CHAPTER I

INTRODUCTION

1.1 Cracking process

Ethylene is almost exclusively produced from ethane, propane and heavier paraffins from crude oil (naphtha and gas oil). Generally plants produced ethylene from light paraffins, particularly ethane and propane, are expected to be built in areas with abundant natural gas supply. The light feed material is produced as a gaseous product mixture and fed to pyrolytic crackers. The cracked product stream also contains quantities of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide and other pyrolytic side reaction products besides the olefins.

In an ethylene plant, the ethane feed stock is first reacted 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 is then rapidly quenched by various streams and cooling water in the transfer line exchanger and quench tower. From the quench tower, the cracked gas is compressed in a five stage centrifugal compressor. Acid gases are removed from the charge gas between the fourth and 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 hydrogen. 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. Acetylene 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. 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 olefins plant. Process side fouling reduces the overall operation efficiency of an olefins plant. The fouling is commonly caused by the formation of organic polymers which is in some location may contain small amount of inorganic constituents. The fouling can be measurably reduced if properly selected antifoulant is used.

1.2 Pyrolysis of gases

The pyrolysis of essentially pure components or simple mixtures hydrocarbons is of commercial interest particularly for the light paraffins (ethane, propane, and butanes). Simple characterizations of feedstocks and of product compositions were logical starting point for pyrolysis modeling. Hence many models at different sophistication level have been proposed for ethane, propane, butane, and more recently their mixtures. Some of these are in reasonable agreement with the experimental data as already mentioned. Difficulties have been experienced in the modeling of gas mixtures co-cracking, particularly involving ethane, versus the pure-additivity rule; contradictory interpretations of the experimental results sometimes occur.

Similar problems are also noted for pyrolysis of "pure" gases, when considering the prediction problem of the formation and interactions of minor products. Actually, in the range of high severity decomposition, the description of a "pure component" pyrolysis becomes almost equivalent to decomposition and interactions of a complex mixture.

Gas composition of cracked gas effluent or caustic tower feed comprise many components as shown in Table 1.1. For plants which produce 400-600 klb/hr of cracked gas, the average mol. wt. is typically with 20-24, CO_2 concentration of 100-300 mol. ppm., H_2S concentration 600-1100 mol. ppm. and acetaldehyde concentration 10-100 mol. ppm.[1]

Table 1.1: Gas composition in cracked gas [1]

Components	Caustic tower feed (Kgmol/H)
Hydrogen	1759.69
Carbon monoxide	5.65
Carbon dioxide	1.82
Hydrogen sulfide	0.30
Methane	607.27
Acetylene	18.45
Ethylene	1710.16
Ethane	829.88
MAPD (C_3H_4's)	4.17
Propylene	81.23
Propane	21.27
Butadienes	39.82
Butenes	12.59
Butanes	6.75
C5 hydrocarbons	8.75
C6 hydrocarbons	6.88
Benzene	19.28
Toluene	2.75
Xylene / ethylbenzene	0.34
Styrene	0.65
C9 hydrocarbon-204°C	1.86
204 °C plus	0.10
Steam / water	23.15

1.3 Yellow oil problem

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 solution. 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 tower typically has a weak and a strong caustic strength sections. In addition, water wash section is used to remove entrained caustic from the treated cracked gas. Circulation loops keep the caustic strength in each section relatively constant. The tower uses either trays or packing for mass transfer. The tower is typically found in the higher-pressure section of the cracked gas compressor system.

The formation of yellow or red oil in the caustic tower may result in a variety of operating problems. The red oil deposits occur 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 which will result in the lower efficiency of acid gas removal.

A high level of yellow or red oil in the recirculating caustic solution promotes foaming in the caustic tower. This increases the pH of the water wash section and effects the treatment of the water wash stream. Severe foaming causes the carryover of caustic laden wash water into the cracked gas compressor. Caustic corrosion and salt fouling of the compressor may result. Foaming may also result in incomplete removal of acid gas and increased caustic makeup requirements.[2,3]

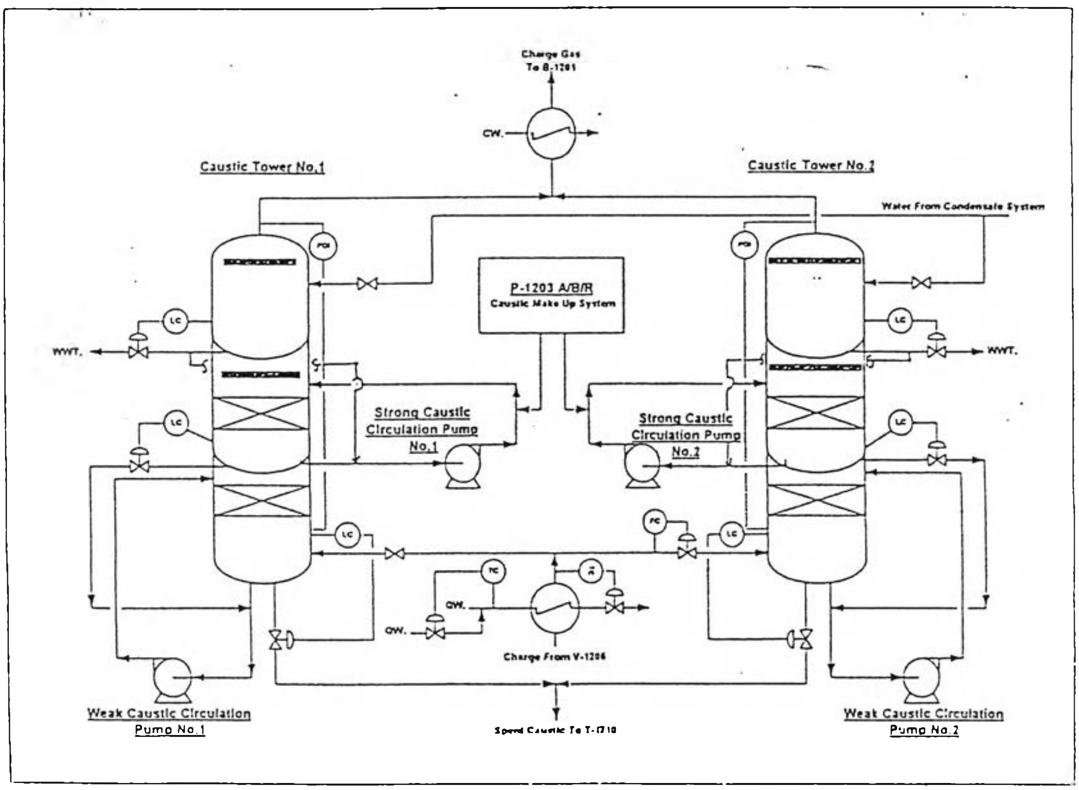

Figure 1.1: Caustic tower diagram

1.4 The Objectives of the Research

The objectives of this thesis are:

1.4.1 To study the effect of various factors on yellow oil formation

- effect of oxygen
- effect of temperature
- effect of iron solution
- amount of acetadehyde and caustic soda

1.4.2 To study the effectiveness of inhibitor to yellow oil formation

- hydrazine solution
- hydroxylamine hydrochloride

1.5 Scope of Research

This research will focus on the effect to yellow oil formation by oxygen, temperature, iron solution, and inhibitors using acetadehyde as precursor in the experiments and compare the results. In the experiment, the occurred solids and solution were studied by comparison to reference (blank solution) using UV-visible Spectrophotometer for measurment of α, β unsaturated aldehyde (λ 293 nm show absorption of carbonyl group). The effect of amount of acetaldehyde and caustic soda also forms part of the study. In addition the effectiveness of inhibitors, hydrazine and hydroxylamine hydrochloride, will be investigated.