

CHAPTER II

LITERATURE SURVEY

In this chapter, background on the fouling formation will be provided. Then, a number of proposed mechanisms of the formation will be discussed. After having some ideas on the fouling formation, the chemical treatment technique used in the industry to reduce or inhibit the fouling will follow.

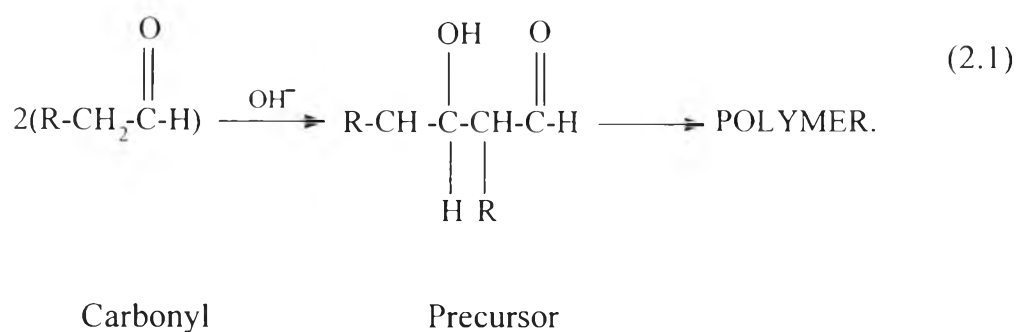
2.1 Fouling Mechanism

While the precise mechanism of fouling processes in the caustic tower is not known with certainty, typically two mechanisms have been identified that are responsible for the foulant formed in the caustic units. According to Martin (1998), the two mechanisms are the free-radical polymerization of dienes initiated by heat and metal and the aldol condensation of carbonyl compounds in the presence of caustic. Unsaturated components in the cracked gas, particularly dienes and higher acetylenes, react to form polymeric compounds in the scrubber solution by means of the free-radical mechanism. On the other hand carbonyl compounds, which are formed in the cracking process, are condensed into the caustic system and undergo the aldol condensation polymerization. The basic environments provided by the caustic system, heat and residence time catalyze and promote the reaction.

Of the two mechanisms described above, it appears that the aldol condensation is the predominant reaction in ethane cracker plant due to the relatively small quantity of dienes produced from the cracking reaction of ethane. For the benefit of ethane cracker operators, this study is, therefore, directed toward the aldol condensation only.

2.2 Carbonyl Fouling Mechanism

Typical set up of caustic tower in ethylene plants cracking ethane is shown in Figure 2.1. Based on the carbonyl fouling mechanism, the fouling deposits accumulated in the caustic tower, are results of the aldol condensation reaction.



Carbonyl compounds such as acetaldehyde and other aldehydes, formed in the cracking furnaces, remain with the cracked gas until it reaches the caustic tower. Inside the caustic tower, the aldehydes are condensed into the caustic system and the aldol reaction starts. The amount of the aldehydes removed from the cracked gas stream by means of this mechanism depends on operating temperature, pressure, number of caustic recirculation stages, caustic recirculation rate, and type of tower internals. The tower removes between 50 and 95% of the acetaldehyde from the cracked gas. The presence of the dilute caustic solution that serves as a catalyst for the reaction is suitable for promoting the aldol condensation. The aldols formed are essentially insoluble in the caustic solution, therefore deposit upon the internal surfaces of the caustic tower.

In the presence of the dilute caustic solution, aldehyde undergoes dimerization reactions, which result in increasing its molecular weight. The polymerization rate increases as temperature rises. At a certain point, the

reaction products become insoluble in the recirculating caustic, and deposit on the tower trays. These deposits have an orange-brown color and physically look like free radical generated polymer. Martin (1988) also showed that using certain proprietary chemicals that interfered the polymerization reaction could reduce the carbonyl fouling.

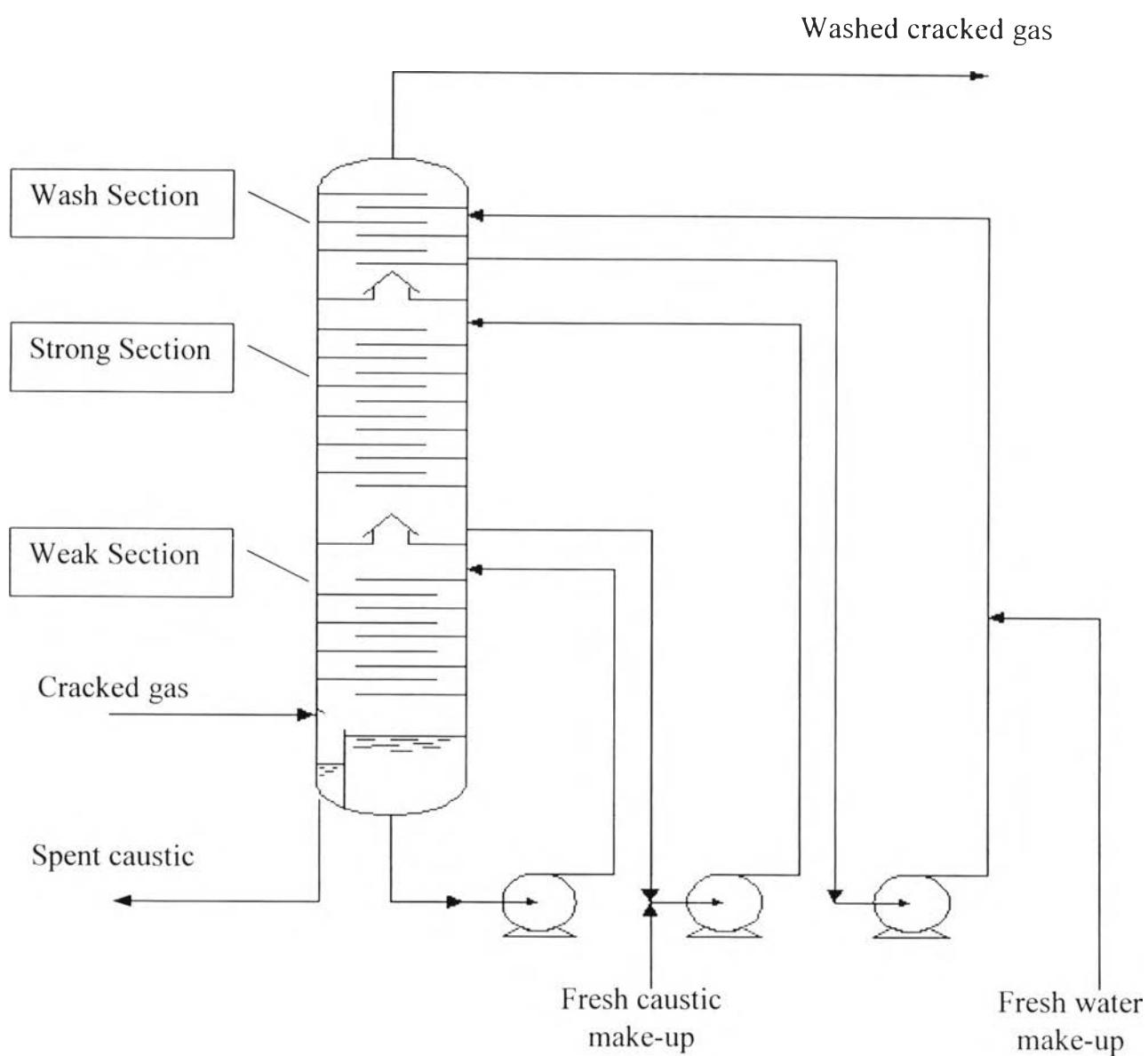
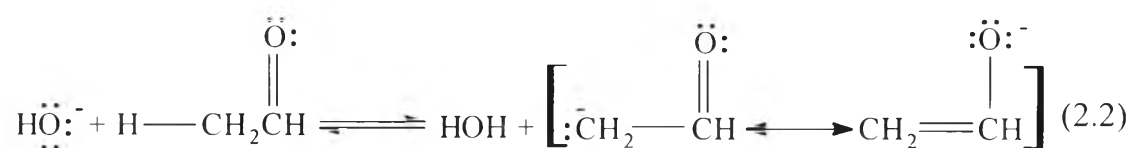


Figure 2.1 Caustic tower.

A more specific mechanism to the aldol condensation of acetaldehyde was proposed by Graham (1990). The mechanism includes four steps.

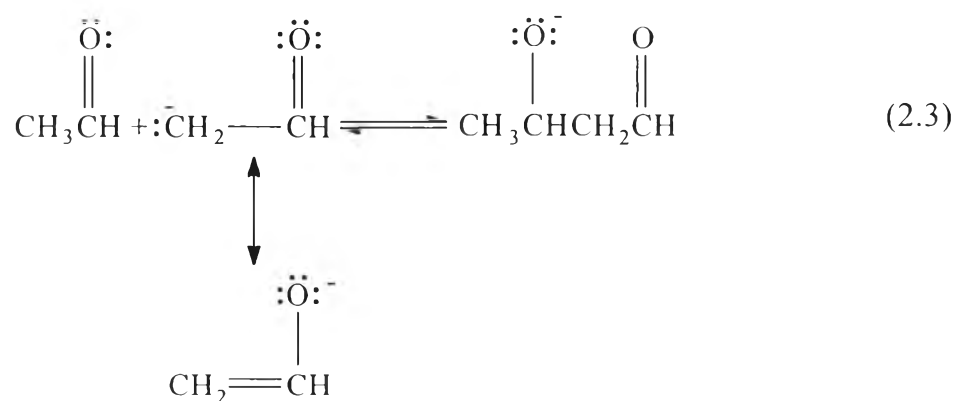
Step 1

The base (hydroxide ion) abstracts a proton from the α -carbon of one molecule of acetaldehyde to give a resonance-stabilized enolate ion.



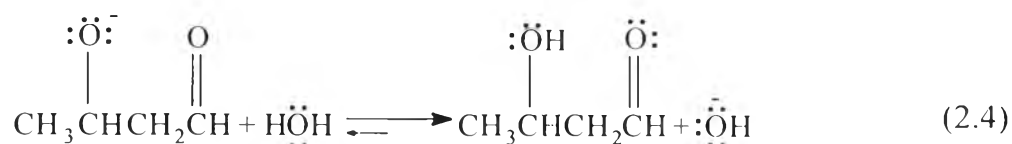
Step 2

The enolate ion acts as a nucleophile – as a carbanion – and attacks the carbonyl carbon atom of a second molecule of acetaldehyde. This step gives an alkoxide ion.



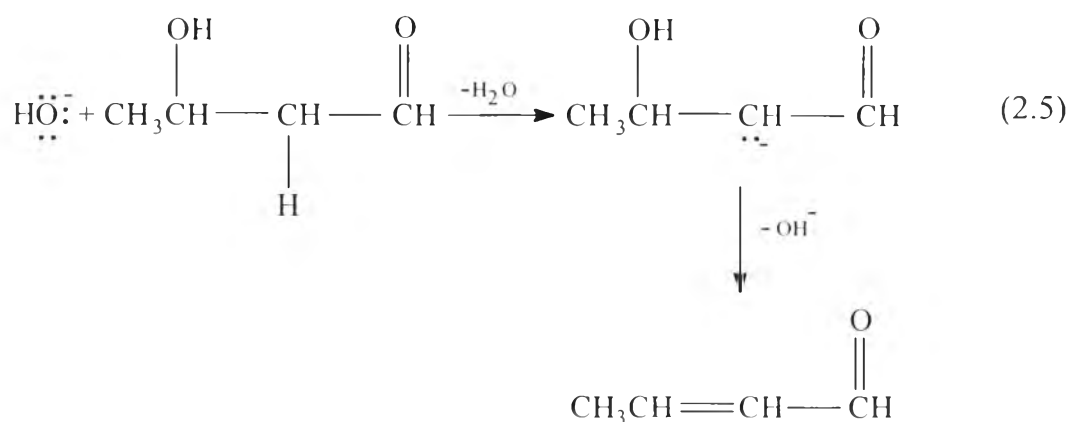
Step 3

The alkoxide ion abstracts a proton from water to form aldol. This step takes place because the alkoxide ion is a stronger base than a hydroxide ion.



Step 4

The dehydration of addition product from step 3



Precursor for polymerization

2.3 Reduction of the Fouling in a Caustic Tower

Hydroxylamine and its hydrochloride and sulfate salts have been used to inhibit the polymer formation caused by the condensation of aldehydes contained in caustic scrubber units (Roling, 1987). Similarly, hydrazide compounds can inhibit the formation and deposition of the polymer-based fouling materials after the caustic scrubbing of hydrocarbon streams (Lewis, 1994). Despite the tremendous success of such treatments, the hydroxylamine

and hydrazide compounds are expensive and must be overfed to the caustic scrubber units.

Ethylenediamines and water soluble salt forms thereof have been used to inhibit the carbonyl based fouling, particularly aldehyde fouling, that often occurs during the caustic scrubbing of liquid or gas phase hydrocarbon streams (Awbrey, 1990). Amino-containing aryl compounds have been applied as inhibitors for the formation and deposition of the fouling materials during the caustic washing of hydrocarbon gases (Dunbar, 1993). However, not all amine-containing aryl compounds are effective for this purpose. Moreover, some of them are not even soluble under the caustic washing conditions.

Acetoacetate ester has been used to inhibit the polymer based fouling in basic ($\text{pH} > 7$) wash systems of the type adapted to remove impurities from liquid or gas phase hydrocarbon mediums (Roling, 1993). Additionally, a solution of a percarbonate of a Group I or Group II metal has been used to inhibit the formation and deposition of the fouling materials during the basic washing of hydrocarbons contaminated with oxygenated compounds (McDaniel, 1993).

An aromatic amine selected from the group consisting of 2-aminophenol, 4-aminophenol, 4-aminobenzenesulfonic acid and salts thereof, 4-amino-o-cresol, 3-aminophenol, 2-aminobenzoic acid and salts thereof, 3-aminobenzoic acid and salts thereof, and 4-aminobenzoic acid and salts thereof to the caustic solution can reduce the fouling in the caustic tower. A preferred substituted aromatic amine has been the sodium salt of 4-aminobenzenesulfonic acid in aqueous solution (Lewis, 1998a).

Non-enolizable carbonyl compounds have been useful for the inhibition of the oxygenated hydrocarbon fouling in the caustic scrubber. Preferred non-enolizable carbonyl compounds have been formaldehyde,

glyoxal, benzaldehyde, p-anisaldehyde, formic acid, glyoxalic acid and paraformaldehyde (Lewis, 1998b).