STUDY OF DEGRADATION OF SULFOLANE SOLVENT AND THE CORROSION IN AROMATICS EXTRACTIVE DISTILLATION UNIT

By

Ahmed Mostafa Abdel-Fattah Ahmed Abo Bakr

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
in
Chemical Engineering

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
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Under the Supervision of

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FACULTY OF ENGINEERING, CAIRO UNIVERSITY
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Title of Thesis:

Study of degradation of sulfolane solvent and the corrosion in aromatics extractive distillation unit.

Key Words:

Sulfolane degradation, chlorides, corrosion rate, extractive distillation, linear polarization resistance.

Summary:

In this thesis, the degradation of sulfolane solvent was studied at different concentrations of chlorides and oxygen. Then, the corrosion rate of three different alloys (namely: carbon steel A 106, 304 SS and 316 SS) in the degraded samples was measured by linear polarization resistance method. After that, monoethanolamine (MEA) was added to the most severely degraded sample to neutralize it. Finally, the corrosion rate of that three alloys was measured in the neutralized sample.

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Dedication

I dedicated this work to my parents Dr. Mostafa Abdel-Fattah and Dr. Samia Tag El-Deen.

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Abstract

Sulfolane is a polar solvent which is used in aromatic extractive distillation units to produce benzene (C_6H_6), which is used widely in the petrochemical industry. Unfortunately, severe corrosion usually takes place in sulfolane extractive distillation units due to sulfolane degradation into acids during processing. This causes frequent shutdowns and replacement of equipment and pipelines. The conventional method to control the corrosion rate in the extractive distillation units is to add monoethanolamine (MEA) in batch wise manner to neutralize the sulfolane. The degradation of sulfolane is caused by several factors. The main factors are temperature, oxygen ingress and accumulation of chlorides in circulating sulfolane. The effect of temperature and oxygen was studied extensively in previous literatures. However, the role of chlorides in the degradation process remains unstudied in laboratory and not fully understood. In addition, the corrosion rate of different metals in sulfolane after degradation and the effectiveness of MEA to mitigate the corrosion have not been studied. Therefore, in this thesis, the effect of different chlorides concentrations (0, 100, 500 and 1000 ppm) on sulfolane degradation was studied in laboratory with and without oxygen ingress at the operating temperature of sulfolane unit. In addition, the corrosivity of the degraded sulfolane samples were measured for three different alloys; namely, carbon steel (CS), 304 SS and 316 SS. The corrosion rate was measured by linear polarization resistance method. Then, the effect of adding MEA to the degraded sample on its corrosivity toward these alloys was determined. It was found that as chlorides content increased, the degradation of sulfolane and its corrosiveness also increased. In addition, it was found that carbon steel was usually susceptible to high corrosion rate even at low chlorides concentration. In contrast, 304 SS and 316 SS exhibited good corrosion resistance at low to moderate concentrations of chlorides (0 to 500 ppm), while their corrosion rate increased drastically at high chlorides concentration (1000 ppm). Finally, it was found that adding MEA is not effective in mitigation of the corrosion of carbon steel (only around 37% reduction of corrosion rate was measured), while it was able to greatly reduce the corrosion of 304 SS and 316 SS up to 80%.

Keywords: Sulfolane Degradation, Chlorides, Corrosion Rate, Extractive Distillation, Linear Polarization Resistance.

Chapter 1 : Introduction

1.1. Overview

Benzene (C_6H_6) is one of the most important materials in the petrochemical industry. It is usually used in preparation of many chemicals used in manufacturing of plastics, drugs, dyes, detergents and insecticides [1]. One of the widely used technology to produce benzene is the extractive distillation process [2]. In this process, benzene is extracted from light reformate (the light portion of reformate, which is the effluent of naphtha reformer reactor and contains around 30 wt % benzene) by a highly polar sulfolane solvent in the extractive distillation column. Since the aromatics (benzene and toluene) are more polar than non-aromatics compounds, sulfolane tends to dissolve the aromatics and form the heavy component and go down the extractive distillation column. On the other hand, less polar non-aromatic compounds left undissolved and form the light component which rises as vapors to the overhead of the column and pumped back to the refinery. The aromatics are then separated from the sulfolane in the recovery column which operates under vacuum. Finally, the aromatics are fractionated into benzene and toluene [3], [4].

Unfortunately, corrosion is a chronic problem in the sulfolane extractive distillation units. The corrosion takes place due to the degradation of sulfolane into acids and polymerized solids. The acids cause corrosion while the solids induce erosion-corrosion, especially in pumps and elbows [5]. In addition, these solids cause blockage and fouling of heat exchangers tubes and distillation columns trays, which necessitates frequent shutdowns for cleaning [6]. There are several factors affecting the degradation of the sulfolane including: temperature, oxygen ingress and accumulation of chlorides [7]–[9].

Temperature is one of the major factors that determine the severity of sulfolane degradation. However, it was found that only at temperatures above 220-230 ℃ the sulfolane thermal decomposition becomes noticeable [10]. Therefore, the sulfolane temperature is always kept below 180 ℃ to minimize sulfolane thermal degradation. Another important factor affecting sulfolane degradation is the presence of oxygen. Several laboratory experiments were carried out to determine the exact effect of oxygen on sulfolane degradation. The conclusion from these experiments was that sulfolane reacts with oxygen to form weak acids, strong acids, acidic polymers and non-acidic polymers. It was found that the presence of oxygen accelerates the degradation of sulfolane at high temperatures [11]–[13]. For example, the degradation of sulfolane at atmosphere containing oxygen at 200 ℃ is five times higher than that at 200℃ in an inert atmosphere [3]. Therefore, all measures should be taken to reduce or eliminate the oxygen ingress into the extractive distillation unit [14]. Another important factor is the presence of chlorides [15]. Chlorides are entrained with the light reformate feed into the unit and tend to accumulate in the circulating sulfolane solvent [16]. The accumulation of chlorides in the sulfolane extraction system increases the sulfolane degradation by ring-opening hydrolysis of sulfolane molecules. In addition, presence of chlorides itself intensifies the corrosion of equipment in the extractive distillation units [11], [17].

Several countermeasures are taken to control sulfolane degradation and the subsequent corrosion [18]. Firstly, continuous monitoring of sulfolane condition is of vital importance to ensure that sulfolane is in a good state and to take the necessary corrective actions if a deviation took place. Monitored parameters include pH value, acid number and color. In addition, it is a common practice to use neutralizers such as monoethanolamine (MEA) to control acidity of the sulfolane. However, the corrosion continue to deteriorate the equipment even after adding the neutralizer [11], [19]. Therefore, the effectiveness of the neutralizers in preventing the corrosion in sulfolane units is questionable. Another way to control the solvent condition is by regenerating the solvent to remove solidified degradation product. This is done by taking a small slip stream from the circulating solvent to the solvent regenerator. In the solvent regenerator, a steam with aid of stab-in reboiler are used to strip the clean solvent form OVHD, while the heavy polymers remain at the bottom. After specific period of operation, the vessel should be taken out of service and dump the deposited material [20], [21]. Finally, material upgrading could be considered for equipment which undergo sever corrosion. Some plants changed the material of high temperature heat exchanger from carbon steel (which corroded severely) to be 304 stainless steel, which resulted in extending the life time of these heat exchangers [13].

1.2. Objective and organization of the thesis

In this research, the effect of chlorides content on the sulfolane degradation was investigated to provide more insight on the effect of chlorides on sulfolane degradation process. To do that, sulfolane samples with different chlorides concentrations; 0, 100, 500, and 1000 ppm were heated at the operating temperature in both inert and oxygen-rich atmospheres for two hours. Then, the pH and color of the degraded samples were measured to determine the extent of degradation in each sample. After that, the general corrosion rate of three different alloys (A 106 carbon steel, 304 stainless steel and 316 stainless steel) in the degraded sulfolane samples was determined by linear polarization technique (LPR). Finally, the effect of adding monoethanolamine (MEA) on sulfolane acidity and corrosivity on the same three alloys were also studied.

By studying these subjects, a better understanding of the degradation process of sulfolane could be developed. This would provide a guide of ways to reduce the solvent degradation. In addition, it is expected to provide a sound base for better corrosion control of the sulfolane extractive distillation units, which would result in decreasing the unit downtime and equipment damage due to high corrosion rates.

The thesis is organized in following sections:

i) Introduction
ii) Literature review
iii) Experimental
iv) Results and discussions
v) Conclusions.

Chapter 2 : Literature Review

2.1. Sulfolane

Sulfolane (tetrahydrothiophene 1,l dioxide), is a colorless, highly polar, water-soluble solvent used in several industrial applications. The first description of sulfolane in chemical literature was in 1916 [22]. Sulfolane is generally produced by a method developed by Shell Oil in 1940s. This method depends on the reaction of sulfur dioxide (SO_2) with a sulfolene precursor to form a sulfolene. Then, the sulfolene is hydrogenated to form the sulfolane over suitable catalyst. A preferred catalysts are those containing nickel, cobalt, platinum, copper, etc. [23]. The reaction formula is show in figure 2.1.

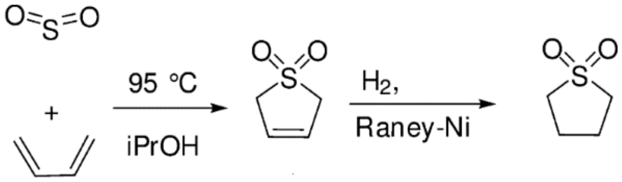

Figure 2.1 Sulfolane production formula

The total worldwide production of sulfolane is estimated at between 18,000 and 36,000 tons per year. Commercially, sulfolane is available as anhydrous sulfolane and as sulfolane containing 3% deionized water [24].

Prior to 1941, benzene, toluene and xylenes were recovered as by-products from coke oven operations and coal-tar distillation, where partial purification of the individual aromatics was accomplished by fractional distillation before removal of the remaining non-aromatics by treatment with concentrated sulfuric acid. However, these processes were of restricted aromatics recovery and purity. In addition, the quantity of aromatics produce by processing coal was very limited.

The petroleum industry has provided a suitable mean for aromatics mass production with desirable purity and recovery. The first step was the introduction of platforming technology, which converted naturally-occurring petroleum naphthenes to aromatics, by reforming naphtha over a platinum-based catalyst to produce high octane number gasoline. The second development was the use of liquid-liquid extraction to separate BTX from non-aromatics hydrocarbons with a very high selectivity using a specialize solvent.

Of many solvents which have been proposed for extraction of aromatics, sulfolane exhibits superior properties over other solvents. Results of research and development studies on its use for this purpose were first released publicly at the Fifth World Petroleum Congress in 1959. The first commercial applications began at the Shell refineries at Stanlow, England and Rho, Italy in 1962, and were described at the Sixth

World Petroleum Congress in 1963. These units demonstrated the practicality and excellent performance of sulfolane [25].

2.1.1. Sulfolane Properties

Sulfolane is an organosulfur compound, containing a sulfonyl group with a sulfur atom double-bonded to two oxygen atoms. The double bond is highly polar, but the carbon ring has high non- polar stability. Sulfolane is readily soluble in water due to the highly polar sulfur–oxygen double bonds. Shell Chemical found the solubility to be 1,266 g/L at 20°C (68°F). The physical and chemical properties of sulfolane is shown in Table 2.1 [18], [22]:

Table 2.1 Sulfolane physical and chemical properties

Property	Unit	Value
CAS registry number		126-33-0
Molecular formula		$C_4H_8SO_2$
Molecular weight	$g.mol^{-1}$	120.17
Melting point	°C	28.5
Boiling point	°C	287.3
Specific gravity		1.266
Flash point	°C	165-178
Vapor Density (air = 1)	$g.L^{-1}$	4.2
Vapor pressure		
150 °C	mmHg	14.6
200 °C	mmHg	86.2
287 °C	mmHg	760.0
Viscosity		
30 °C	Cp	10.3
100 °C	Cp	2.5
200 °C	Cp	0.97
Heat Capacity		
30 °C	J/(kg. °C)	1339.8
100 °C	J/(kg. °C)	1465.4
200 °C	J/(kg. °C)	1674.7

The relative solubility of various hydrocarbon in sulfolane is influenced by temperature, water content and the composition of the hydrocarbon in equilibrium with the solvent [25]. Consequently, relative solubility change from point to point in an extractor, as the composition of the hydrocarbon phase changes. At conditions that could exist at one point in an operating extractor, the solubility of various species, relative to benzene, are shown in figure. 2.2.

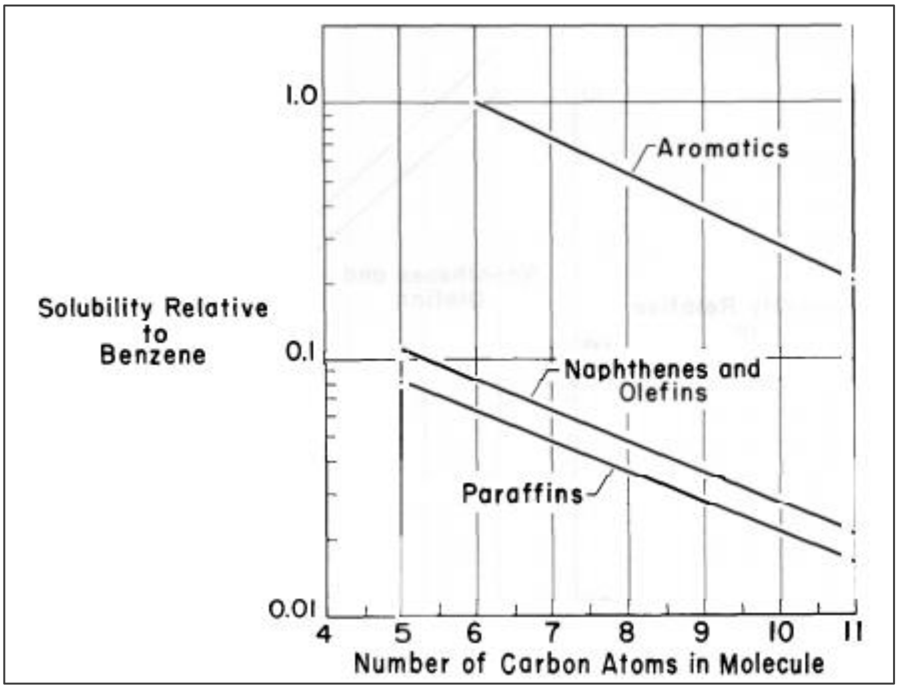

Figure 2.2 Relative solubility of different hydrocarbons in Sulfolane

2.1.2. Sulfolane Uses

2.1.2.1. Extractive Solvent

Sulfolane is used principally as a solvent for extraction of benzene, toluene, and xylene from mixtures containing aliphatic hydrocarbons. In general, the sulfolane extraction unit consists of four basic parts: extractor, extractive stripper, extract recovery column, and water–wash tower. The hydrocarbon feed is first contacted with sulfolane in the extractor, where the aromatics and some light non-aromatics dissolve in the sulfolane. The rich solvent then passes to the extractive stripper where the light non-aromatics are stripped. The bottom stream, which consists of sulfolane and aromatic components, and which at this point is essentially free of non-aromatics, enters the recovery column where the aromatics are removed. The sulfolane is returned to the extractor. The nonaromatic raffinate obtained initially from the extractor is contacted with water in the wash tower to remove dissolved sulfolane, which is subsequently recovered in the extract recovery column. Benzene and toluene recoveries in the the process are routinely greater than 99%, and xylene recoveries exceed 95%.

2.1.2.2. Extractive Distillation Solvent

Extractive distillation is a technique for separating components in narrow boiling range mixtures which are difficult to separate by ordinary fractionation. The process consists of allowing a higher boiling liquid that has a special affinity for one or more of the components in the mixture to flow downward in a distillation column countercurrent to the ascending vapors and thereby to enhance differences in volatility of components of the mixture. Sulfolane is a suitable extractive–distillation solvent for carrying out the separation of close boiling alcohols and chlorosilanes; mono- and