Replacement of Commercial Anti-Corrosion Material with a More Effective and Cost Efficient Compound Based on Electrolytic System Simulation

Saeid Khajehmandali, Fattah Mollakarimi, and Zohreh Seyf

Abstract—There was a high rate of corrosion in Pyrolysis Gasoline Hydrogenation (PGH) unit of Arak Petrochemical Company (ARPC), and it caused some operational problem in this plant. A commercial chemical had been used as anti-corrosion in the depentanizer column overhead in order to control the corrosion rate.

Injection of commercial corrosion inhibitor caused some operational problems such as fouling in some heat exchangers. It was proposed to replace this commercial material with another more effective trouble free, and well-known additive by R&D and operation specialists.

At first, the system was simulated by commercial simulation software in electrolytic system to specify low pH points inside the plant. After a very comprehensive study of the situation and technical investigations ,ammonia / monoethanol amine solution was proposed as neutralizer or corrosion inhibitor to be injected in a suitable point of the plant. For this purpose, the depentanizer column and its accessories system was simulated again in case of this solution injection.

According to the simulation results, injection of new anti-corrosion substance has no any side effect on C5 cut product and operating conditions of the column. The corrosion rate will be cotrolled, if the pH remains at the range of 6.5 to 8 . Aactual plant test run was also carried out by injection of ammonia / monoethanol amine solution at the rate of 0.6 Kg/hr and the results of iron content of water samples and corrosion test coupons confirmed the simulation results.

Now, ammonia / monoethanol amine solution is injected to a suitable pint inside the plant and corrosion rate has decreased significantly.

Keywords—Corrosion, Pyrolysis Gasoline, Simulation, Corrosion test copoun.

I. INTRODUCTION

IN petrochemical complexes, cracking operations in presence of steam in ethylene plants will produce very different hydrocarbon cuts which are used as feed stock of down-stream plants.

The feed-stocks of ethylene plants usually can be selected from a wide range of materials such as Ethane gas, LPG,

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Naphtha, Gas oil, and etc. Normally all these feed-stocks are contaminated with sulphur and chlorine containing compounds. Some of the cracking products could be polluted with these impurities causing various operational problems and difficulties in down-stream plants. One of the heavy cuts separated in different sections of the ethylene plant is called crude gasoline, which normally will be sent to pyrolysis gasoline hydrogenation (PGH) plant for total hydrogenation.

Usually, this cut (crude gasoline) contains impurities such as sulphur compounds and chlorine containing organic acids, which causes equipment and pipeline corrosion in presence of water [1]. In some cases the intensity and severity of corrosion is so high that it is impossible to keep the plant running. This will obligate you to have an un-wanted plant shut-down and stoppage of gasoline (a strategic material) production.

In PGH plant of Arak Petrochemical Company (ARPC), due to sever corrosion problems in some sections of the plant, a commercial compound had been used as anti-corrosion material based on plant designer suggestion.

Due to its un-effectiveness in complete control of corrosion, precipitation in heat exchanger tubes reducing their efficiency, and many other operational difficulties happened during injection of this material.

ARPC's R&D experts decided to replace this compound with another well-known and more effective material.

In this regard, a research project with the title "viability and feasibility study of replacement of commercial anti-corrosion compound with another more effective compound" was defined.

In first stage of this research project, simulation of depentanizer column of PGH plant was performed based on electrolytic system to control the pH through using ammonia solution. Based on the results obtained from this simulation, practically some actual tests were performed inside the plant [2].

Since using only ammonia solution as corrosion inhibitor could cause operational difficulties in other parts of the plant and/or product quality problems [2], authors decided to modify it to prevent all these problems.

Again through simulation of depentanizer column in various cases of:

1. Column operation simulation without using any material as corrosion inhibiter.

2. Column operation simulation with using only ammonia solution as corrosion inhibitor, and

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3. Column operation simulation with using a mixture of ammonia solution and mono-ethanol amine as corrosion inhibitor.

The best results were obtained in the third case.

To prove this practically, many actual tests were performed inside the plant. The pH values were measured regularly at different points and very successful results were obtained. This was proved also by installing some corrosion test coupons inside various equipments.

Through simulation study results and actual plant tests, the optimum recipe was obtained for the new anti-corrosion compound including the composition of the new compound and the dosing amount.

II. PGH PLANT PROCESS DESCRIPTION

As we told before, the feed of PGH plant is crude gasoline separated in various points of the ethylene plant.

Crude gasoline normally is composed of hydrocarbon compounds from C5 to C7+ including olefinic, di-olefinic, aromatic, and cyclo-Diene materials. Sulphur containing organic compounds and chlorine containing carboxcylic acids are also included as contaminants. The purpose of PGH plant is to convert all the di-olefinic compounds included in crude gasoline to saturated olefinic compounds through complete hydrogenation in a single stage hydrogenation process. The next step is the separation of impurities and various classes of materials. These operations are performed in three consecutive distillation columns called depentanizer column, dehexanizer column, and deheptanizer column.

In these three columns C5, C6, and C7 cuts are separated and collected in their respective storage tanks. Later on these three main separated compounds are mixed in definite proportions and final pyrolysis gasoline product will be available for sale [1]. The schematic drawing of PGH plant process is shown on Fig. 1.
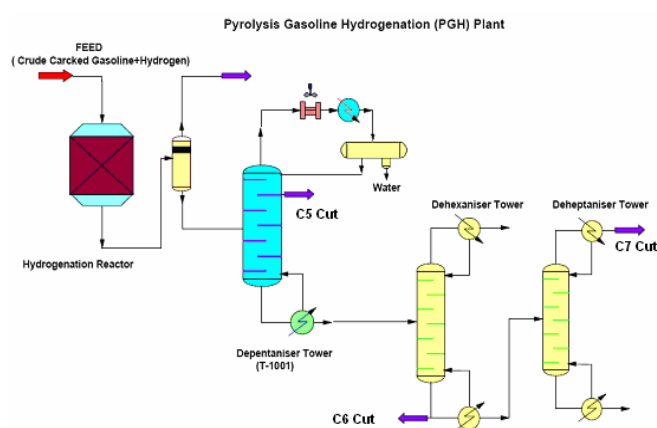

Fig. 1 Schematic process flow diagram of pyrolysis gasoline hydrogenation plant [1]

As it was described, PGH plant is composed of two different sections; hydrogenation reaction section and fractionation section. Due to the presence of some impurities in feed-stock, we have encountered corrosion phenomenon in both sections.

In the reaction section, because of very high sensitivity level of catalyst to additive materials, the corrosion rate is controlled through performing some corrective actions.

In fractionation section, the suggested compound by the plant designer was a commercial anti-corrosion. This material is a mixture of a film forming material and a neutralizer material. This compound is soluble in water and is injected to depentanizer column overhead stream with a weight proportion of 30 ppm.

Replacing this imported material with other easily accessible (domestic production), cheaper, and more effective compound will decrease the production cost and will improve the plant productivity.

In this regard, in substitution of this material, well known composition of new compound, its availability in our country, and its lower cost in comparison to the commercial material were considered in this research project.

Based on preliminary studies, performed researches, use of practical experiences in PGH plant and also in some refinery plants, and study of many technical papers, ammonia solution was recommended as first suggestion [2].

After more comprehensive study and research, another compound (a mixture of ammonia solution and mono-ethanol amine) was proposed. After practical employment and finding the optimum recipe of injection, outstanding results were achieved [2,3,4,5,6,7].

Performance evaluation of this new compound is demonstrated through laboratory test of pH on separated water phase of this system and also by measuring free ferrous content of this water phase. This monitoring and control of pH and free ferrous content was performed for duration of three months.

III. ELECTROLYTIC SYSTEM SIMULATION FOR CONTROLLING pH

A. Tower Simulation without Chemical Injection

Depentanizer is the first fractionating column in PGH plant. This tower contains 46 valve trays. Hydrogenated pyrolysis gasoline enters on tray NO 16 (from bottom) as tower feed. C5 cut product is withdrawn from tray NO 42 as side product and a blend of C6 and C7 cuts exit from column bottom as bottom product.

Separated vapors from top of the tower, passes through an air condenser (AE-1003) and a water cooler (E-1004) and are liquefied at 40° C and 5.4 Bar absolute. This liquid contains hydrocarbons and water, which is accumulated in V-1004 and separated in two phases.

Hydrocarbon phase is returned back to the tower as reflux and the aqueous phase will accumulate in V-1004 boot and goes out. Some operational observations and inspection tests show that severe corrosion begins from the top of tower and terminate in V-1004 boot. These tests also confirm that wherever aqueous phase exists (e.g. Boot V-1004), corrosion rate would be maximized [1].

Severe corrosions were seen in top section of the tower and in order to control the corrosion, some commercial anti-corrosion material is injected into overhead stream of the tower.

Gas chromatograph test (GC) was carried out in R&D department to determine contaminants in the feed of the tower. The test shows that about 50 ppm of sulphur and 2 ppm of chlorine compounds are present in the feed stream entering the column. GC test, identifies sulphur compounds as tiophens and mercaptanes and chlorine compounds as chlorine carboxylic acids. To consider worst case for corrosion condition inside the tower and its accessories, hydrogen sulfide (H_2S) and hydrochloric acid (HCL), were selected as representatives of sulphur and chlorine compounds respectively.

The reactions which result to corrosion are written based on electrolytic equilibrium system as follows [2]:

$$H_2O \rightleftharpoons H^+ + OH^- \quad (1)$$
$$Ln\ K_{eq} = 140.932 - 13445.9/T - 22.4773\ Ln(T) \quad (T\ in\ °K)$$

$$H_2S \rightleftharpoons H^+ + HS^- \quad (2)$$
$$Ln\ K_{eq} = 218.599 - 12995.4/T - 33.5471\ Ln(T) \quad (T\ in\ °K)$$

$$HCl \rightleftharpoons H^+ + Cl^- \quad (3)$$
$$Ln\ K_{eq} = -19.93 + 8938.1/T \quad (T\ in\ °K)$$

Simulation of the process was carried out based on PFD documents of PGH plant and by using commercial simulation software.

Electrolyte species were introduced to the software and a combination of NRTL/NRTL1986 was selected as thermodynamic system to model molecules electrolyte system. Fig. 2 below shows depentanizer column and its accessories without any anti-corrosion material injection.
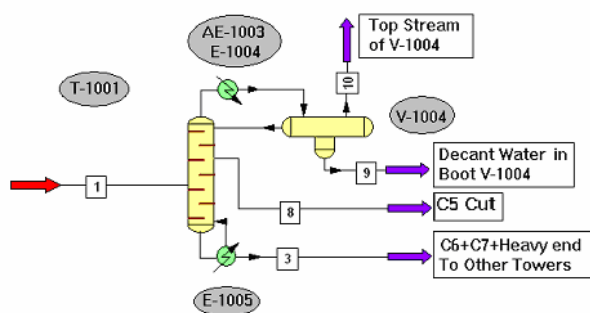

Fig. 2 Simulation of corrosion condition in depentanizer tower (without chemical injection)

In Fig. 3, actual temperature profile of the tower are compared with simulation results representing very good conformity between them.

Simulation results predict that in the aqueous phase of V-1004, the pH value would be about 3.9. Since fabrication material of this vessel is carbon steel, severe corrosion should

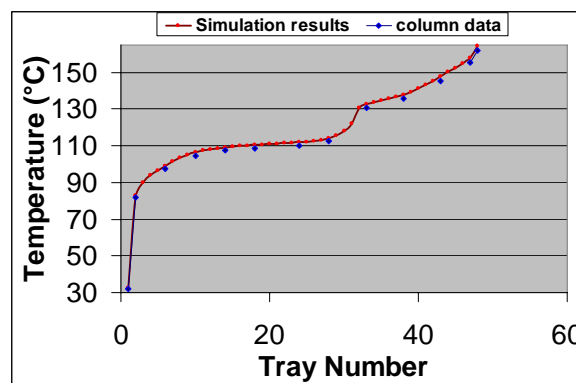happen in this vessel. Actual conditions of the plant completely confirm this situation.

Fig. 3 Real temperature profile vs. simulation results in depentanizer tower (without chemical injection)

B. Tower Simulation with Ammonia/Amine Solution Injection

In this case, ammonia solution and mono-ethanol amine (C_2H_7NO), streams NO 4 & 5 in Fig. 4, are mixed in a separate vessel and this basic solution is used as anti-corrosion additive. This solution is injected into the overhead stream of the tower before air cooler (AE-1003).

A new simulation must be carried out to determine required amount of anti-corrosion solution to neutralize acidic agents in the overhead stream before and after condensers and inside the accumulator (V-1004).

There are additional electrolytic reactions that take place in the overhead stream as follows [2]:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (4)$$
$$Ln\ K_{eq} = 2.76 - 3335.7/T + 1.4971\ Ln(T) - 0.0370566\ T$$
$$(T\ in\ °K)$$

Chlorine ion causes the following reaction:

$$NH_4Cl + H_2O \rightleftharpoons NH_4^+ + Cl^- \quad (5)$$
$$Ln\ K_{eq} = 3$$

And dissociation reaction of mono-ethanol amine would be as follows:

$$C_2H_7NO + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (6)$$
$$Ln\ K_{eq} = 0.7996 - 8094.81/T - 0.07484\ T \quad (T\ in\ °K)$$

Simulation of depentanizer column was carried out by considering above reactions and all assumptions mentioned in previous section. A graphical representation of tower simulation is shown in Fig. 4.

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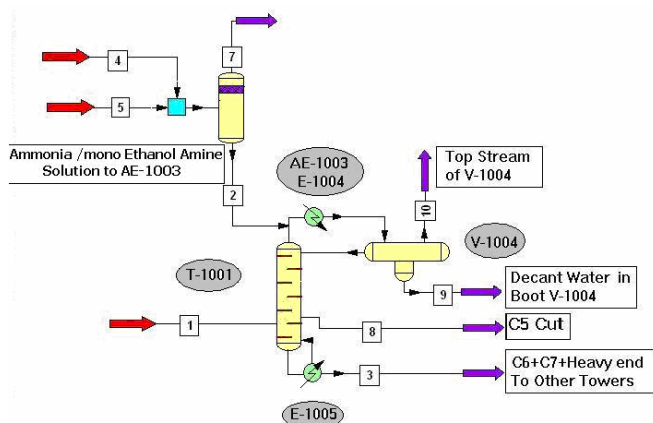International Journal of Materials and Metallurgical Engineering
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Fig. 4 Simulation of depentanizer tower after new anticorrosion injection

Table I shows some simulation results for with/without anti-corrosion injection cases in the top of tower stream.

TABLE I
SIMULATION RESULTS FOR WITH/WITHOUT ANTI-CORROSION INJECTION

Condition / Parameter	Before anti-corrosion injection	After anti-corrosion injection (Ammonia /Monoethanol amine solution)
Top tower temp (°C) Bottom Tower temp(°C)	82.5 164.5	82.5 164.5
Operating pressure (bar abs)	5.6	5.6
Decanted water pH	3.9	8.2
Water content in C5 cut (ppm)	1.2	2.0
Ammonia/amine content in C5 cut (ppm)	nil	nil

This result shows that pH value increases from 3.9 to 8.2 inside the accumulator (V-1004), and protects it against corrosion in case of injection of 0.6 kg/hr new anti-corrosion substance.

Table I, also shows that ammonia and mono–ethanol amine contents in C5 cut side stream product are nearly equal to zero and only about 2 PPM of free water may be present in this stream.

Mass flow rate of side cut remains constant respect to previous case (no injection) and all other operating conditions of the tower (pressure, temperature profile, reflux flow rate, bottom product flow rate, etc.…) would remain unchanged and the same as previous case.

Simulation results ensure us that no any unexpected phenomenon will occur during practical injection of new anti-corrosion substance.

C. Simulation of Column Overhead Accessories

Top of tower accessories consist of two heat exchangers (AE-1003, E-1004) and overhead accumulator vessel (V-1004) and inter-connecting pipelines. These equipments are shown in Fig. 5.
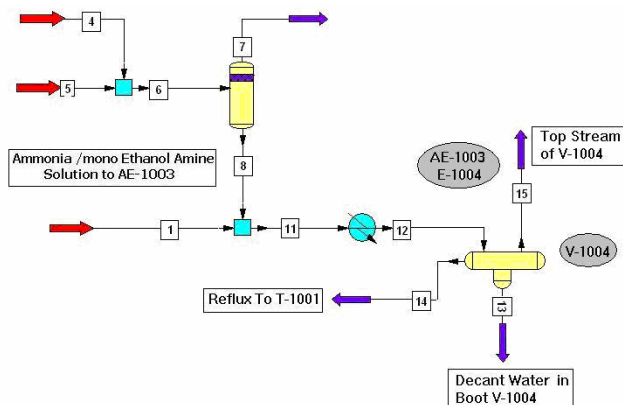

Fig. 5 Depentanizer overhead accessories

This section is simulated separately to ensure that all equipments and connecting lines would be protected against corrosion. This simulation is carried out based on previous chemical reactions and assumptions. The most important result in this section is pH values which are shown in Table II. According to this table, all pH values inside the equipments and connecting lines would be about 8.2, which guarantees the performance of new anti-corrosion material.

TABLE II
PREDICTED PH VALUES BEFORE AND AFTER NEW ANTI-CORROSION INJECTION

Stream number	pH before chemical injection	pH After ammonia\amine solution injection
8 (ammonia\amine solution)	3.9	12.6
11 (before air cooler AE-1003)	3.9	8.2
12 (after air cooler AE-1003)	3.9	8.2
13 (decanted water V-1004)	3.9	8.2

IV. PRACTICAL APPLICATION IN OPERATING PLANT

Based on the simulation results, experimental application of new compound (mixture of ammonia solution and mono-ethanol amine) was performed on 1 March 2007.

The initial flow rate was 0.6 kg/hr. During the injection pH value and free ferrous content of water phase separated in V-1004 boot were measured regularly and based on the obtained results, the injection flow rate is changed to keep the results in an acceptable range. Some of these results are shown on Table III.

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TABLE III
pH VALUE AND FREE FERROUS CONTENT OF SEPARATED WATER PHASE

Date	Aqueous phase pH	Free ferrous content in water (ppm)
3/3/2007	6.2	160
5/3/2007	7.05	120
7/3/2007	7.4	65
8/3/2007	7.1	45
9/3/2007	6.9	38
11/3/2007	8.0	21
12/3/2007	7.2	15

During the practical execution all the peripheral effects of new compound injection on column performance and operating conditions were monitored. No negative effects were seen. Also we never encountered any contamination of ammonia and/or mono-ethanol amine material in C5 cut product.

In addition to these pH and free ferrous content tests and for better monitoring of corrosion phenomenon after application of this substituted anti-corrosion material, some corrosion test coupons were installed inside more susceptible equipment.

The photo of one of these test coupons after one month of continuous operation is shown in Fig. 6.

Installed test coupon in boot V-1004 of PGH plant

Initial weight : 11.9775 gr   at 01 June 2007
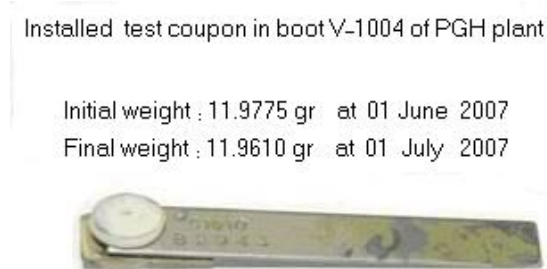Final weight : 11.9610 gr   at 01 July 2007

Fig. 6 Installed test coupon in boot V-1004 of PGH Plant

The corrosion test coupon used was made of carbon steel grade 1010. Calculation of corrosion rate was performed by using the following formula [7].

$$MPY(miles / year) = \frac{W \times 534}{\rho \times A \times T}$$

In which:
W: weight difference in mg
ρ: density of coupon in gr/cm3
A: coupon surface area in in2
T: test time in hr

Based on the actual results obtained and calculation of corrosion rate using the above formula, corrosion rate was about 1.5 MPY. Based on famous references MPY < 2 is a sign of very low and controlled corrosion [7].

V. CONCLUSION

1. Simulating the operating status of PGH plant by using suitable software based on electrolytic system predict acidic environment with low pH values which is an indication of corrosion occurrence. This is confirmed totally by actual sever corrosion in PGH plant.

2. Based on simulation results of depentanizer column and its related facilities, injection of ammonia solution and mono-ethanol amine does not have any negative effect on column performance. It does not change the column operating conditions. Tower side-cut and bottom products are totally free of these materials as contaminants. This claim is proved by practical execution of the project in running plant.

3. Based on the results obtained from software, after injection of ammonia solution and mono-ethanol amine, the pH values of streams which previously was in acidic range, changes to neutral range and excess basic solutions are transferred to water phase and separated from hydrocarbon phase in the boot of column reflux drum. From this point the water phase containing excess basic solutions are withdrawn from the system.

4. During the experimental application of ammonia solution and mono-ethanol amine injection, by keeping constant the pH in the range of 7.0 – 8.5, the free ferrous content of water is a good indication of corrosion rate. The results obtained from test coupon installed into the system (MPY=1.5) confirms reduction of corrosion rate.

5. Replacement of imported unknown commercial material with a mixture of ammonia solution and mono-ethanol amine (produced in our company) has the following positive features for our company.

- Controlling sever corrosion in PGH plant
- Decreasing operational problems and difficulties
- Cost saving of about $ 55,000 per year

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