in naphthene composition of both samples played a part in the level of hydrogen produced as the reaction responsible for hydrogen production is dependent on the naphthene composition.

4. Conclusion

1. The operating temperature of the continuous catalyst regeneration (CCR) reforming process affects the volume of hydrogen produced. At 440°C the yield of hydrogen for the two samples was about 0.6% by volume whereas at 540°C the yield was above 2% by volume. The endothermic nature of dehydrogenation and dehydrocyclization are favoured at high temperatures. Limitation will be imposed by material of construction of the reactors.

2. The naphthene content of the reforming feed affects the hydrogen yield. The higher the naphthene content, the more the hydrogen yield. Stability and susceptibility of naphthene to form cyclic compounds increases the hydrogen formation.

3. In order to maximize the production of hydrogen in a catalytic reformer the process temperature should be considered. Using Le Chatelier’s Principle, higher temperatures will favour higher hydrogen yield. However, the value of the temperature has to be a compromise between reactor materials and economy of the quantity of hydrogen yield viz-a-viz the cost of high temperature operations and environmental impact. Also, catalytic stability at higher temperatures is a limiting factor.

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