

## **Overview of Butadiene chemical reaction fouling in Steam Crackers and its control by Carbon Steel surface modification**

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### **Abstract**

The main objective of the Steam Cracker is to produce monomers prone to polymerization. The drawback is that polymerization can occur in the Steam Cracker itself. The main monomers fouling precursor is Butadiene. All along the separation process, Butadiene concentration and process temperature change. This implies step changes in polymer structure and fouling level. Several techniques are used to control this fouling, including oxygen ingress control, the use of additives such as antioxidants and free radical scavengers. By a catalytic effect, the metal surfaces can also be a polymerization initiator. The objective of passivation is to modify the Carbon Steel surface into stable magnetite and maghemite. Using electrochemistry to characterize different Carbon Steel samples, we were able to improve our passivation procedure. And when applying metal passivation, we were able to increase run length of Depropanizer reboilers limiting the fouling rate and its impact on operation.

### **Introduction**

The main objective of the Steam Cracker is to produce monomers prone to polymerization. The drawback is that polymerization can occur in the Steam Cracker itself. The main monomers Ethylene

and Propylene are not so reactive to induce big fouling problems in the Steam Cracker. This is not the case with Butadiene. Depending on the feedstock the yields are completely different regarding Butadiene production (FIGURE 1).

FIGURE 1: Typical of cracking yields from different feedstocks

Feedstock		Naphtha	Ethane
Hydrogen	H <sub>2</sub>	1,5%	4,2%
Methane	CH <sub>4</sub>	15%	6,4%
Ethane	CH <sub>3</sub> -CH <sub>3</sub>	4%	29,2%
Ethylene	CH <sub>2</sub> =CH <sub>2</sub>	30%	52,9%
Propylene	CH <sub>2</sub> =CH-CH <sub>3</sub>	15%	1,5%
Butadiene	CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	4%	2%
Butenes (1 double bond)		5%	
C5's		5%	
Benzene	C <sub>6</sub> H <sub>6</sub>	6%	1,2%
Toluene	C <sub>6</sub> H <sub>5</sub> -CH <sub>3</sub>	3%	
C6-C8 non aromatics + C8+		8%	

All along the process, as separation progress, Butadiene concentration and temperature increase (FIGURE 2). This implies a modification in polymerization kinetic and fouling structure. The

result is a fouling level and aspect that changes all along the Steam Cracker and Butadiene production unit separation process.

FIGURE 2: Typical concentrations and temperatures at different locations.

Feedstock	Full Yields		Bottom Deethanizer (65°C)		Bottom Depropanizer (100°C)	
	Naphtha	Ethane	Naphtha	Ethane	Naphtha	Ethane
Hydrogen	1,50%	4,2%				
Methane	15%	6,4%				
Ethane	4%	29,2%				
Ethylene	30%	52,9%				
Propylene	15%	1,5%	39%	32%		
Butadiene	4%	2%	11%	43%	17%	63%
Butenes (1 double bond)	5%		13%		22%	
C5's	5%		13%		22%	
Benzene	6%	1,20%	16%	26%	26%	38%
Toluene	3%		8%		13%	
C6-C8 non aromatics + C8+	8%					

The diversity of polymer aspect is due to differences in crosslinking level and solvency properties of the matrix it comes from. We can have fouling with “honey-type” polymer (FIGURE

3), “pancake” polymer (FIGURE 4), foam polymer (FIGURE 5) and “popcorn” polymers (FIGURE 6) in relation to the level of cross linking of the polybutadiene...

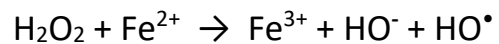


FIGURE 3 to 6: Different butadiene polymers aspects

The most dangerous Butadiene polymers are the popcorn polymers we find mostly in Butadiene units. These polymers are so strong that they can induce loss of containment. Using the internal cracks during popcorn polymer expansion, we are now able to detect them using acoustic emission [1] & [2].

The aspect and the quantity of fouling is also depending on the way the polymerization is initiated. In the case of Butadiene polymerization, we have a complex reaction scheme, including the reaction with Oxygen traces. Oxygen traces in hydrocarbons produce peroxide. The heat exchangers and metal surfaces participate to the

polymerization initiation. This action of the surface is, for example, coming from the Fenton reaction.



The free radical generated by this way initiates a polymerization chain. This shows the interest of having stable metal surfaces. The initiation of polymerization is highly induced by metal surface, especially on rusted Carbon Steel pieces of equipment.

FIGURE 7 summarizes the complex chemical reactions around initiation butadiene fouling from Carbon free radical (**R**·).

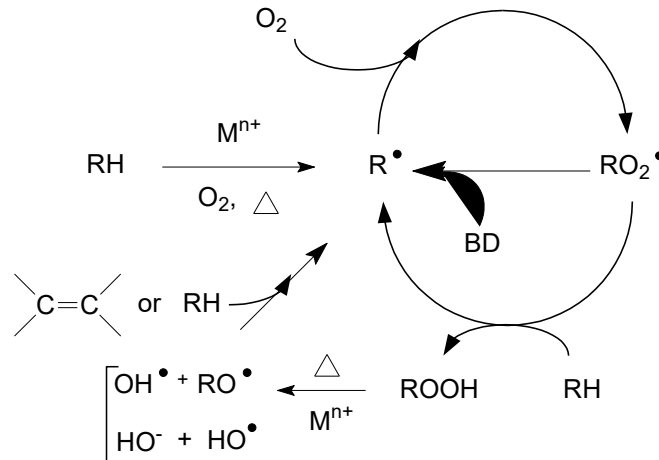


FIGURE 7: Chemical reactions involved in initiation of butadiene fouling

Several techniques are used to control this fouling, including Oxygen ingress control, the use of additives such as antioxidants and free radical scavengers. The most efficient free radical scavengers are based on the TEMPO (TEtraMethylPiperidineOxyl) family of additives (FIGURE 8). The drawback of these additives is their molecular weight: they are heavier than Butadiene, therefore in specific locations they are “unactive”.

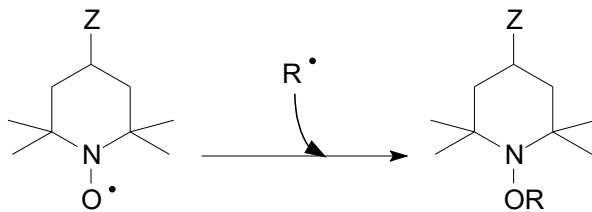


FIGURE 8: Free radical scavenging reaction of TEMPO family additives.

One of the surface modifications that can be used is the metal passivation. This is used on Butadiene units since a long time. But this procedure is sometimes difficult to apply on industrial scale because we need to apply nitrite solutions at temperature around 100°C. And all heat exchangers, distillations columns, piping... must be passivated for a complete passivation of the unit.

This passivation technique has been reported since the forties [3]. Since then, other passivation technologies have been described [4], but nitrite remains the most used. The objective is to modify the Carbon Steel surface into stable magnetite and maghemite. Magnetite formula is  $\text{Fe}_3\text{O}_4$ , this is mix of two iron oxidation state. Maghemite formula is  $\text{Fe}_2\text{O}_3$ . Both has a spinel crystalline structure.

### Experimental

Using electrochemistry, we were able to improve our passivation procedure [5].

We applied different procedures to passivate P 235 GH grade Carbon Steel (standard EN 10028-2: 2017). The electrochemical tests consisted essentially in following the Open Circuit Potential in a classical 3 electrodes device. Reference electrode is Saturated Calomel Electrode (SCE) and counter electrode is platinum. Low potentials are attributed to non-passivated steels and high potentials (above -150 mV) are associated to well passivated steels. All the electrochemical measurements were made on a slightly alkaline de-aerated solution under argon with no agitation at 50°C. The different treatments are described in FIGURE 9 and 10.

FIGURE 9: Different treatments of first sample set, impact of passivation and reoxidation

Parameters		Ref	T1	T2
Pickling	Aeration	Under air		
	Duration	8H		
	Temperature	50°C		
	Composition	3%w citric acid + 0,2%w corrosion inhibitor + pH~4 via NH3		
Reoxidation		no	no	Yes
Passivation	Aeration	-	Under air	Under air
	Duration	-	24H	24H
	Temperature	-	90°C	90°C
	Composition	-	3%w NaNO <sub>2</sub>	3%w NaNO <sub>2</sub>

FIGURE 10: Different treatments of second sample set, impact of atmosphere over passivation solution

Parameters		T1A	T1B
Pickling	Aeration	Under air	
	Duration	8H	
	Temperature	50°C	
	Composition	3%w citric acid + 0,2%w corrosion inhibitor + pH~4 via NH3	
Reoxidation		no	no
Passivation	Atmosphere	Nitrogen	Under air
	Duration	24H	24H
	Temperature	90°C	90°C
	Composition	3%w NaNO <sub>2</sub>	3%w NaNO <sub>2</sub>

Aeration under air means that the solution was kept in contact with air during the passivation procedure. Reoxidation consisted of immersing the sample in an NaCl solution with a concentration between 40 and 60 g/L, at room temperature.

Immersion for 7 days was completed by drying in the open air for 7 days.

In FIGURE 11 we see the open circuit potential evolution with time of the different Carbon Steel samples we prepared compared to a non-treated Carbon Steel sample. We see that the non-treated Carbon Steel sample is reactive with a potential

decreasing down to -800 mV/SCE. The treated Carbon Steel samples are clearly passivated with a potential remaining high over -100 mV/SCE.

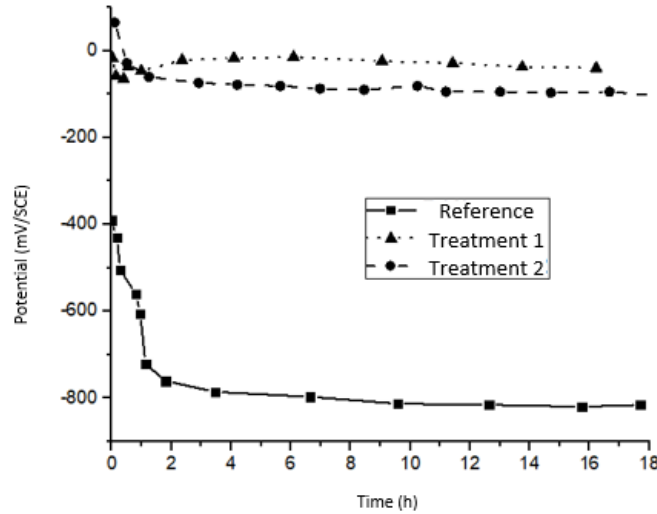


FIGURE 11: Open circuit potential evolution of prepared Carbon Steel samples

In FIGURE 12 we see that the Carbon Steel sample that was treated without any oxygen (treatment 1A) remains active with a potential around -550

mV/SCE. By contrast, the sample treated in presence of oxygen (treatment 1B) is passivated and unactive with a potential over -100 mV/SCE.

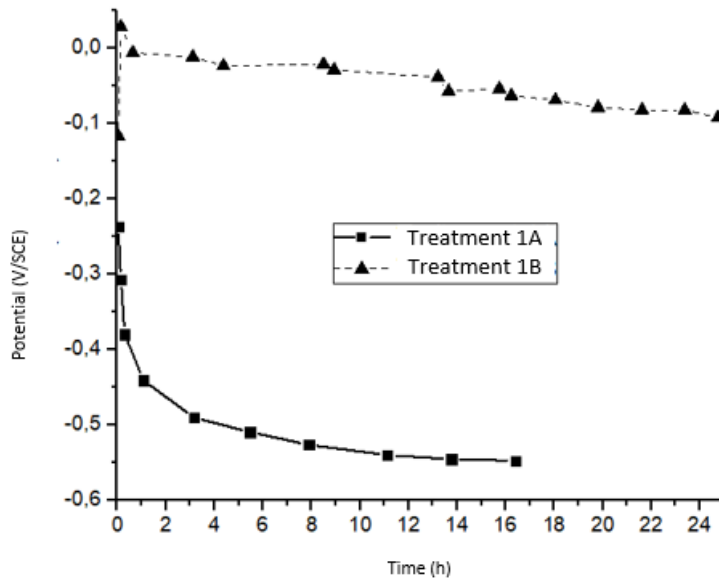


FIGURE 12: Open circuit potential of prepared Carbon Steel samples

And when applying metal passivation, we were able to increase run length of Depropanizer reboilers limiting the fouling rate and its impact on operation. Before applying any passivation on Depropanizer reboilers, their run length was limited at 3 to 4 months. When applying Carbon Steel passivation, the run length jumped immediately over one year.

### Conclusion

The objective of passivation is to modify the Carbon Steel surface into stable magnetite and maghemite. Using electrochemistry to characterize different Carbon Steel samples, we were able to improve our passivation procedure. And when applying metal passivation, we were able to increase run length of Depropanizer reboilers limiting the fouling rate and its impact on operation.

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