

## CHAPTER II

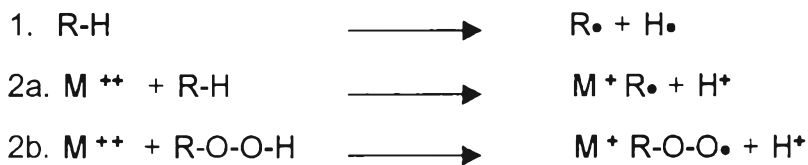
### THEORY AND LITERATURE REVIEW

#### 2.1 Mechanisms of carbonyl formation

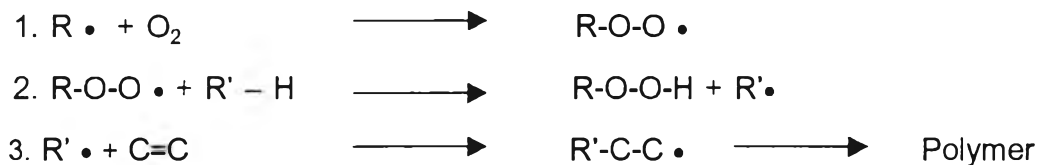
The mechanism involves the condensation of carbonyl compounds in the presence of caustic solution. The carbonyl compounds are formed in the cracking process and like the dienes are condensed into the caustic system. The caustic system provides the basic environment, heat and residence time needed to catalyze and promote aldol condensation polymerization.

Free radical polymerization occurs in three steps:

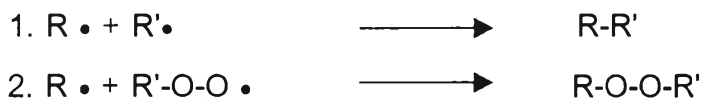
##### A.Chain initiation



##### B.Chain Propagation



##### C.Chain Termination



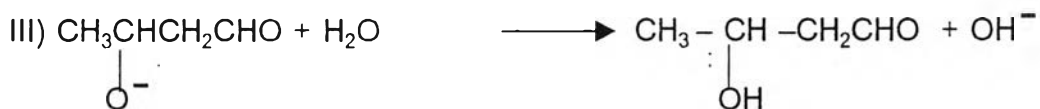
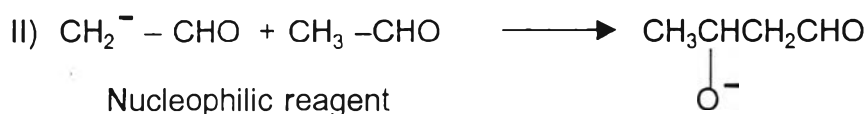
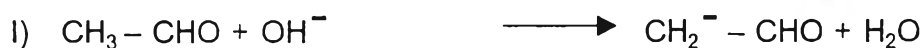
Where  $\text{R}\cdot$  = reactive polymer, monomer

M = metal

Free radical polymerization can be catalyzed by oxygen, peroxides <sup>4</sup>

## 2.2 Mechanisms of aldol condensation

Under the influence of dilute base or dilute acid, two molecules of an aldehyde or a ketone may combine to form a  $\beta$ -hydroxy aldehyde or  $\beta$ -hydroxy ketone. This reaction is called the aldol condensation. In every case the product results from addition of one molecule of aldehyde (or ketone) to a second molecule in such a way that the  $\alpha$ -carbon of the first becomes attached to the carbonyl carbon of the second.

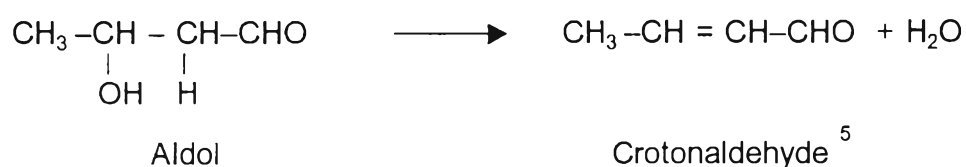


The generally accepted mechanism for the base-catalyzed condensation involves the following steps, acetaldehyde being used as an example. Hydroxide ion abstracts (step I) a hydrogen ion from the  $\alpha$ -carbon of the aldehyde to form carbanion, which attacks (step II) carbonyl carbon to form ion. Ion (an alkoxide) abstracts (step III) a hydrogen ion from water to form the  $\beta$ -hydroxy-aldehyde, regenerating hydroxide ion. The purpose of

hydroxide ion is thus to produce the carbanion, which is the actual nucleophilic reagent.

#### Dehydration of aldol products

The  $\beta$ -hydroxy aldehydes and  $\beta$ -hydroxy ketones obtained from aldol condensations are very easily dehydrated; the major products have the carbon-carbon double bond between the  $\alpha$ -carbon and  $\beta$ -carbon atoms.



### 2.3 Reaction of carbonyl compound with hydroxide

Yellow or red oil is a polymer containing carbonyl group. The carbonyl polymer forms in ethylene plant caustic tower due to the presence of acetaldehyde and other aldehydes in cracked gas. Aldehydes are formed in the cracking furnaces and remain in the cracked gas until they reach the caustic tower. The caustic tower scrubs the aldehydes from the cracked gas stream. The amount removed depends on operating temperature, pressure, and number of caustic recirculation stages, caustic recirculation rate and the type of tower internals. The tower can remove about 50 to 95 % of the aldehydes 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 aldol condensation reaction. This is an addition polymerization reaction as shown in the simplified reaction below:

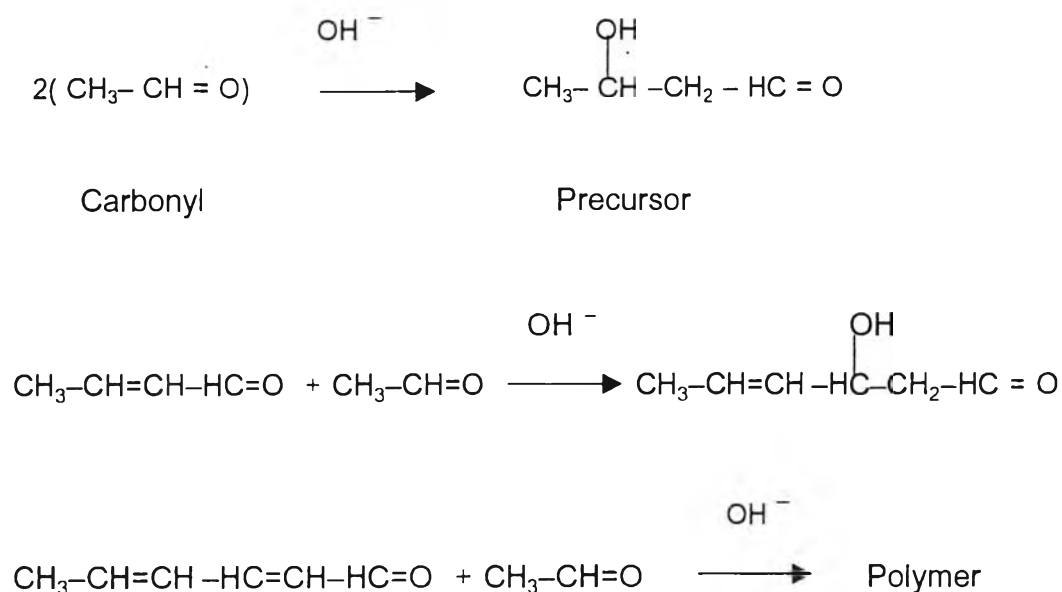


Figure 2.1: Aldol condensation reaction

This reaction is an equilibrium process. This is because the hydroxide solution 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 reaction. Caustic towers generally have a large caustic recirculation flow and 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 recirculating caustic loop.<sup>2,6</sup>

## 2.4 Literature Reviews

Texas Eastman Co., reported considerable fouling problems in their caustic tower, although it was red oil, not yellow oil. However, they had used lake water as a diluent for caustic with no nitrogen purge. They do not draw off the yellow oil from the caustic tower and put it in drums.

The cracked gas stream has been exposed to heat, metals and trace levels of oxygen. All these conditions are known to catalyze polymerization and oxidation of olefinic species. Oxidation of olefins will result in the formation of ketones, aldehydes and other carboxylic acids. In the presence of basic conditions (i.e., in the caustic tower), these products will undergo aldol condensation reaction and result in fouling deposits on the trays of the caustic tower.<sup>7</sup>

Nalco Chemical Co., described the fouling at acid gas removal system. At some point in the compression system, a caustic tower and a monoethanolamine (MEA) tower were used to scrub carbon dioxide, hydrogen sulfide and other acid gases to prevent the contamination in the ethylene stream. With MEA scrubbing systems, corrosion and fouling caused by degradation of the amine, oxygen contamination and buildup of corrosion products and salts formed during the reaction.<sup>3</sup>

J.F.Martin, Betz Process Chemicals, Inc. (1988) explained that organic fouling of acid gas removal systems could be caused by two mechanisms. Condensed or dissolved dienes and other higher acetylene can polymerize to form polymeric compounds by means of the free-radical mechanism. On the

other hand carbonyl compounds which were formed in the cracking process can undergo the aldol condensation polymerization. He presented the remedy that water base antifoulants may help increase run length. Certain proprietary chemicals that interfered with the polymerization reactions could reduce the carbonyl fouling. If aldehydes and/or ketones are present in the cracked gas, these will tend to condense into the recirculating caustic solution. In the presence of dilute caustic, aldehyde and ketones undergo dimerization reaction 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 deposit 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 chemical to interfere with these polymerization reactions.<sup>5</sup>

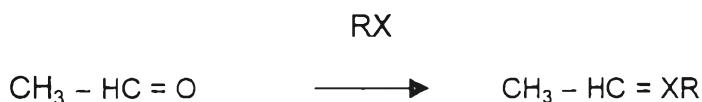
Chemlink international explained that small quantities of reactive species other than the olefins themselves, specifically carbonyl compounds, can polymerize rapidly in the presence of basic catalysts such as caustic or amines. This reaction is called aldol condensation and the products are polyaldehydes. Due to the large concentration of olefins and dienes, free radical polymerization is also possible. In untreated systems polymers can quickly build up in the scrubber towers causing poor unit performance and in some severe cases, plugged tower trays and associated piping.

Another common problem is the build up of viscous oligomers. These low to medium molecular weight polymers are insoluble in the caustic and form a hydrocarbon layer in the tower. This layer can trap solids such as iron

sulfide and organic polymers forming a rag layer and leading to foaming in the tower. If foaming is severe, tower efficiencies are reduced and liquids can be carried over into the compressor train.<sup>8</sup>

Weismiller Michael described that the fundamental solution to prevent fouling is to reduce or eliminate polymer formation caused by aldol condensation. Nalco/Exxon has a patented inhibitor that reacts with aldehydes, and prevents them from participating in the aldol condensation reaction.

To inhibit polymer growth under these condition, the carbonyl group of acetaldehyde must be changed. This is the function of an inhibitor, such as Nalco/Exxons inhibitor.



The above equations show how the inhibitor deactivates both acetaldehyde and crotonaldehyde (acetaldehyde dimer) towards polymerization. The "X" represents the active portion of the inhibitor. It reacts with the carbonyl group and effectively replaces the oxygen. (This displaced oxygen becomes part of a water molecule, which is the by product of this reaction.) The inhibitor has, in essence, scavenged the carbonyl group. Once the carbonyl group of the reactive aldehyde has been replaced, the molecule is no longer susceptible to attack by caustic, and it can no longer participate in the polymerization process.<sup>9</sup>

The formation of the fouling at acid gas removal unit was discussed. The fouling at caustic scrubber is a carbonyl polymer, which forms in the caustic tower due to the presence of aldehyde and ketone. Aldehyde and ketone formed in the cracking furnaces and remain with the cracked gas unit it reaches the caustic tower. The caustic tower scrubs the aldehyde and ketone from the cracked gas stream. The fouling increases with higher aldehyde concentration in recirculating caustic and with higher temperature.<sup>10</sup>

Paul V. Roling, described that hydroxylamine and its hydrochloride and hydrogen sulfate salts have been used to inhibit polymer formation caused by condensation reaction of aldehydes contained in caustic scrubber units. However, despite the tremendous success of such treatments, these compounds are expensive and must be overfed to the caustic scrubber units in light of their apparent selectivity toward the ketone contaminant.<sup>11</sup>

Spencer S. Awbrey, described that ethylenediamines and water soluble salt formed thereof have been used to inhibit carbonyl based fouling, particularly aldehyde fouling, that often occurs during caustic scrubbing of liquid or gas phase hydrocarbon streams.<sup>12</sup>

Vincent E. Lewis, described that carbohydrazide has been disclosed as useful for inhibiting polymeric fouling deposits during the caustic scrubbing of pyrolytical-produced hydrocarbons contaminated with oxygen containing compounds.<sup>13</sup>



Paul V. Roling, described that acetoacetate ester are used to inhibit polymer based fouling in basic (pH >7) wash systems of the type adapted to remove impurities form liquid or gas phase hydrocarbon mediums.<sup>14</sup>

Cato R. McDaniel, described that a solution of a percarbonate of a group I or group II metal is used to inhibit the formation and deposition of fouling materials during the basic washing of hydrocarbons contaminated with oxygenated compounds.<sup>15</sup>

Vincent E. Lewis, described that hydrazide compound has been disclosed as useful for inhibiting polymeric fouling deposits during the caustic scrubbing of pyrolytically-produced hydrocarbons contaminated with oxygen-containing compounds.<sup>16</sup>

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, has been studies. A preferred substituted aromatic amine is the sodium salt of 4-aminobenzenesulfonic acid in aqueous solution.<sup>17</sup>

Non-enolizable carbonyl compounds have utility for the inhibition of oxygenated hydrocarbon fouling in the caustic scrubber. Preferred non-enolizable carbonyl compounds are formaldehyde, glyoxal, benzaldehyde, p-anisaldehyde, formic acid, glyoxalic acid and paraformaldehyde.<sup>18</sup>