CHAPTER I
INTRODUCTION

1.1 An Overview of an Ethylene Plant

Ethylene is almost exclusively produced from ethane, propane, and heavier paraffins and from the virgin crude oil fractions naphtha, kerosene and gas oil. Plants to produce ethylene from light paraffins, particularly ethane and propane, are expected to be built in areas with abundant natural gas supply. The large-scale production of ethylene is carried out by pyrolysis (cracking) of hydrocarbon feedstocks in the presence of steam in large, multiple pyrolysis furnaces and the subsequent separation of the resultant gas mixture is carried out through a complex sequence of unit operations.

The simplest paraffin and the most widely used feedstock for producing ethylene is ethane. Cracking ethane can be visualized as a free radical dehydrogenation reaction where hydrogen is a coproduct.

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \qquad \text{..........................(1)}$$

Theory of the dehydrogenation reaction is simple but the process of producing ethylene is rather complicated. There are many steps in purifying and separating ethylene for use as a feedstock for polymerization purpose in the downstream industries. Accordingly the plant encounters problems that can reduce plant efficiency.

In an ethylene plant, the ethane feedstock is first contacted with amine to remove carbon dioxide. It is then saturated with water vapor before being sent to the cracking heater. In the cracking heater, ethane is cracked at high temperature and rapidly quenched by cooling water in the transfer line exchangers. From the quench tower, the cracked gas is compressed in a five-stage centrifugal compressor. Condensed water and hydrocarbon from the compression system are collected and sent to the bottom of quench tower. Acid gases are removed from the charge gas between the fourth and the fifth stages of compression. The compressed gas is then dried. The dried charge gas is sent to the benzene wash tower to remove heavy components which would freeze in the chilling train. The over head vapor from the benzene wash tower is chilled with propylene and ethylene refrigerant for separating certain gases such as H_2. Demethanizer separates methane from the cracked gas. The bottoms from the demethanizer go to the deethanizer which separates ethane, ethylene, and acetylene to the top. Acethylene is hydrogenated to ethylene by the acetylene converter. Finally ethane and ethylene are fractionated by ethylene fractionator. Ethane leaving the bottom of the ethylene fractionator is recycled and cracked to extinction. Figure 1.1 has shown the simplified olefin block flow diagram.

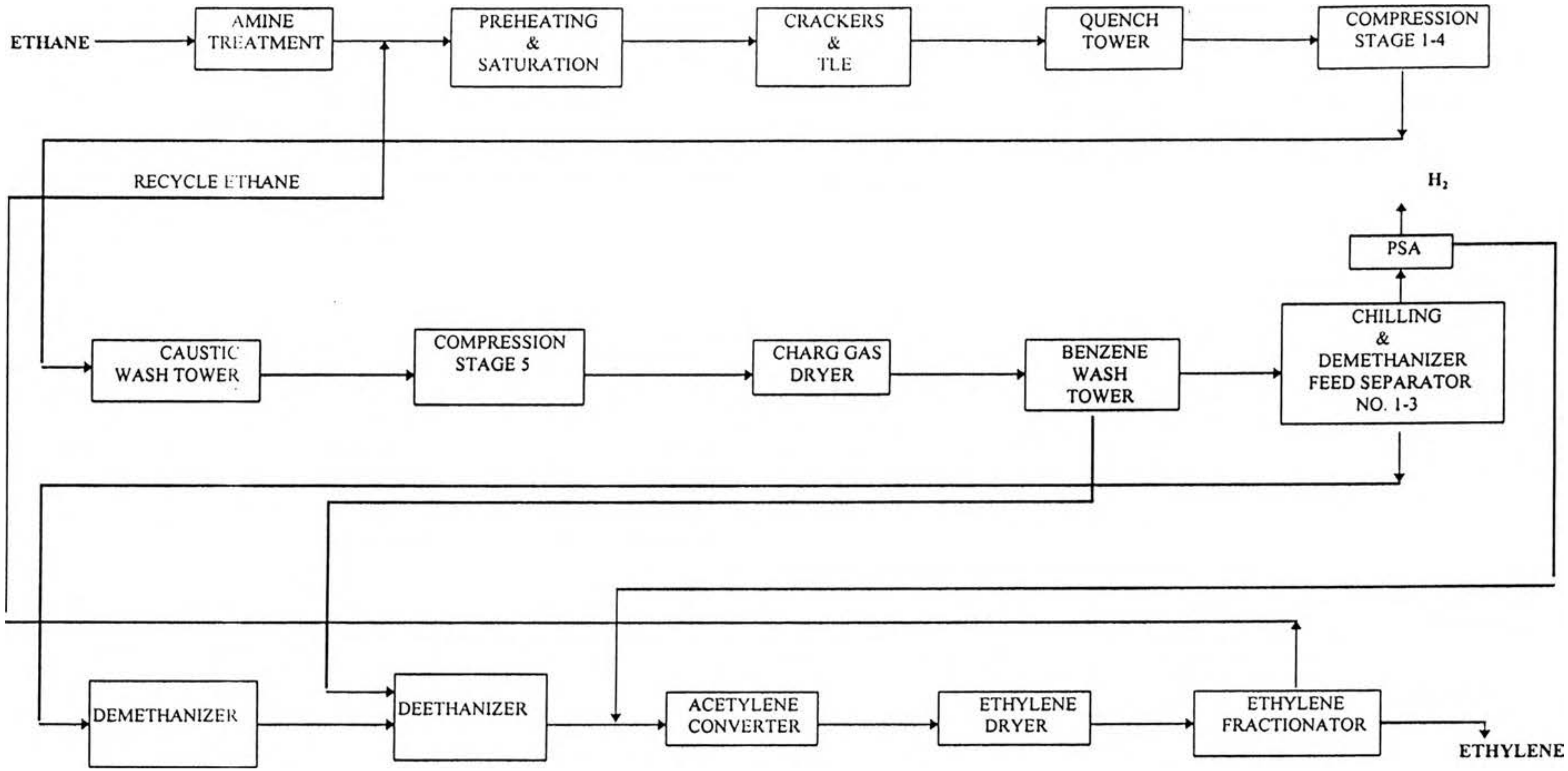

Figure 1.1 The simplified olefin block flow diagram.

In each operation unit, one of the serious problems that reduce ethylene plant efficiency is the fouling. Fouling can occur in many parts of an olefin plant. Process-side fouling reduces the overall operating efficiency of an olefin plant. The fouling is commonly caused by the formation of organic polymers which may can contain small amounts of inorganic constituents. The fouling is measurably reduced if a properly selected antifoulant is used.

1.2 Yellow Oil Formation in the Caustic Tower Operation

In the production of olefins, a caustic tower removes acid gases such as carbon dioxide and hydrogen sulfide from cracked gas. The operation basically washes the cracked gas with a counter current flow of caustic. This removes the acid gases by reactive absorption. The tower must decrease the level of acid gases to very low levels to meet ethylene product quality requirements.

The towers typically have a weak and a strong caustic strength section to provide complete removal of the acid gases. Also, a water wash section removes entrained caustic from the cracked gas. Circulating loops keep the caustic strength in each section relatively constant. The towers use either trays or packing for mass transfer. The towers is found between the fourth and the fifth stages of the cracked gas compressor system.

The formation of yellow oil in the caustic tower may result in a variety of operating problems. The yellow oil deposits onto tower internals. These deposits can lead to high pressure drop and a reduction of acid gas removal capabilities. This may reduce plant production rate and possibly require an unscheduled shutdown to clean the tower.

The material can also build up in the caustic recirculation lines. This may reduce the caustic recirculation rate to the tower. The lower recirculation rate may also result in lower acid gas removal.

This master thesis studies the case of an olefin plant which experienced fouling in its packed caustic tower where hydrogen sulfide and carbon dioxide are removed from the pyrolysis gas by scrubbing with caustic soda solution. The caustic tower is between the fourth and fifth stages of the compression system. The fouling product at caustic tower is called yellow oil.

Yellow oil is formed in the caustic tower. The operating temperature there is 50°C and the pressure is 20 bars. The effluent from the ethane cracker is sent to quench tower to knock out the water which is injected into the ethane cracker and after that, it is sent to the compressor to build up the pressure before being sent to the caustic tower.

Yellow oil is the oil accumulating on the top of spent caustic. Normally the operators will skim this oil out to prevent it from flowing with the spent caustic. Spent caustic will be sent to spent caustic storage tank and pumped to the spent caustic oxidation. If yellow oil flows with spent caustic to spent caustic storage tank, it will form a polymer which will deposit at the bottom of storage tank. This polymer will clog up the pumps.

Attempts have been made to solve the problem by heating the solution in the caustic storage tank but the polymerization becomes more serious. Another method was by skimming the yellow oil at caustic tower and reducing the temperature at the caustic storage tank. Finally, nitrogen sealing has been introduced to the caustic storage tank.

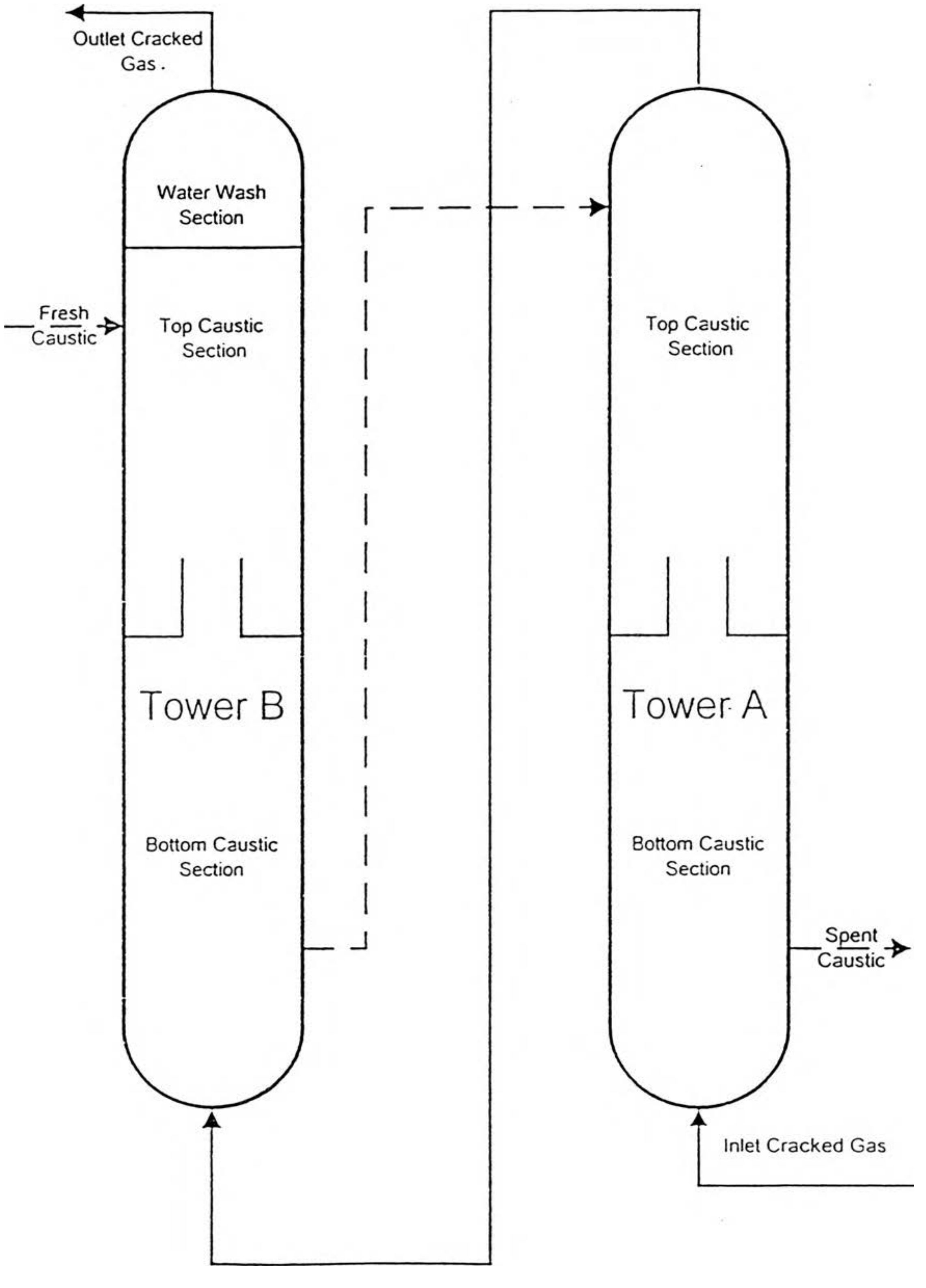

Figure 1.2 Flow diagram of caustic scrubber system.

1.3 Carbonyl Fouling Mechanisms

In 1996 Eighth Annual Ethylene Producers Conference AIChE spring national meeting, the formation of the fouling at acid gas removal unit was discussed. The producers have consensus that fouling or yellow oil is a carbonyl polymer. The carbonyl polymer forms in ethylene plant caustic towers is due to the presence of acetaldehyde and other aldehydes in cracked gas. Aldehydes form in the cracking furnaces and remain with the cracked gas until it reaches the caustic tower. The caustic tower scrubs the aldehydes from the cracked gas stream. The amount removed depends on operating temperature, pressure, number of caustic recirculation stages, caustic recirculation rate and the type of tower internals. The tower removes between 50 and 95% of the acetaldehyde from the cracked gas. Fouling increases with higher aldehyde concentration in recirculating caustic and with higher temperature.

Aldehyde in the presence of caustic undergoes a classic condensation reaction. This is an addition polymerization reaction as shown in the simplified reaction below:

$$2\,(\mathrm{R\text{-}CH_2\text{-}}\overset{\overset{\displaystyle \mathrm{O}}{||}}{\mathrm{C}}\mathrm{\text{-}H}) \xrightarrow[\text{Base}]{\mathrm{OH^-}} \mathrm{R\text{-}CH_2\text{-}}\overset{\overset{\displaystyle \mathrm{OH}}{|}}{\mathrm{C}}\mathrm{\text{-}CH\text{-}}\overset{\overset{\displaystyle \mathrm{O}}{||}}{\mathrm{C}}\mathrm{\text{-}H} \qquad \text{...........(2)}$$

Carbonyl Base **Precursor**

$\downarrow$

POLYMER

Figure 1.3 The aldol condensation reaction of carbonyl compound.

The reaction is an equilibrium process. This is because sodium hydroxide is not strong enough to completely deprotonate acetaldehyde. Therefore, both an anion and a neutral molecule exist in the solution. The anion attacks the neutral aldehyde which leads to polymerization through multiple aldol condensation reactions. Caustic towers generally have a large caustic recirculation flow and a relatively low blowdown rate. This allows a long residence time for the polymerization to occur. A series of color changes occurs as the reaction progresses. The low molecular weight aldol creates a light yellow color. The color changes to orange and then to red as the polymer reaction and molecular weight grow. A deep red liquid is produced, from which the term red oil is derived. Finally, the reaction forms a reddish sludge in the recirculation caustic loop.

1.4 Literature Reviews

Lummus Global Inc.(1996) has reported that the general consensus on the cause of the yellow oil formation is that it is a result of carbonyl compounds (aldehydes and ketones) which are formed in the cracking heater. The source of the problem is the presence of oxygen. Often the source of oxygen is the caustic storage tank. The caustic storage tank should have a nitrogen blanket and use an oxygen free water for dilution.

Texas Eastman also has had considerable fouling problem in their caustic tower, although they produce a “red oil” and not a yellow oil. However, they use lake water as a diluent for caustic with no nitrogen purge.

Nalco Chemical Co., Texas has described the fouling at acid gas removal system. At some point in the compression system, a caustic tower and a monoethanolamine (MEA) tower are used to scrub carbon dioxide, hydrogen sulfide and other acid gases to prevent the contamination of the ethylene. With MEA scrubbing systems, corrosion and fouling are caused by degradation of the amine, oxygen contamination and buildup of corrosion products and salts formed during the reaction.

J.F.Martin, Betz Process Chemicals, Inc.(1988) explained that organic fouling of acid gas removal systems can be caused by two mechanisms. Condensed or dissolved dienes and other unsaturated hydrocarbons in the rich amine can polymerize. He presented the remedy that water based antifoulants may help increase run length. The free radical polymers that deposit in alkanolamine systems are treated with proprietary water soluble antioxidants, chain-stoppers and oxygen scavengers. Another mechanism which causes fouling is the aldol-condensation reactions. If aldehydes and/or ketone organics are present in the cracked gas, these will tend to condense into the recirculating caustic. In the presence of dilute caustic, aldehyde and ketones undergo dimerization reactions where the molecular weight is continually increased. The rate of polymer forming reaction increases as temperature increases. At a certain point the reaction products become insoluble in the recirculating caustic and deposits form on tower trays. These deposits have an orange-brown color and physically look like free radical generated polymer. However, peroxides do not catalyze these reactions. Carbonyl fouling can be reduced by using certain proprietary chemicals that interfere with these polymerization reactions.

1.5 Objectives

The objectives of this thesis works are :

1. To study the mechanism of yellow oil formation and identify the chemical structure of the yellow oil.

2. To carry out some experiments to find ways to prevent the formation of yellow oil.