A Case Study for Benzene Reduction in the Final Gasoline Pool of Existing Refineries

Babak Behnejad'

Tehran Oil Refining Company babak_behnejad@yahoo.com

Abstract

The Environmental Protection Agency (EPA) has developed recent limitations regarding fuel specifications and pollutants, which refiners are required to follow. Based on Mobile Source Air Toxics (MSAT) II regulations, the average benzene content in the gasoline pool should not exceed 0.62 vol. % [1].

Designers of new refineries are able to consider the mentioned limitations from the beginning. In contrast, existing refineries have to modify the operating conditions of existing units, or in the event of failure add new units by spending high expenses, in order to achieve mentioned environmental restrictions.

Since the gasoline production processes depend on refineries' configurations, the quality of the final gasoline pool would depend on their relevant process units. In some cases, refiners have to inject other imported materials as octane booster to the final gasoline pool in order to obtain the desired gasoline specifications (e.g. Research Octane Number (RON) and benzene content).

This article attempts to investigate a conventional crude oil refinery challenge for achieving benzene content as per MSAT II regulations for various research octane numbers.

Keywords: Benzene Reduction, Gasoline Pool, Refinery, EPA, MSAT II.

¹⁻ Head of Process Engineering Department, Project Engineering Affairs

1- Introduction

Benzene is present in crude oil and is also formed in the catalytic and thermal processes within the refinery. Gasoline produced from Catalytic reformer and Fluid Catalytic Cracking (FCC) units are two important components which contain the most amount of benzene in the final gasoline pool [1].

By studying the final gasoline pool of the refineries, it becomes obvious that the contribution of benzene from catalytic reformed gasoline and FCC gasoline are 70-85% and 10-25% respectively. Because catalytic reformed gasoline is the largest source of benzene content in the gasoline pool, the key to lowering the content of benzene in the gasoline is reducing the content of benzene in the reformed gasoline. Thus, the best approach to obtain reduced benzene content in the gasoline is to focus on reformate gasoline. The benzene content in reformate gasoline can be controlled by removing either compounds from the reformer feed or benzene from reformate [1].

Refineries' owners prefer to solve this problem with the minimum cost impact. Methods of reducing benzene content in the reformed gasoline are as follows:

1- Pre-fractionation Processes: By reducing benzene precursors in catalytic reformer feed via fractionation and saturating benzene contained in light straight-run (LSR) or other gasoline sources.

However, in many cases, any effort for using pre-fractionation processes will not cover benzene in 0.62 Vol. %.

2- Post-fractionation Processes: (A) By removing benzene through the chemical conversion method (Revamping or adding a new reformer splitter to produce a benzene-rich stream followed by hydro-processing to remove benzene). (B) By removing benzene by physical separation method (Reduction benzene from reformate via solvent extraction benzene in gasoline).

Benzene saturation process is a simple process with relatively low capital and operating cost. The hydrogenation saturation method is a proven benzene reduction technology but will inevitably result in the loss of octane value in reformed gasoline and hydrogen consumption challenges. Whereas for benzene extraction method storing, handling and access market for extracted benzene will be significant [3].

2- Experimental

Benzene is present in crude oil and is also formed in the catalytic and thermal processes within the refinery. Gasoline produced from Catalytic reformer and Fluid Catalytic Cracking (FCC) units are two important components which contain the most amount of benzene in the final gasoline pool [1].

This article tries to show further problems that a conventional refinery will face when attempting to simultaneously reduce benzene and obtain desired RON. In this study the throughput of the crude oil refinery, 100,000 BPSD has been considered. Gasoline is produced from the Catalytic Reforming Unit (CRU), Hydrocracking and Isomerization units. Approximate values of flow rates, RON and benzene content of Platformate and Isomerate have been shown in table 1. Since yield and RON in the start of run (SOR) is different from the end of run (EOR), and strongly depends on the catalyst performance of the unit, these parameters have been calculated based on average octane-barrel during one life cycle.

| | Platformate | Isomerate | | | |
|------------------|-------------|-----------|--|--|--|
| Flow Rate (BPSD) | 9,800 | 7,000 | | | |
| RON | 96 | 86 | | | |
| Benzene (Vol. %) | 3.9 | 0 | | | |

Table 1-Flow rates. RON and benzene content of Platformate and Isomerate

The octane loss can be offset by increasing reforming severity or reducing the volume of Platformate gasoline produced. Another alternative for compensating octane number is adding volumes of alcohol base compounds to gasoline, although this option has limitations [1]. As per table 1, it is obvious that by adding Isomerate to Platformate, RON of the combined stream will be reduced. In this study, in order to compensate for the reduced RON to the desired values, imported MTBE or premium gasoline sources have been considered. Refining processes with benzene reduction unit and gasoline outsourcing has been illustrated in figure 1.

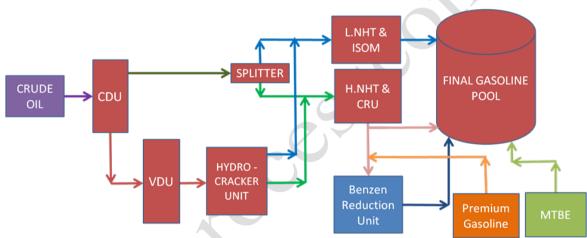


Figure 1-Refining processes with benzene reduction unit and gasoline outsourcing

In order to compensate for the loss of RON, maximum tolerable MTBE (10 Vol. %) is injected in the final gasoline pool. In addition, outsource premium gasoline (RON=98 and benzene content 6 vol. %) from Continuous Catalytic Reforming (CCR) would be used in case of required higher RON. Based on calculations done in this study, since benzene content in the premium gasoline is higher than the existing produced gasoline, the entire amount of the imported premium gasoline should be sent to the new benzene reduction unit. By adding premium gasoline, RON in the final gasoline pool will be corrected, but benzene content will be increased. Therefore, both the amounts of RON and benzene content should be corrected simultaneously.

In this article, both benzene extraction and saturation units have been studied. The summary of the calculations to achieve RON 95 is presented in tables 2 and 3 respectively. Note that blending RON has been calculated based on the linear volumetric method.

Table 2-Case study for Benzene Extraction Unit (RON=95 & Benzene Content = 0.62 Vol. %)

| | Existing Platformate to Benzene Unit | Imported Platformate to Benzene Unit | Combined Platformate to Benzene Unit | Produced Low Benzene Reformate | Isomerate to the Gasoline Pool | Existing Platformate to the Gasoline Pool | MTBE to the Gasoline Pool | Final Gasoline Pool |
|---------------------|---|---|---|---|---|---|------------------------------------|---------------------------|
| Flow Rate (BPSD) | 7,850 | 9,500 | 17,350 | 16,656 | 7,000 | 1,950 | 2,561 | 28,167 |
| RON | 96.0 | 98.0 | 97.1 | 96.6 | 86.0 | 96.0 | 108.0 | 95.0 |
| Benzene (Vol. %) | 3.9 | 6.0 | 5.0 | 0.60 | 0 | 3.9 | 0 | 0.62 |

Table 3-Case study for Benzene Saturation Unit (RON=95 & Benzene Content = 0.62 Vol. %)

| | Existing Platformate to Benzene Unit | Imported Platformate to Benzene Unit | Combined Platformate to Benzene Unit | Produced Low Benzene Reformate | Isomerate to the Gasoline Pool | Existing Platformate to the Gasoline Pool | MTBE to the Gasoline Pool | Final Gasoline Pool |
|---------------------|---|---|---|---|---|---|------------------------------------|---------------------------|
| Flow Rate (BPSD) | 7,810 | 10,400 | 18,210 | 18,174 | 7,000 | 1,990 | 2,716 | 29,880 |
| RON | 96.0 | 98.0 | 97.1 | 96.3 | 86.0 | 96.0 | 108.0 | 95.0 |
| Benzene (Vol. %) | 3.9 | 6.0 | 5.1 | 0.60 | 0 | 3.9 | 0 | 0.62 |

Although refiners must consider the benzene restriction, they have some opportunities to survey other octane numbers for more flexibility in the gasoline production of their refinery. The result of this survey has been presented by implementing of the new extraction or saturation units in tables 4 and 5 respectively.

Table 4-Calculated Various RON for Benzene Extraction Unit

| Imported Premium Platformate (BPD) | Imported MTBE (BPD) | RON |
|---------------------------------------|----------------------------------|---|
| 0 | 0 | 91.5 |
| 0 | 455 | 92.0 |
| 0 | 1580 | 93.0 |
| 3600 | 1994 | 94.0 |
| 9500 | 2561 | 95.0 |
| | Platformate (BPD) 0 0 0 3600 | Platformate (BPD) MTBE (BPD) 0 0 0 455 0 1580 3600 1994 |

Table 5-Calculated Various RON for Benzene Saturation Unit

| Case | Imported Premium Platformate (BPD) | Imported MTBE (BPD) | RON |
|------|---------------------------------------|---------------------------|------|
| 1 | 0 | 0 | 91.4 |
| 2 | 0 | 550 | 92.0 |
| 3 | 0 | 1,678 | 93.0 |
| 4 | 4,000 | 2,078 | 94.0 |
| 5 | 10,400 | 2,716 | 95.0 |

3- Results and Discussion

Because the type of benzene reduction processes would be influenced by the flow rate and RON of the final gasoline pool, choosing the suitable benzene reduction process would be the key parameter. Both conventional benzene saturation and extraction processes have so far been the most common processes in the world [3].

In tables 4 and 5, results show that, in the case of RON below 92, only the implementation of benzene reduction unit is required and it is not necessary to adding any octane booster to the final gasoline pool. To achieve final gasoline to RON 92-93, only MTBE as octane booster is necessary, whereas beside MTBE, premium gasoline should be used to reach RON 94-95.

For eliminating or reducing dependence on outsourcing, besides implementing each type of benzene reduction unit, utilization of the following higher octane gasoline sources should be investigated by refiners: revamping or installing a new naphtha splitter for sending benzene

precursors to Isomerization unit, revamping or implementing a new Isomerization unit, sending butane to the final gasoline pool, revamping the existing CRU, replacing the existing CRU with a CCR unit, adding FCC and Alkylation units[4].

4- Conclusions

This study demonstrates that, since gasoline is a major profitable product in the refineries, in order to meet the recent gasoline specifications and environmental restrictions, refiners have to switch to using the new technologies. Choosing benzene extraction, saturation or other benzene reduction processes strongly depends on the infrastructure of the existing refineries.

Total investment, Internal Rate of Return (IRR) and payback time of the investment for each refinery will be unique. In order to minimize the total cost of the refinery, all possible scenarios (RON: 91–95) should be estimated by adding benzene reduction or extraction units.

References

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