



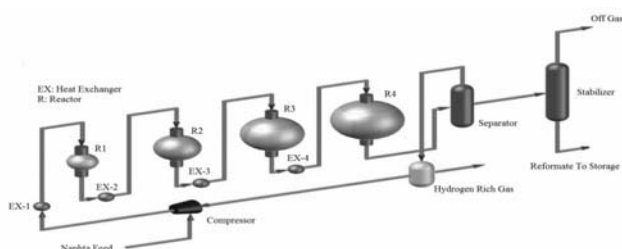
INDUSTRIAL ANALYSIS OF CATALYTIC REFORMING REACTORS

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Catalytic reforming is a very important process in chemical industry. The aim of this process is to transform treated naphtha (paraffins, olefins, naphthenes, aromatics) into reformates with a better yield in aromatics such as benzene, toluene, and xylenes (BTX) that are very important petrochemical materials providing a high octane number. In this work, activity and selectivity were checked in terms of expected aromatics at the start of a cycle of a Pt-Re/Al₂O₃ bi-functional catalyst. This was carried out in four fixed bed catalytic reactors of the naphtha catalytic reforming plant placed in series. The results obtained showed that the catalyst was relatively deactivated but remained selective.



INTRODUCTION

In order to protect environment, various legislations are passed including an increase in octane number. One of the key processes in the petroleum refining and petrochemical industries is catalytic naphtha reforming. This is used extensively to convert low-octane hydrocarbons of naphtha to more valuable high-octane gasoline components.¹⁻⁷

Naphtha is a fraction of petroleum or a complex mixture consisting of hydrocarbon molecules with 5 to 12 carbon atoms. It also includes mainly paraffins, olefins, naphthenes, and aromatics. The product reformat in catalytic naphtha process includes valuable aromatics such as benzene, toluene, and, xylenes (BTX) that are intensely needed in our modern life.⁸⁻⁹

Catalysts used in catalytic reforming are often bi-functional involving two metallic functions, the Platinum (Pt) and Rhenium (Re). The Platinum (Pt) is responsible for the naphthenes dehydrogenation and

olefin hydrogenation.¹⁰⁻¹² The Rhenium (Re) has the same function as the Platinum (Pt), but tends to strongly favor hydrogenation. This enhances the catalyst stability and life duration. This confers the catalyst a higher resistance against progressive deposits of coke.¹³⁻¹⁹ The catalyst contains also an acid function which comes from the (Al₂O₃) support. This acid function contributes to the reactions of isomerization and cyclization. To maintain an optimal degree of acidity of this catalyst, an injection of a chlorinated component is carried out at the upstream reactors. This will compensate the loss in chlorine during the factory magnaforming processing. Chlorine excess is adjusted by injecting water.²⁰⁻²¹

OBJECTIVE

The main objective of this work is to check the activity and selectivity in terms of expected aromatics at the start of a cycle of a Pt-Re/Al₂O₃

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bi-functional catalyst in a fixed bed reactor. This reactor is located at the catalytic reforming naphtha plant in the city of Skikda in Algeria. This will generate a maximum of (BTX) aromatics from a charge poor in aromatics.

DESCRIPTION OF THE PROCESS

The synoptic scheme of magnaforming factory of Skikda is described in Figure 1:

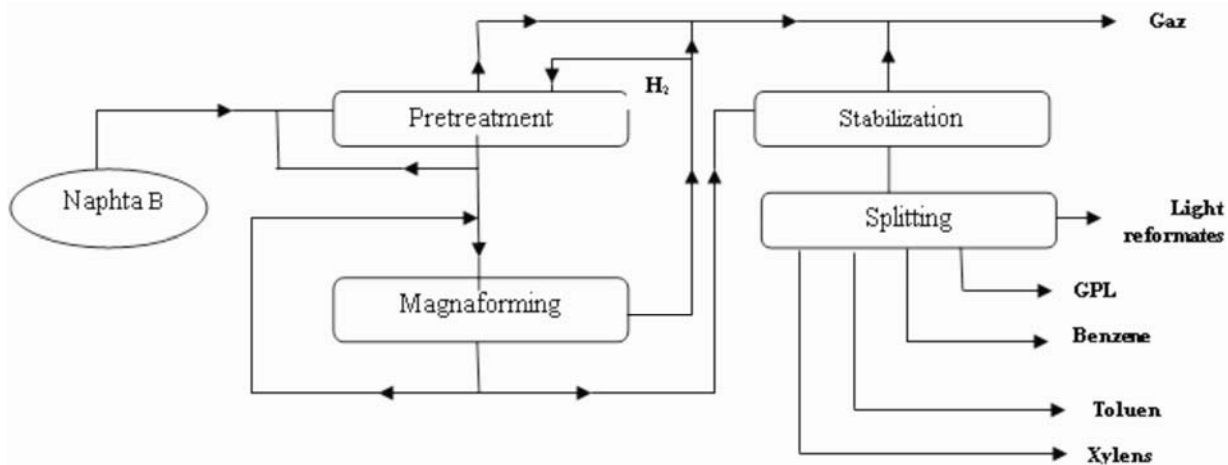


Fig. 1 – Synoptic scheme of Magnaforming Plant.

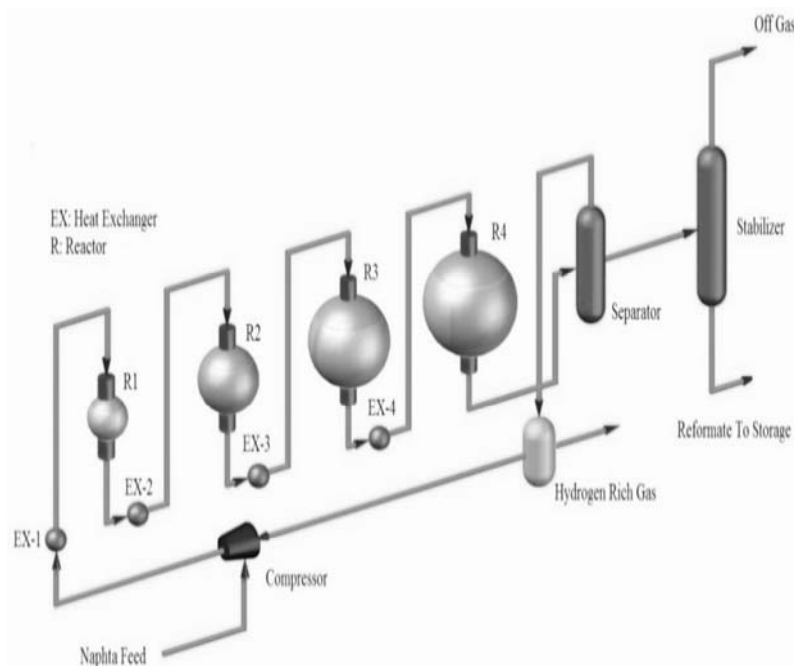


Fig. 2 – The catalytic naphtha reformer.

The magnaforming section uses a bimetallic catalyst (Platinum and Rhenium) E801-E803 (E = Engelhard), with an alumina basis support (acid). This will confer a high activity to the catalyst. The catalyst characteristics are summarized in Table 1.

The section also includes four reactors (R1, R2, R3 and R4) in series. Between two reactors, a heat exchanger is placed. This heat exchanger readjust

the inlet temperature, to the desired value, for each reactor. This is imposed by the endothermic nature of the chemical reactions in each reactor ($F1 = 2.8$ kcal/h, $F2 = 14.0$ kcal/h, $F3 = 57.6$ kcal/h, $F4 = 162.0$ kcal/h). The presence of these heat exchangers will thus regulate the process service temperatures.

The characteristics of the reactors are summarized in Table 2.

Table 1
Catalyst characteristics

| Catalyst property | | R | Composition (% wt.) | Catalyst distribution | | | |
|-------------------------|--|---|------------------------|---------------------------|------------------|--------------|-----------------|
| | | | | Cat. (m ³) | Cat. (% vol.) | Cat. (kg) | Cat. (% wt.) |
| Type | Pt-Re / Al ₂ O ₃ | 1 | Pt: 0.26 –Re:0.26 | 8.477 | 9.325 | 6100 | 09.545 |
| D (mm) | 1.5 | 2 | Pt: 0.26 –Re:0.26 | 12.273 | 13.5 | 8529 | 13.346 |
| L (mm) | 5 | 3 | Pt: 0.22 –R e:0.42 | 35.079 | 38.587 | 24664 | 38.595 |
| d (kg/cm ³) | 0.7208 | 4 | Pt: 0.22 –Re:0.42 | 35.079 | 38.587 | 24612 | 38.513 |

Table 2
Reactor characteristics

| | R 1 | R 2 | R 3 | R 4 |
|---------------------------------------|-------|-------|--------|--------|
| Diameter (m) | 3.660 | 4.270 | 6.405 | 6.405 |
| Section (m ²) | 10.52 | 14.32 | 32.22 | 32.22 |
| Volume (m ³) | 25.67 | 40.76 | 137.58 | 137.58 |
| Bead volume (m ³) | 8.59 | 14.25 | 51.25 | 51.25 |
| Height of catalyst bed in reactor (m) | 0.806 | 0.857 | 1.089 | 1.089 |

Table 3
Feed and Product characterization

| Feed | | Reformate | |
|-----------------|-------|-----------------|-------------|
| Volume Fraction | | Volume Fraction | |
| Paraffin | 63-65 | Paraffin | 32.52-33.43 |
| Olefine | 00.00 | Olefine | 1.01-1.54 |
| Naphthene | 28-29 | Naphthene | 1.93-2.89 |
| Aromatic | 6-8 | Aromatic | 62.89-63.96 |

Table 4
PONA content within charge and reformates

| | | P | O | N | A |
|----------|----------------|---------|------|-------|-------|
| | | (%vol.) | | | |
| 30 days | Treated charge | 64.15 | 0.00 | 28.99 | 6.85 |
| | Reformates | 32.52 | 1.11 | 2.89 | 63.48 |
| 60 days | Treated charge | 65.08 | 0.00 | 28.12 | 06.8 |
| | Reformates | 32.85 | 1.26 | 1.93 | 63.96 |
| 90 days | Treated charge | 63.72 | 0.00 | 28.71 | 07.57 |
| | Reformates | 32.69 | 1.54 | 2.34 | 63.43 |
| 120 days | Treated charge | 64.05 | 0.00 | 29.92 | 08.03 |
| | Reformates | 33.43 | 1.01 | 2.67 | 62.89 |
| 150 days | Treated charge | 63.08 | 0.00 | 29.12 | 07.8 |
| | Reformates | 33.34 | 1.33 | 2.01 | 63.2 |

In these four reactors, the transformation of naphtha into reformat takes place after a series of chemical reactions (dehydrogenation, dehydrocyclization, isomerization, hydrocracking). The naphtha enters the magnaforming section through a centrifuge turbo compressor which also brings an H₂-rich gas.

The effluent of the last reactor, after a cooling process, enters a separator balloon. At the exit of the balloon, the liquid phase enters the fractioning section and the hydrogen rich gaseous phase is resent to the turbo compressor.

The reforming charge is generally defined by its PONA which gives its composition in basic hydrocarbons. The charges, rich in promoters of aromatics (Naphthenes), are also called naphthenic, provided $N + 2A \geq 44.5$. These latter are reformatted into a high octane number under low conditions of severity. The charge rich in paraffin, is also called paraffinic, when $N + 2A < 44.5$. These

latter transform paraffin by cracking or by cyclization to provide a high octane number. This results in a severe increase in temperature.

From the data in Table 4, the formability number, $N + 2A$, is equal to 44.7. Consequently, this will classify our considered naphtha into an aromatic precursor charge.

SELECTIVITY OF THE BI-FUNCTIONAL CATALYST

The following table gives both content and volumetric flow for each hydrocarbon family within the charge and reformates.

The computation method for paraffin and naphthene selectivity in aromatics (see Tables 6 and 7) requires the volumetric flow and PONA content (see Table 5) in the charge and reformates.

Table 5

PONA volumetric flow in the charge and reformates

| | | P | O | N | A | volumetric flow |
|----------|----------------|-------------------------------|------|-------|-------|-------------------|
| | | vol. flow (m ³ /h) | | | | m ³ /h |
| 30 days | Treated charge | 89.81 | 0.00 | 40.59 | 9.59 | 140 |
| | Reformates | 29.92 | 1.02 | 2.66 | 58.40 | 92 |
| 60 days | Treated charge | 91.11 | 0.00 | 39.37 | 9.52 | 140 |
| | Reformates | 30.22 | 1.16 | 1.78 | 58.84 | 92 |
| 90 days | Treated charge | 89.21 | 0.00 | 40.19 | 10.60 | 140 |
| | Reformates | 30.07 | 1.42 | 2.15 | 58.36 | 92 |
| 120 days | Treated charge | 89.67 | 0.00 | 41.89 | 11.24 | 140 |
| | Reformates | 30.76 | 1.41 | 2.46 | 57.86 | 92 |
| 150 days | Treated charge | 88.31 | 0.00 | 40.77 | 10.92 | 140 |
| | Reformates | 30.67 | 1.22 | 1.85 | 58.25 | 92 |

Table 6

Method of Computation of the paraffin selectivity in aromatics

| Paraffin selectivity in aromatics |
|--|
| $S_p = \frac{P \rightarrow A}{\% P_{charge} - \% P_{reformat}} \times 100$ |
| Paraffins conversion |
| $T_p = \frac{\text{Paraffins transformed}}{\text{initial Paraffins}} \times 100$ |
| Paraffins transformed into aromatics |
| $P \rightarrow A = \left(\frac{\text{Volumic flow of the aromatics in the reformat}}{\text{Volumic flow of the charge}} \times 100 \right) - A\% - (N \rightarrow A)$ |

Table 7

Method of Computation of the naphthenes selectivity in aromatics

| | |
|--|---|
| Naphthenes selectivity in aromatics | |
| $S_N = \frac{N \rightarrow A}{\%N_{\text{Charge}} - \%N_{\text{Reformat}}} \times 100$ | |
| Naphthenes conversion | |
| T_N | $\frac{\text{Naphthenes transformed}}{\text{initial naphthenes}}$ |
| Naphthenes transformed in aromatics | |
| $N \rightarrow A = 0.952 (T_N \times \% N_{\text{Charge}})$ | |

Table 8

Paraffin and naphthenes selectivity in aromatics

| | T_p | T_N | S_p | S_N |
|----------|-------|-------|-------|-------|
| 30 days | 66.69 | 93.45 | 28.69 | 98.80 |
| 60 days | 66.83 | 95.49 | 30.00 | 97.59 |
| 90 days | 66.29 | 94.64 | 26.57 | 98.10 |
| 120 days | 65.70 | 94.14 | 21.18 | 98.38 |
| 150 days | 65.27 | 95.46 | 24.70 | 97.60 |

The value, 0.952, was supplied by the catalyst manufacturing company (Engelhard). They assume that 95.2% of naphthenes are transformed into aromatics.

The results of the computation of the paraffin and naphthenes selectivity in aromatics are given in Table 8.

According to these results, a low paraffin selectivity, “ S_p ” is observed in aromatics. This suggests that paraffins are cracked instead of being aromatized by dehydrocyclization or dehydrogenated into naphthenes. The deposition of the coke on the catalyst surface is unavoidable. This results in the slowing of the kinetics of dehydrogenation of the cyclohexanic and cyclopentanic naphthenes.

Consequently, the naphthenes selectivity in aromatics “ S_N ” is affected by coking.

HYDROCARBONS FAMILIES YIELDS IN EACH REACTOR

In order to compute the yields of aromatics, naphthenes and paraffins in each reactor, (Table 9), the inlet and outlet temperatures of each reactor as well as the decrease in paraffins and naphthenes, and the increase in aromatics in each reactor must be known (Table 10).

Table 9

Computation of aromatic, naphthenes and paraffin yields in each reactor

| The first reactor $k=1$ | The other reactors $k=2,3,4$ | The decrease of the P, N and increase of A in each reactor |
|---|---|---|
| $\eta_{A_1} = A_{\text{Charge}} + \Delta A_1$ | $\eta_{A_k} = \eta_{A_{k-1}} + \Delta A_k$ | $\Delta A_k = \left(\frac{\Delta T_k}{\Delta T_{\text{total}}} \right) \Delta A$ |
| $\eta_{N_1} = N_{\text{Charge}} + \Delta N_1$ | $\eta_{N_k} = \eta_{N_{k-1}} + \Delta N_k$ | $\Delta N_k = \left(\frac{\Delta T_k}{\Delta T_{\text{total}}} \right) \Delta N$ |
| $\eta_{P_1} = P_{\text{Charge}} - \Delta P_1$ | $\eta_{P_k} = \eta_{P_{k-1}} + \Delta P_k$ | $\Delta P_k = \left(\frac{\Delta T_k}{\Delta T_{\text{total}}} \right) \Delta P$ |
| | A % Aromatics _{Reformat} - % Aromatics _{Charge} | |
| | N % Naphthenes _{Reformat} - % Naphthenes _{Charge} | |
| | A % Paraffins _{Reformat} - % Paraffins _{Charge} | |

Table 10
Temperature drop along the catalytic bed (°C)

| | 1 st Reactor | | | 2 nd Reactor | | | 3 rd Reactor | | | 4 th Reactor | | | ΔT_{total} |
|----------|-------------------------|---------|--------------|-------------------------|---------|--------------|-------------------------|---------|--------------|-------------------------|---------|--------------|--------------------|
| | T_1^e | T_1^s | ΔT_1 | T_2^e | T_2^s | ΔT_2 | T_3^e | T_3^s | ΔT_3 | T_4^e | T_4^s | ΔT_4 | |
| 30 days | 431 | 384 | -47 | 488 | 443 | -45 | 514 | 487 | -27 | 514 | 502 | -12 | -131 |
| 60 days | 446 | 391 | -55 | 488 | 450 | -38 | 514 | 489 | -25 | 514 | 505 | -9 | -127 |
| 90 days | 439 | 383 | -56 | 488 | 443 | -45 | 516 | 489 | -27 | 516 | 507 | -9 | -137 |
| 120 days | 443 | 382 | -61 | 488 | 444 | -44 | 516 | 490 | -26 | 516 | 508 | -8 | -139 |
| 150 days | 442 | 382 | -60 | 488 | 442 | -46 | 518 | 495 | -23 | 518 | 511 | -7 | -136 |

Table 11
Absolute Reactors Pressure (kg/ cm²)

| | | |
|---|----|------|
| Absolute Reactors Pressure (kg/ cm ²) | R1 | 14.6 |
| | R2 | 13.5 |
| | R3 | 12.3 |
| | R4 | 11.3 |

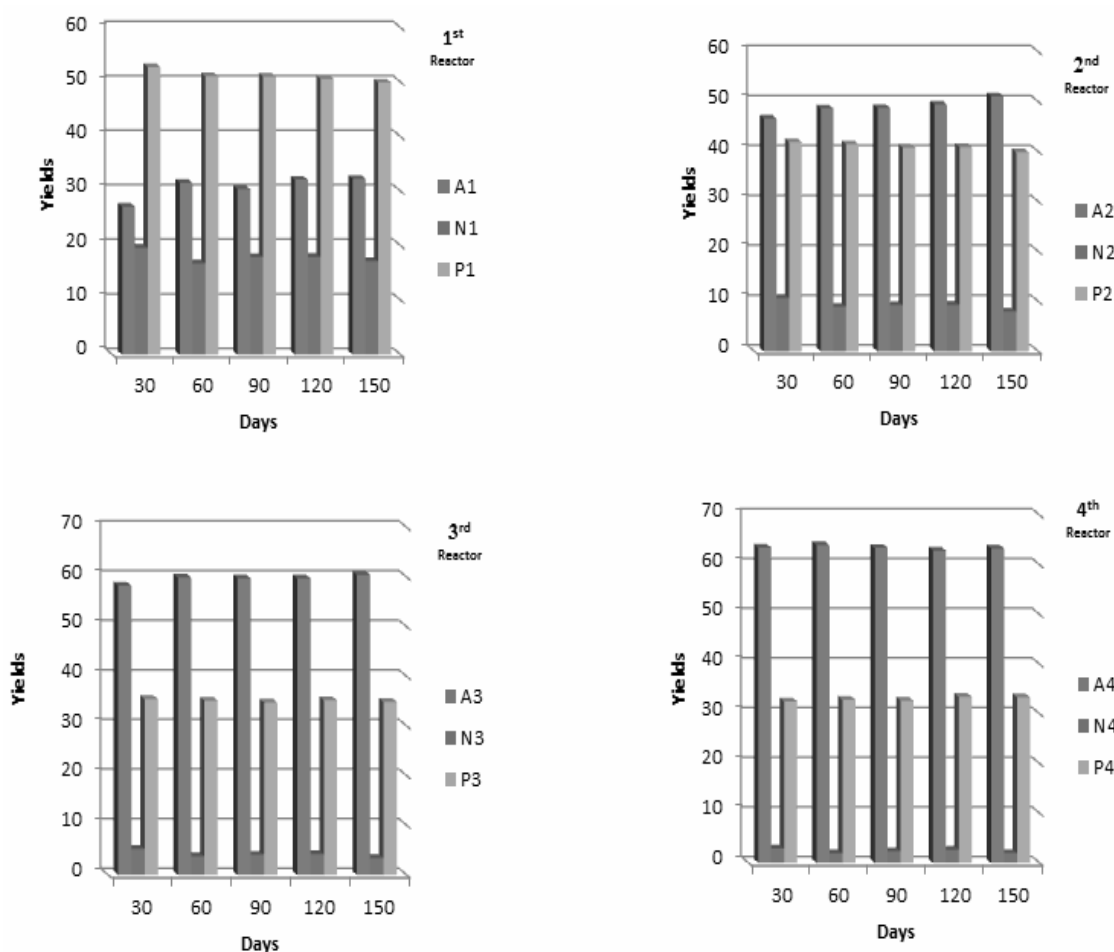


Fig. 3 – Hydrocarbon family yields in each reactor.

Differences in yields for the hydrocarbon family were observed in the four reactors. This is probably due to:

A speedy and almost total conversion of naphthenes, and simultaneously an increase in aromatics. This suggests that the main reaction in

the reactors is the naphthenes dehydrogenation which is the fastest of the reactions.

A low consumption of paraffins in the four reactors is probably due to the low rate of the paraffin dehydrocyclization reaction.

The operating conditions, *i.e.*: (i) The low purity and volumetric flow of hydrogen have a negative impact on the ratio (H_2/HC) and consequently on the paraffins that are cracked instead of being aromatised; (ii) A 1% content in chlorine in the catalyst guarantees an optimal acidity. An over chlorinated catalyst leads to an increase in isomerisation and cracking. While the octane number of the reformat increases for a given temperature, the yield in reformat decreases; (iii) The low value of ΔT in the second reactor leads to a pursuing of the dehydrogenation naphthenes in the reactors 3 and 4 at the expense of the dehydrocyclization of the paraffin, this latter being a key reaction in the production of aromatics.

CONCLUSION

The performances of a bi-functional catalyst were industrially analyzed in a series of four successive fixed bed catalytic reactors of the catalytic reforming unit whose aim is to produce a maximum of aromatics (BTX). The catalyst was found to be partially deactivated but remained selective.

LIST OF SYMBOLS

| | |
|-------------|---|
| <i>BTX</i> | Benzene, Toluene, Xylene |
| <i>PONA</i> | Paraffins, Olefins, Naphthenes, Aromatics |
| <i>R</i> | Reactor |
| T^e | Input temperature (°C) |
| T^s | Output temperature (°C) |
| η_P | Paraffins yield |
| η_N | Naphthenes yield |
| η_A | Aromatics yield |
| S_p | Paraffin selectivity in aromatics |
| S_N | Naphthene selectivity in aromatics |
| T_p | Paraffins conversion |

| | |
|-------|--|
| T_N | Naphthenes conversion |
| k | Index indicating the reactor number |
| Fk | Heat Flow in the Heat Exchanger k (kcal/h) |

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