

Examination of the Reasons for the Formation of Red Oil in Spent Caustic from Olefin Plant

Mehdi Seifollahi, Ashkan Forootan, Sajjad Bahrami Reyhan

Abstract—Due to the complexity of olefinic plants, various environmental pollutants exist such as NO_x , CO_2 , Tar Water, and most importantly Spent Caustic. In this paper, instead of investigating ways of treating this pollutant, we evaluated the production in relation to plant's variable items. We primarily discussed the factors affecting the quality of the output spent caustic such as impurities in the feed of olefin plant, the amount of injected dimethyl disulfide (DMS) in furnaces, variation in feed composition, differences among gas temperatures and the concentration of caustic solution at the bottom of the tower. The results of the laboratory proved that in the formation of Red Oil, 1,3butadiene and acetaldehyde followed free radical and aldol condensation mechanism respectively. By increasing the injection rate of DMS, Mercaptide amount increases in the effluent. In addition, pyrolysis gasoline accumulation is directly related to caustic concentration in the tower. Increasing naphthenes in the liquid feed augments the amount of 1,3butadiene, as one of the sources of Red Oil formation. By increasing the oxygenated compound in the feed, the rate of acetaldehyde formation, as the main source of Red Oil formation, increases.

Keywords—Olefin, spent caustic, red oil, caustic wash tower.

I. INTRODUCTION

AMONG the most important and strategic plants are olefins and their derivatives such as Ethylene, propylene, butadiene, low-density polyethylene, high-density polyethylene, polypropylene, poly-alpha-olefin, and Polybutadiene.

In one of the olefin plants' designs, gas feed (including ethane) and liquid feed (mostly consisting of C_3 , C_4 , and C_5 cuts) enters cracking furnace and after cracking and reaction, products such as Ethylene, Propylene, Methane, Hydrogen, Acetylene, Methyl acetylene, Propadiene, and Pyrolysis gasoline are produced. Then cracked gas decoked and cooled in hot section and its heavy combinations separate as fuel oil. The rest of the ingredients enter the compressor, and its pressure rises and goes to the cold section after drying. At this stage, hydrogen and methane are removed. Afterwards, C_2 products including ethylene and ethane are separated. Accompanying acetylene is converted to ethylene and ethane by a hydrogenation reaction. Then, C_3 products such as propylene, propane, methyl acetylene and propadiene are removed. Propadiene and acetylene are converted to propylene and propane by hydrogenation. After that, C_4 products such as butadiene, butene, etc. as well as C_5 and higher cuts are separated as pyrolysis gasoline. C_4 cuts hydrogenated in

hydrogenation reactor and injected to liquid furnaces as the liquid feed.

When ethylene and other olefinic products are being produced in the pyrolysis unit of olefin plant, compounds such as H_2S and CO_2 are also produced. The formation of hydrogen sulfide is due to the presence of sulfide compounds such as sulfide compounds in feed or added dimethyl disulfide (DMS) for poisoning the nickel of furnace coils so as to reduce coke formation. Also, carbon dioxide increased in the cracking and coke removal operations.

In this study, however, we discussed the problems related to the spent caustic system from the beginning to neutralization in an olefin plant. With an increased understanding of the factors affecting the formation and increasing this material, we tried to eliminate or control it. Also, by recovering it, the profit increased, and pollution effluents could be reduced at the plant.

Given the importance and complexity of olefin plants, various research projects have been considered. For Example, Nowowiejski et al., have studied on fouling and forming a polymer in caustic wash tower [1]. Maugans et al. and Ellis et al. have studied on treating spent caustic wastewater with WAO method [2]-[4]. In addition, Sheu et al. did neutralization and Fenton reaction combined method [5].



Fig. 1 Separated phases in the tower output sample

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One of the most contaminated waste waters is caused by emitted hydrogen sulfide, and mercaptans from hydrocarbon gasses washed in caustic solutions; therefore, special attention should be paid to controlling and managing such harmful pollutants.

As far as dealing with pollutants is concerned, most researchers have focused less on the production and recycling of the waste and more on the final disposal of the waste and the related methods such as Wet Air Oxidation[2]-[4], Neutralization [5], [6] and Advanced Oxidation.

CO₂ gas forms hydrate and caused freezing in cold section, and H₂S is a poison for hydrogenation reactors (palladium-based catalysts), hence the fact that they must be removed from the system [7]. To remove these gasses, the cracked gas is washed in the tower with caustic solution.

Caustic wash tower is a vertical gas-liquid tower under pressure with a temperature ranging from 30 to 50°C. Caustic towers are usually composed of three or four parts: the upper part employs boiler feed water, the middle part uses high concentrate caustic, and the bottom part makes use of low concentrate caustic so as to wash. Each level consists of a reservoir or a liquid container at the bottom. Furthermore, gas contact with the liquid is made possible by circulating the upper part of the container and spraying the caustic. A part of the liquid at the end of each section is transferred to the bottom section. Finally, a certain amount of the caustic solution is emitted from the end of the tower as the spent caustic. A hydrocarbon oil layer may also be present above each part of the caustic solution. Caustic towers are supposed to allow a minimum holdup time for the condensed hydrocarbons and formed red oil (A hydrocarbon compound (varying from orange to red or dark red based on its long life and is famous in industry for its color) accumulates above the caustic surface in caustic wash tower) as a higher holdup time increases the polymerization rate of such hydrocarbons.

The middle part of the reservoir is designed to transfer liquid from top to bottom with a line in which oil floats and moves to the next section, reducing the holdup time in the process. The design is based on a bottom floor skimmed by the operator in order to remove the hydrocarbons from the caustic. This hydrocarbon oil, routinely and periodically removed from the system due to the shorter chains, is light and can easily be removed from the system. Nonetheless, with the increase in the life of hydrocarbons, the chain and the tendency to form polymer increase.

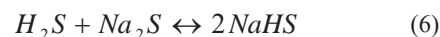
In this tower, polymerization reactions are temperature dependent. Accordingly, by increasing the temperature to more than 49 °C, the formation rate of Red Oil in the tower rises. (Fig. 1) Excessive increase in the temperature of tower's feed is not recommended [2], [8].

A. The Tower Caustic Reactions

1. Irreversible Reactions



2. Reversible Reactions:



Depending on its composition, spent caustic stream can be divided into the following three groups:

TABLE I
CLASSIFICATION OF SPENT CAUSTIC TYPES [4], [9]

Usages	Pollutant	spent caustic types
Ethylene of LPG Scrubbing	sulfide and mercaptans	Sulfidic
Scrubbing Kerosene Diesel	sulfide and Naphtenic	Naphtenic
Scrubbing Gasoline Washes	sulfide and phenol	Cresylic

Sulfidic spent caustic is the only included caustic and sulfide. The composition of the sulfidic stream in petrochemical units includes 0.5% to 4% sulfide (S²⁻) and 0.1% to 4% mercaptides. Naphtenic spent caustic mostly includes naphtenic acid (greater than 15%) and a small amount of sulfide, a combination with a very high tendency to foam. Cresylic spent caustic contains a large amount of phenol, cresols and organic acids. The amount of phenol in the composition can reach up to 2000 ppm [10].

B. Physical Characteristics of the Spent Caustic

Suspended solids (SS): The spent caustic usually contains colloidal particles (in the case of polymer) whose amount ranges from 0.2 to 0.5 g / l and are not easily removed through refining operations and do not generally measure them.

- Hydrocarbons (HC) exist in three forms:
 - Solution (with light and aromatic compounds)
 - A thin layer which includes two groups:
 - Non-stable emulsion(Paraffin)
 - Stable emulsion(Asphaltenes)
 - Solution (with polar compounds (naphtenate) separated only by acid hydrolysis)

The amount of hydrocarbons in caustic consumptions is between 0.05% -4%, and because of their volatility, hydrocarbons are hazardous if evaporated in the air. Generally, the properties and composition of spent caustic are as follows:

C. The Cause and Mechanism of Polymer Formation in Caustic Tower

Depending on the olefin plant feed, the behavior of the caustic wash tower differs for polymer, emulsion and foam. Liquid cracking plants have long history of choking caustic tower due to the diene compounds and hydrocarbon condensation in the cracked gas entering the tower. Choking, emulsion, and foam are the three major hazards occurring in

caustic towers and, if not seriously taken care of, might shut down the olefin plant

Dienes are aliphatic with two active double bonds. The choking caused by such materials is due to the absorption and condensation in caustic circulation direction. If dienes are allowed to accumulate in the system, they might lead to tower shutdown.

TABLE II
COMPOSITION OF SPENT CAUSTIC [3], [11]

Composition	Material
0.5%-6%	NaHS
1%-5%	Na ₂ CO ₃
1%-4%	NaOH
0.1%-4%	NaSR
500-1500 ppm	Soluble Oil
6000-20000 ppm	TOC
20000-60000 ppm	COD
1080-1100 Kg/m ³	Density

Condensation of hydrocarbons in the caustic tower is caused by the formation of red oil which chokes the tower and its equipment. Moreover, the rate of polymer formation by Aldol condensation increases with the increase in the temperature and concentration of acetaldehyde.

Washing the Cracked gas with caustic, increases the risk of polymer formation of unsaturated compounds by condensation and choking tower's packing. Polymer formation rate is totally dependent on the partial pressure of butadiene, the concentration of the caustic in the tower and other impurities such as oxygenated compounds that act as polymerization initiators. In the present olefin plant case study, the amount of butadiene in cracked gas was higher than other gas crackers. Due to the high partial pressure of butadiene on the fourth level of the compressor, caustic wash tower was located at the outlet of the third level.

Choking in caustic tower is identified via the increase in the pressure drop, the stability of acid gas eliminating efficiency or the production of solid particle.

At first, a little soluble dimer in caustic remains and then it started to grow and lightening, then form insoluble oil floating on the surface, at which point it was very simple to skim the tower. The remaining polymers which instigated polymerization reactions, created longer chain lengths and remained suspended in the caustic. Larger polymers were very difficult to remove from the system as they did not float due to their heaviness and metal surfaces [7], [8].

Depending on the amount of polymerization, hydration, and impurities, the polymer can appear as red, yellow, green or other colors. This material can absorb other organic materials from cracked gas and corrosion products in the tower and increase its volume in the process.

Foaming phenomenon is recognized by the increase in the pressure difference of the tower and the increase in the level of the water washing section. Emulsion increase is due to the increase in the amount of hydrocarbons in the tower because of the temperature which is lower than the normal or incomplete

separation of hydrocarbons in the compressor inlet drums (knock out drum) [12], [13].

D. The Mechanism of Polymer Formation

In general, idea that choking of the towers is a function of the acetaldehyde concentration and reactions due to aldol condensation exists. However, regardless of injection inhibitors (anti polymers), why the polymer formation does not reduce? Why the carbonyl group removal agents do not stop the polymer formation? A theory has been proposed that the polymer formation is the result of free radical polymerization. It should be noted that free radical polymerization, usually occurs in hotter areas like the cracked gas compressor's blades or cooling exchangers of the compressor interstages. Therefore, the lower temperature of the towers is the reason for lowering the strength of the free radical theory. In spite of that, Claud et al. have shown that free radical polymerization can happen in caustic systems and even can be the main and dominant mechanism [14].

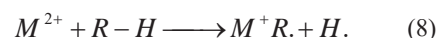
E. Various Mechanisms of Polymer Formation

Organic chockings in amine or caustic systems can be due to two mechanisms:

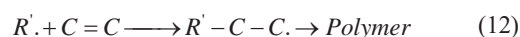
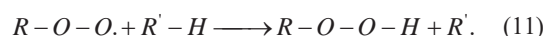
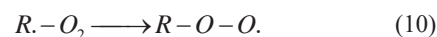
- Free radical polymerization
- Aldol condensation

1. Free Radical Reactions

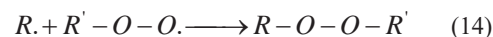
a) Chain Initiation



b) Chain Propagation



c) Chain Termination



where R = Reactive Polymer monomer or oligomer and M = Metal. In free radical mechanism, unsaturated compounds in cracked gas such as 1,3butadiene and acetylene have a significantly recognizable solubility in caustic solution and can be polymerized with free radical mechanism at the tower pressure [11], [13]. At a suitable temperature, peroxide decomposes into free radicals. If a free radical is added to a monomer the resulting chain will grow up to three times its size and will even gain higher molecular weights. Compounds that generate free radicals are:

- Azo compounds
- Peroxide
- Oxygen and metallic oxides which often exist in caustic towers.

Polymers formed in caustic towers have other properties. One side of the macromolecule is hydrophilic and the other is hydrophobic, hence is the cause of spherical shapes formation.

The hydrophilic polymer in the aqueous solution is drawn to the outer side of the sphere while the hydrophobic side is pulled to the inner side. A symbolic form of macro-molecules is shown in Fig. 3.

Aromatics cannot be dissolved in water yet according to the specific shape of the polymer, they can accumulate in the polymer's hydrophobic center, and that is why certain amounts of aromatics can be spotted in spent caustic [8], [15].

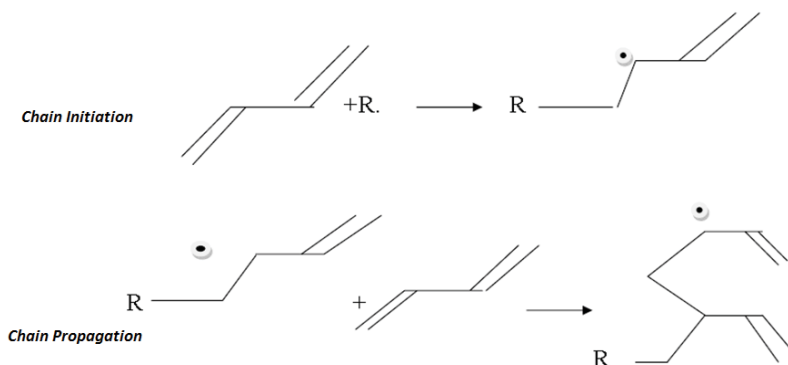


Fig. 2 Polymer formation steps

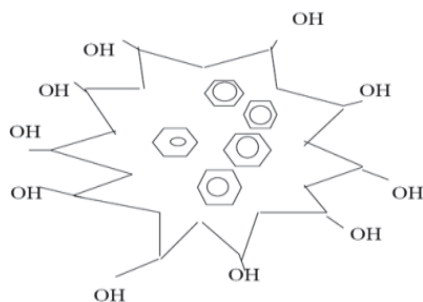


Fig. 3 Symbolic form of macro-molecules

Polymer formation continues after effluents exiting from spent caustic tower, because unreacted monomers and precursors (methyl acetylene/Propadiene and vinyl/ethyl acetylene which have high solubility in alkaline solutions) continue the polymerization process if there is a proper temperature and pressure. Furthermore, in the case of oxygen entree, polymerization actually increases. Inappropriate quality of fresh caustic can also increase the rate of polymer formation as impurities keep accumulating. These impurities include heavy metals and other compounds (Mercury, iron, nickel, Magnesium, Silica, calcium, lead and copper) that can act as initiators.

Metallic compounds directly react with sulfur and form compounds known as Chalcogen metal group. Such compounds are also known as initiators and accelerators of the polymerization reaction. To prevent the formation of these substances, fresh caustic should be independent of starter materials from the outset. [11].

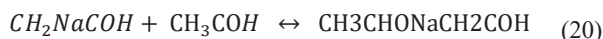
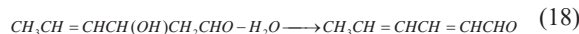
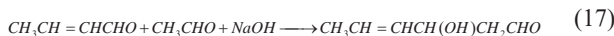
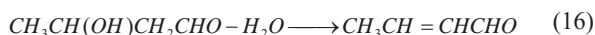
Carbonyl compounds exist along with unsaturated compounds in cracked gas and in the presence of caustic, carbonyl compounds change into heavier materials through the

process of condensation, also known as Aldol condensation. In general, Aldol condensation occurs when ketones, aldehydes and carbonyl are condensed in the cracked gas.

Aldol condensation can be identified via hydrocarbon layers (above the spent caustic) with colors ranging from orange-red to red-brown and red and through granular orange to brown particles and yellow polymer layers (existing in skimmed layers). The red layer which is very sticky and considered as a hazardous material, is also called red oil.

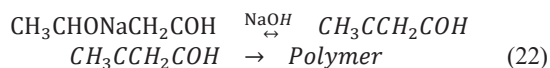
In system's process conditions, the molecules of aldehyde and ketone form beta-hydroxy aldehyde or hydroxy ketone. The reaction continues owing to the presence of C=O groups. Moreover, the dehydration product changes into a dual-band structure and a polymer due to reaction with carbonyl groups.

2. Aldol Condensation

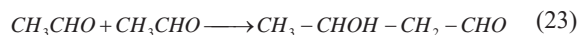


If more than six molecules (with a double bond structure) participate in the polymerization process, the resulting polymer will be red.





More than 70% of carbonyls in cracked gas are absorbed by caustic solution in caustic tower. The amount of polymer formed in these towers is dependent on temperature, pressure and the amount of acetaldehyde. Ketones, however, have slower reactions because of the steric inhibition of the structure.



Cracked gas contains a wide range of carbonyl compounds which may react with Aldol condensation mechanism, but experiments show that acetaldehyde is the most common material which is directly converted into red oil. Carbonyl groups found in cracked gas are Acetone, Acrolein, acetaldehyde, Propionaldehyde and formaldehyde. Formaldehyde concentration is not noticeable in cracked gas because it cannot sustain the high temperature involved in cracking.

Sometimes, the color of the fouling indicates the mechanism. Yellow polymers are caused by diene reactions, while red and orange polymer compounds result from Aldol condensation. Nevertheless, it should be noted that color is not a reliable indication of the type of composition and its mechanism.

Color darkens as the number of carbon-carbon double bonds increases. A change in the color (resulting from the formation of viscous oily liquid) is also visible as the reaction progresses [13].

In olefinic plants, Aldol condensation can be limited by certain reactions. Carbonyl eliminators are among the compounds that react with carbonyl groups and successfully reduce Aldol condensation of aldehydes [16].



II. DISCUSSION

A. The Relationship between Olefin Feed Impurities and Tower Effluent

As was stated, the presence of impurities such as oxygenated compounds in the cracking furnaces form aldehyde and ketone compounds. Furthermore, based on the described mechanisms such materials form red oil polymer through the process of Aldol condensation. Fig. 4 illustrates the relationship between oxygenated compounds in the olefin liquid feed and the amount of acetaldehyde entering the caustic wash tower.

As can be seen, with the increase in the oxygenated compound in the olefin feed, the amount of acetaldehyde increases, heightening the formation rate of red oil in the tower.

B. Injection of DMDS to Olefin Plant Furnaces and Its Effect on the Caustic Tower Effluent

As was already mentioned, DMDS was injected to poison the nickel surface of furnace coils. The amount and duration of DMDS injection varied depending on the type of feedstock (gas

or liquid). The change in the manner of injection altered the rate of mercaptan entering the caustic tower.

Entered mercaptans reacted with caustic tower, producing mercaptide in the process. The increase in mercaptan (R-SH) augments the mercaptide (R-SNa) that moves from the tower directly into the effluent. As shown in Fig. 3, the variation of DMDS is proportional to the change of mercaptan entering the tower.

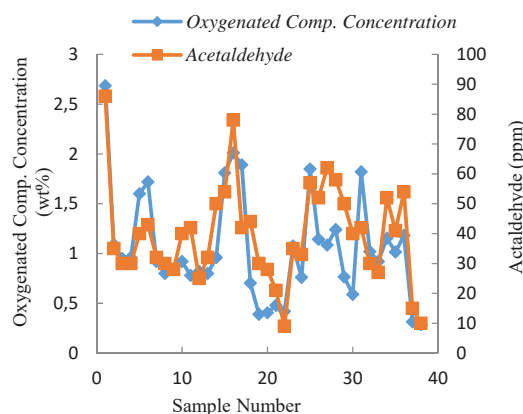


Fig. 4 The percentage of oxygenated compounds in the olefin feed versus the concentration of acetaldehyde at the entrance of the caustic tower

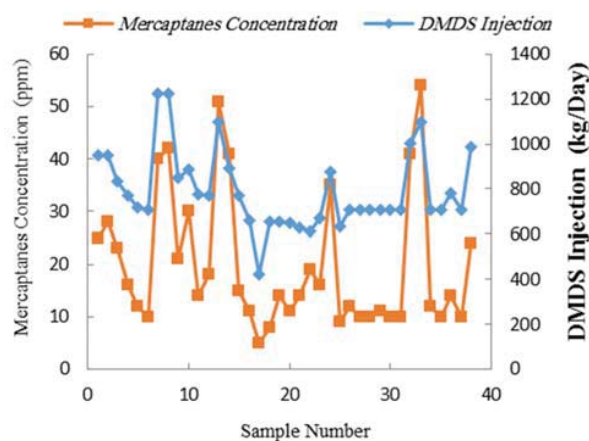


Fig. 5 DMDS injection to the furnaces in relation to mercaptan concentration entering the caustic tower

It is worth noting that the mercaptide in the wastewater was neutralized with sulfuric acid and mercaptans were directed toward the flare along with other gases.

C. The Relationship between Caustic Concentration at the Bottom of the Tower and Pyrolysis Gasoline Discharged from the Caustic Tower to the Effluent

Based on Fig. 4, during the analysis of the samples, the increase in the caustic at the bottom of the tower, led to a rise in the accumulation of Pyrolysis gasoline in the tower. The concentration of caustic at the bottom of the tower which is proportional to the variation of pyrolysis gasoline accumulation

brings about a change in the quality of the effluent from the caustic tower, an increase in the amount of effluent COD and pyrolysis gasoline loss.

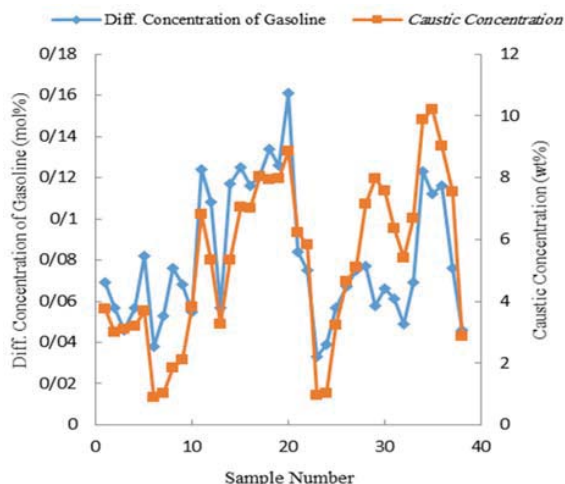


Fig. 6 The change in the caustic concentration at the bottom of the tower with pyrolysis gasoline accumulation

There are two mechanisms involved in the formation of polymer in the caustic tower:

- Free radical polymerization
- Aldol Condensation

Hydrocarbons can be slightly dissolved in the cracked gas based on their concentration and in caustic based on their solubility. Unsaturated compounds in cracked gas are able to form polymer and oxygenated metal ions can enhance the formation of the polymer.

Unsaturated compounds such as 1,3butadiene in cracked gas can be easily dissolved in caustic solution and can form polymer by free radicals at tower's pressure and temperature. Oxygenated compound and metal oxides form free radicals in the tower and form polymer and increase red oil production in compounds such as 1,3butadiene. Moreover, a wide range of carbonyl compounds exist in cracked gas which may react with the aldol condensation mechanism. Nonetheless, as was stated, acetaldehydes are substances that most commonly and directly converted into red oil.

Meanwhile, more than 70% of the carbonyls in cracked gas are absorbed in caustic solution and cause polymer formation. Due to the special shape of the polymer (Fig. 3), with a hydrophilic outer side towards the aqueous solution and a hydrophobic inner side, the aromatic compounds can accumulate and increase the pollution load of aromatic and cyclic compounds in the effluent of the column.

Owing to the fact that more than 70% of pyrolysis gasoline composition consists of aromatics, an increase was observed in the accumulation rate of cyclic compounds as a function of the rise in red oil. According to Figs. 7 and 8, the variation of the accumulation in acetaldehyde with the changes in the concentration of caustic at the bottom of the tower does not fit the variation of 1,3butadiene in the tower with the changes in

the concentration of caustic at the bottom of the tower. This represents the mechanism of Aldol condensation for aldehydes and 1,3butadiene as free radical mechanism.

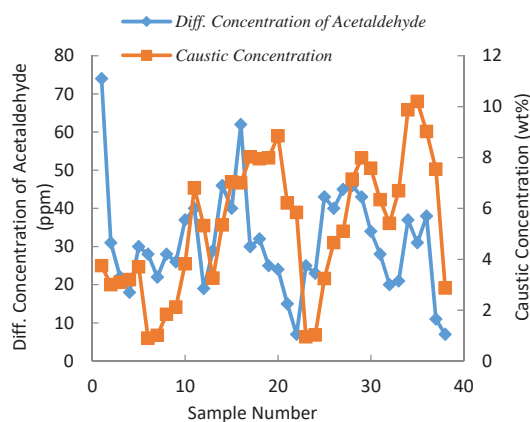


Fig. 7 Caustic concentration in proportion to acetaldehyde accumulation

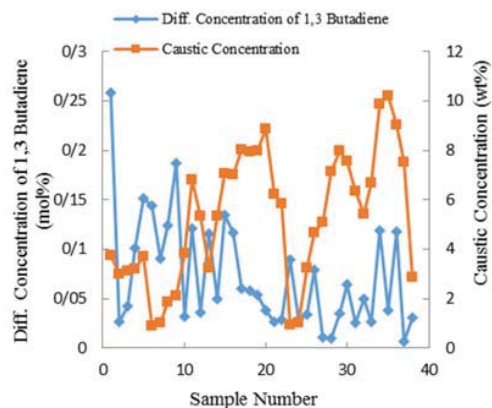


Fig. 8 Changes in the concentrations of 1,3butadiene in proportion to caustic concentration at bottom of the tower

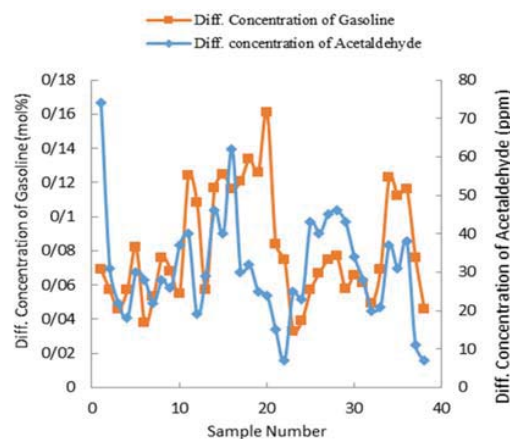


Fig. 9 Acetaldehyde accumulation change in proportion to pyrolysis gasoline accumulation

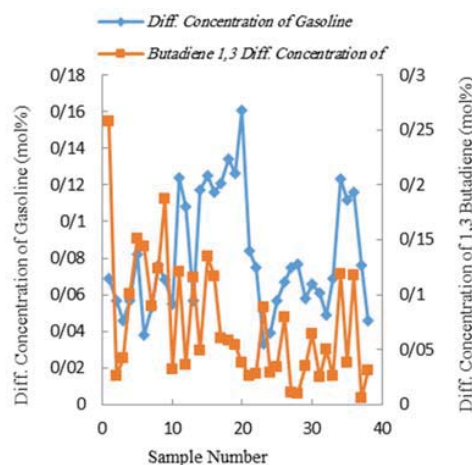


Fig. 10 1,3butadiene change in proportion to pyrolysis gasoline accumulation

The increase in the accumulation of acetaldehyde and 1,3butadiene, increased the formation of red oil and, as previously mentioned, the pyrolysis gasoline accumulation in the caustic tower. In Figs. 9 and 10, the accumulation of acetaldehyde and 1,3butadiene is proportional to pyrolysis gasoline accumulation. Furthermore, with the increase in the red oil, more pyrolysis gasoline leaked from the caustic tower.

D. The Relationship between the Composition of the Olefin Plant Liquid Feed and 1,3butadiene

As it was mentioned, polymerization rate depends on the partial pressure of butadiene, concentration of the caustic in the tower and other impurities such as oxygenated compounds that act as polymerization initiators. In olefin plant case study, butadiene concentration is more than other similar plants because of the differences in liquid feed of olefin plant furnaces. In designing the plant furnaces, the conversion in liquid was in accordance with the following facts:

- Normal paraffins have high ethylene yield.
- Compared with ethylene, i-Paraffin produces more ethane and propylene.
- Aromatics produce heavy compounds such as fuel oil.
- Compared with ethylene, naphthenes and cyclohexanes yield more aromatics and 1,3butadiene, respectively [1].

Therefore, the presence of cyclohexane in feed produces more 1,3butadiene and the existence of the aforementioned impurities heightens the polymer formation in tower. Fig. 11 demonstrates that 1,3butadiene, at the entrance of the caustic tower, is proportional to cyclic compounds in the liquid feed of olefin plant.

III. CONCLUSION

We identified and evaluated the factors affecting the quality of spent caustic at the bottom of the caustic wash tower. These factors are the impurities present in the feed of olefin plant, the injection of dimethyl disulfide to furnaces, composition of feed and caustic concentrations of the bottom of caustic tower.

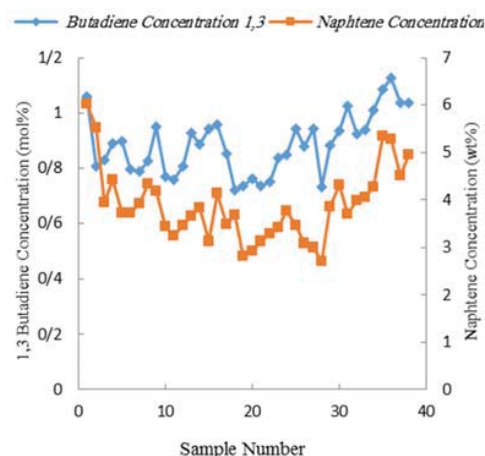


Fig. 11 The changes in the amount of naphthenes in feed in relation to the production of 1,3butadiene

After evaluating these factors, the following results were obtained:

- By increasing the injection rate of DMDS, Mercaptide amount increases in the effluent.
- Pyrolysis gasoline accumulation is directly related to caustic concentration in the tower.
- Increasing naphthenes in the liquid feed augments the amount of 1,3butadiene, as one of the sources of Red Oil formation.
- The formation of Red Oil 1,3butadiene and acetaldehyde were caused by free radicals and Aldol condensation, respectively.

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