

## DMDS

### ANTICOKING OR SPIKING APPLICATION

The manufacture of olefins such as ethylene, propylene and higher types by thermal cracking of hydrocarbons in presence of dilution steam in tubular reactors are greatly affected by undesired side reactions. These side reactions, among which are coke and CO formation, reduce the olefins yield by hampering the heat transfer from the furnace to the process gas and increases the pressure drop over the coil, therefore, limiting equipment performance. (Reyners et al, 1995).

According to Salari, D. et al. (2006), there are three mechanisms by which coke is produced in the coil and transfer line exchange of a cracking furnace:

1. Catalytic coke:

During the startup of a furnace the reacting gas mixture is in contact with the bare reactor walls. Hydrocarbon molecules initially are chemisorbed on a metal crystallite at the surface and converted to coke by a surface reaction.

2. For Radical coke:

At the gas/coke interface layer the polyaromatics are not completely dehydrogenated. At this surface, hydrogen abstraction reactions by free radicals from the gas phase can occur. Hydrogen, methyl and ethyl radicals are the most active species. As a consequence, the concentration of the active sites at the coke surface becomes a function of the gas phase composition.

3. Polyaromatic condensation:

This implies the formation of polynuclear aromatics in the gas phase via free radical reactions. Starting with simple aromatics, condensation and dehydrogenation reactions occurs to produce tar droplets or soot particles that can be liquid or even solid at the conditions prevailing in a thermal cracking reactor. Part of the droplets collides on the tubewall. Some rebound into the gas phase, but it is more likely that they adhere to the surface and are incorporated in the coke layer since the outer surface of the droplets is not completely dehydrogenated. Hence, hydrogen abstraction reactions by gas phase radicals become possible and the coke layer can grow further.

As a result decoking operations are required. Among the different techniques used today to reduce coke formation, the development and use of additives appears to be the most effective and practical method.

Additives such as Organosulfurs compounds play a major role in maintaining optimal performance of a steam cracking furnace, this is supported by industry experience on using organosulfurs to avoid coke formation as shown by Brayden and Srinivas (2011).

Bajus and Baxa (1985) studied the effect of various S-containing additives on coke formation at 820°C and 100kPa in a stainless steel reactor. The presence of sulfur compounds decreases the coke formation. The authors explained that the same sulfur-

containing decomposition or intermediate product is formed and this product suppresses the coke formation irrespective of the properties of the initial sulfur compound added. This product which always forms during the thermal decomposition of sulphur compounds can be  $H_2S$ .

Other authors have also reported the interactions between  $H_2S$  and its effects in coke inhibition; for instance, Wagner (1992) and Rostrup-Nielsen (1984) in Reyners et al. (1995) stated that sulfur clearly acts upon the catalytic gasification of the steam-reforming process, responsible for the CO production. Sulfur components from the gas phase are more readily chemisorbed on the metal particles than water and hydrocarbon molecules. Coverage of metal sites by sulfur then leads to a lower concentration of active oxygen atoms at the surface and hence to a lower catalytic CO production.

Albright and Marek (1988) attributed the reduction of coking by the addition of sulfur to the formation of a passivating layer of metal sulfides. Bajus and Baxa (1985) described the inhibition of coke deposition to an inhibiting effect exerted by a layer of metal sulfides formed by interaction of  $H_2S$  with the metallic wall.

Many Sulphur compounds can be used (EM, TBM, DMS, TNPS 537, TBPS 454) but today DMDS is the most popular choice. Salari et al, (2006) demonstrated that the presence on unshared electron pairs in sulphur compounds can lead to very strong chemisorption on the metal surface. In the case of DMDS, the  $\alpha$  effect enhances the reactivity of the sulphur as compared with Carbon disulphide, therefore, as a consequence, for the same concentration of sulphur in the feed the amount of sulphur actually adsorbed on the surface is the highest for DMDS. The author has pointed out that this is the main reason for the much decreased coke formation.

Bock et al 1982 in Reyners et al, (1995), reported that thermal decomposition of DMDS starts at 575-675°C and yields  $H_2S$ , methanethiol, thioformaldehyde. Carbon disulfide and methane. The formation of  $H_2S$  from DMDS is therefore, expected, even before entering the cracking coil since the pre-heating section reaches 600°C.

## DMDS CHEMICAL REACTION

Vandeputte et al. (2010) studied the radical decomposition mechanism of DMDS theoretically and a kinetic model was developed to account for the formation of all the decomposition products.

The study demonstrated that the decomposition of DMDS is initiated by scission of a S–C bond, forming two radicals which can abstract a hydrogen atom from DMDS. The  $CH_3SSC\cdot H_2$  radicals decompose according to two different paths:

- (a) by  $\beta$ -scission with the formation of  $H_2C=S$  and  $CH_3S$  or
- (b) by an intramolecular substitution reaction with the formation of dithiirane ( $CH_2S_2$ ) and  $CH_3$ .

Addition of  $CH_3$  on  $H_2C=S$  leads to the formation of ethylene and  $H_2S$ , while dithiirane is an important intermediate for the formation of carbon disulfide. Other important decomposition products are  $S_2$  and  $S=CHSCH_3$ .

Brayden and Srinivas, (2011) had reported at the Ethylene Producers Conference that DMDS is H<sub>2</sub>S precursor which is also supported by the reaction shown by Vandeputte et al, (2010).

## REFERENCES TO THE SCIENTIFIC LITERATURE

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## SUMMARY

According to the scientific literature and company experience, Chevron Phillips Chemicals' point of view is that the chemical processing that takes place when DMDS is used in ethylene steam crackers is the transformation of DMDS into H<sub>2</sub>S. It has been shown that a chemical decomposition reaction of DMDS into smaller chemical species leads to the formation of H<sub>2</sub>S. The substance H<sub>2</sub>S formed from DMDS will help to protect the metallurgy in the case for the anti-coking (spiking) application.

Therefore, DMDS is regarded as an intermediate in the manufacture of H<sub>2</sub>S. This is in line with the REACH Regulation Article 3(15) which states that an "intermediate means a substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance". The conversion of DMDS into H<sub>2</sub>S is also in line with the Guidance Document on Intermediates version 2.0 dated December 2010.

This document is also delivered with the presentation from Brayden and Srinivas at the Ethylene Producers Conference in 2011.