

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Aldol condensation reaction (yellow oil formation)

##### 4.1.1 effect of oxygen

In olefins plant, yellow oil occurred in caustic tower have many factors that may be problem. Oxygen is believed to enter the tower through the caustic make-up stream. This experiment shows that both condition has no effect to aldol condensation reaction of acetaldehyde at 25°C and 50°C. The final solutions turned yellow and turbid. At purge air condition with 21 % mol oxygen the results were exactly the same as those with purge nitrogen condition where no oxygen was present for the entire periods of reaction time. However at 50°C, significant amount of aldol products were formed even with the purge nitrogen condition. The temperature of 25°C and 50°C for the experiment was based on the fact that caustic tower in ethylene plant was operated at similar temperature (50°C). Some ethylene plant had used lake water as a diluent for caustic solution with no nitrogen purge and experienced severe yellow oil formation in caustic tower.

**Table 4.1: Result of oxygen effect**

Reaction time (min.)	Observation			
	Temperature 25°C		Temperature 50°C	
	with air	with nitrogen	with air	with nitrogen
30	clear solution	clear solution	little turbidity ,yellow	little turbidity ,yellow
60	clear solution	clear solution	turbidity yellow to orange	turbidity yellow to orange
90	clear solution	clear solution	orange	orange
120	clear solution	clear solution	orange	orange
150	light yellow	light yellow	orange	orange
180	light yellow	light yellow	orange	orange
210	light yellow	light yellow	orange	orange
240	light yellow	light yellow	orange	orange
270	light yellow	light yellow	orange	orange
300	light yellow	light yellow	orange	orange

#### **4.1.2 Effect of temperature**

Aliphatic aldehydes will usually undergo self-condensation under base catalysis called aldol condensation reaction. This experiment was used to study the temperature effect of the reaction. Solid products were weighed by analytical balance. Amount of polymer solids increased with temperature. Temperature thus has direct effect to the reaction because temperature increases reaction rate.

For caustic tower in ethylene plant, temperature of operation can influence the aldol condensation reaction. The temperature has a direct impact on the rate of polymer formation. In addition, the amount of solids that occurred can be used as indicator for the degree of fouling formation in caustic tower.

**Table 4.2: Amount of solid on temperature effect**

Temperature °C	Amount of solid (mg / 100 ml solution)
25	0.43
50	5.92
80	10.52

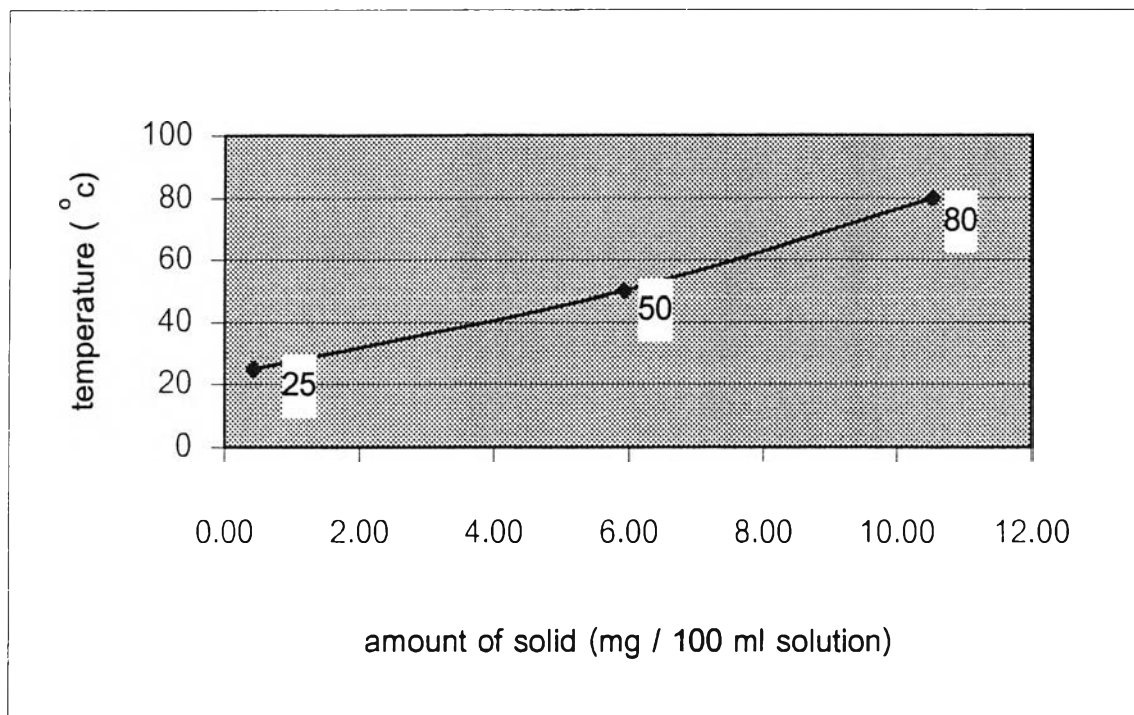


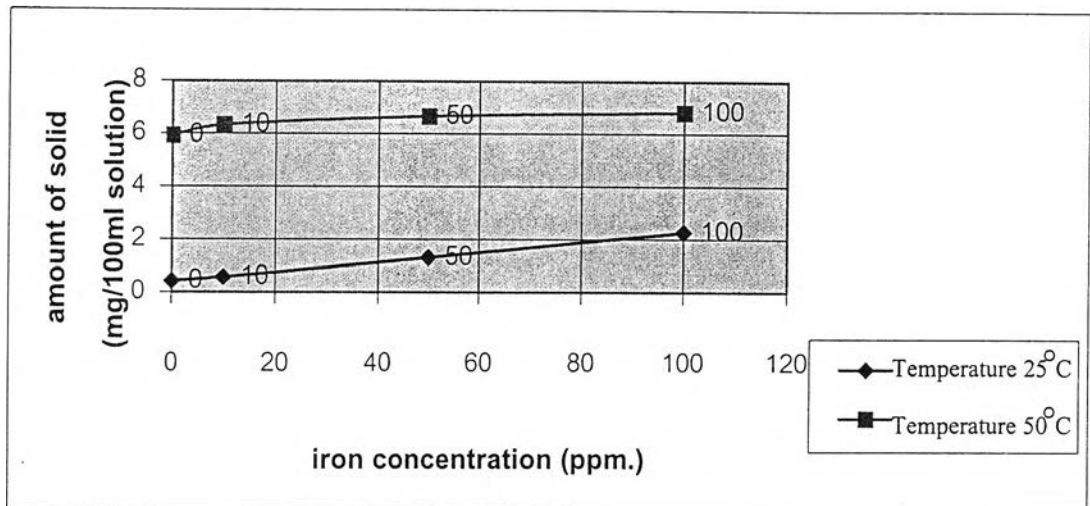
Figure 4.1: The temperature effect on solid formation

### 4.1.3 Effect of iron solution

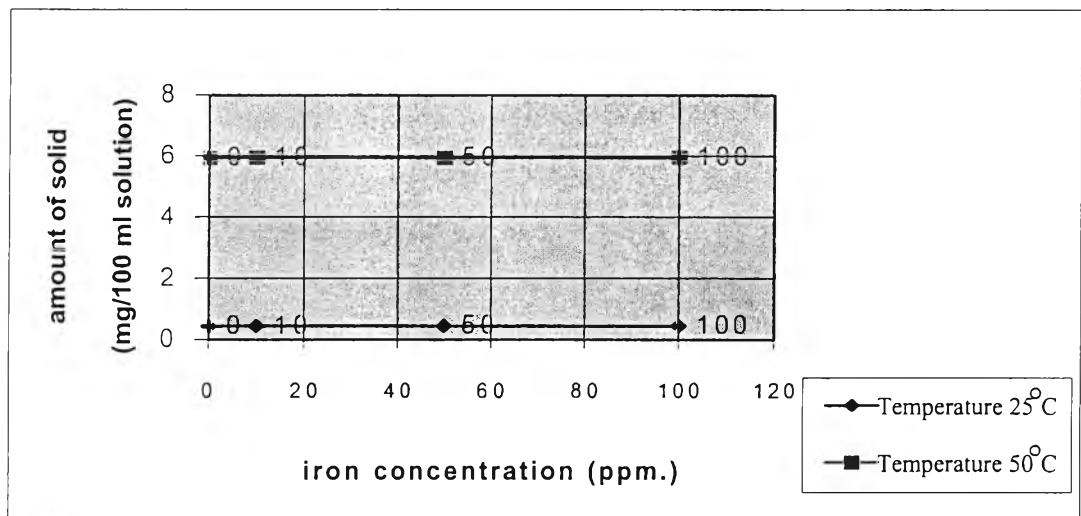
Iron solution ( $\text{Fe}^{+3}$ ) reacted with caustic soda to form iron hydroxide (ferric hydroxide) which precipitated. Result of amount of solid that was washed with acid was less than amount of solid that was not washed with acid. Iron solution cannot react with acetaldehyde and cannot catalyze aldol condensation reaction. Solid polymer product was not increased with iron solution. From this experiment, the increased solid was iron hydroxide. Because the increased solid can dissolve in hydrochloric acid solution but the solid polymer can not. Comparing results at same concentration of acetaldehyde but at different temperature, it was found that amount of solid increases with temperature.

**Table 4.3: Iron solution effect at 25°C and 50°C**

Concentration of iron (ppm.)	mg solid / 100 ml solution			
	at 25°C		at 50°C	
	no washing	washing with acid	no washing	washing with acid
0	0.43	0.43	5.93	5.93
10	0.57	0.44	6.33	5.95
50	1.31	0.45	6.66	5.94
100	2.26	0.45	6.81	5.96



Before washing with acid



After washing with acid

Figure 4.2: Iron solution effect (Before washing with acid and After washing with acid)

## 4.2 Impact of inhibitor on yellow oil formation

### 4.2.1 Hydrazine solution

Acetaldehyde can not undergo aldol condensation reaction when hydrazine solution was added to the mixture. Hydrazine reacted with carbonyl group to form hydrazone. Hydrazine hydrate 0.05 g, 0.2 g, 0.3 g, 0.4 g are equivalent to 0.0010, 0.0041, 0.0062, 0.0082 mol. of hydrazine that were used to react with acetaldehyde 0.1% (0.0018 mol.) in the system. In this experiment, when hydrazine was in excess of the acetaldehyde no polymer occurred. The first reaction solution was not a clear solutions but yellow color because the amount of hydrazine is less than acetadehyde. Other solutions were clear solutions and no color.

Hydrazine was utilized to stop the carbonyl polymerization from aldol condensation reaction. Hydrazine can react with the active aldehyde group to form an inert oxime product. This chemical reaction between acetadehyde (a carbonyl species) and hydrazine is shown below. Hydrazone is soluble in water and caustic solution. This reaction is faster than the aldol condensation reaction.

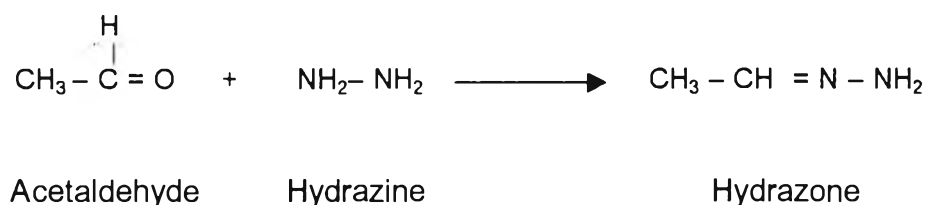


Figure 4.3: Reaction of hydrazine and acetaldehyde

### 4.2.2 Hydroxylamine hydrochloride

Hydroxylamine was another chemical that can stop the aldol condensation reaction. Hydroxylamine hydrochloride 0.05 g, 0.2 g, 0.3 g, 0.4 g are equivalent to 0.0007, 0.00288, 0.0043, 0.0057 mol. that can react with acetaldehyde 0.1% wt. (0.0018 mol.). At 0.1% of hydroxylamine hydrochloride, the aldol condensation reaction can not be completely stopped due to insufficient hydroxylamine hydrochloride in the system. Therefore yellow color occurred. At 0.2%, 0.3%, 0.4% wt. of hydroxylamine hydrochloride there remained excess hydroxylamine hydrochloride in solution and thus no polymer occurred. Clear and colorless solutions were obtained.

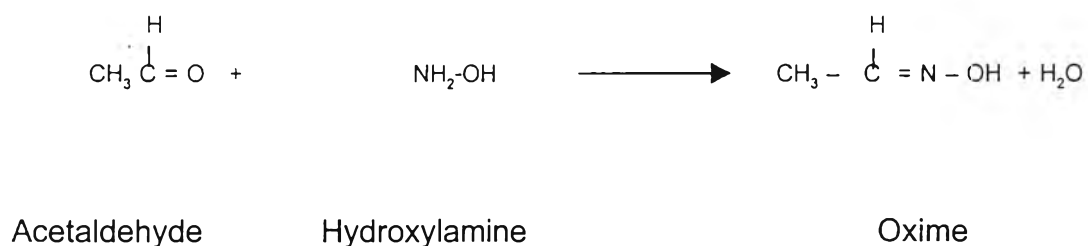


Figure 4.4 : Reaction of hydroxylamine and acetaldehyde



**Table 4.4: Impact of inhibitor hydrazine and hydroxylamine at 25°C**

Hydrazine			Hydroxylamine		
g	mol	appearance	g	mol	appearance
0.05	0.0010	light yellow	0.05	0.0007	light yellow
0.2	0.0041	clear solution	0.2	0.0029	clear solution
0.3	0.0062	clear solution	0.3	0.0043	clear solution
0.4	0.0082	clear solution	0.4	0.0057	clear solution

**Table 4.5 : Impact of inhibitor hydrazine and hydroxylamine at 50°C**

Hydrazine			Hydroxylamine		
g	mol	appearance	g	mol	appearance
0.05	0.0010	light yellow	0.05	0.0007	light yellow
0.2	0.0041	clear solution	0.2	0.0029	clear solution
0.3	0.0062	clear solution	0.3	0.0043	clear solution
0.4	0.0082	clear solution	0.4	0.0057	clear solution

Figure 4.5-4.8 show UV spectrum of inhibited aldol condensation solutions. All spectra show the  $\lambda$  absorption about 200-400 nm. Figure 4.5 at 25°C hydrazine 0.05 g., absorption at  $\lambda$  200 nm of -NOH group has high absorbance and absorption at  $\lambda$  300 nm of carbonyl group has low absorbance. Hydrazine 0.2, 0.3, 0.4 g., absorption at  $\lambda$  200 nm of -NOH group has highest absorbance and absorption at  $\lambda$  300 nm of carbonyl group no absorbance. Figure 4.6 at 50°C hydrazine 0.05 g., absorption at  $\lambda$  200 nm of -NOH group has high absorbance and absorption at  $\lambda$  300 nm of carbonyl group has low absorbance. Hydrazine 0.2, 0.3, 0.4 g., absorption at  $\lambda$  200 nm of -NOH group has highest absorbance and absorption at  $\lambda$  300 nm of carbonyl group no absorbance.

Figure 4.7 at 25°C hydroxylamine 0.05 g., absorption at  $\lambda$  200 nm of -NOH group has high absorbance and absorption at  $\lambda$  300 nm of carbonyl group has low absorbance. Hydroxylamine 0.2, 0.3, 0.4 g., absorption at  $\lambda$  200 nm of -NOH group has highest absorbance and absorption at  $\lambda$  300 nm of carbonyl group no absorbance. Figure 4.8 at 50°C hydroxylamine 0.05 g., absorption at  $\lambda$  200 nm of -NOH group has high absorbance and absorption at  $\lambda$  300 nm of carbonyl group has low absorbance. Hydroxylamine 0.2, 0.3, 0.4 g., absorption at  $\lambda$  200 nm of -NOH group has highest absorbance and absorption at  $\lambda$  300 nm of carbonyl group no absorbance.

Compare Figures 4.5–4.8 with the spectra of a pure yellow oil solution (concentration of yellow oil about 10 ppm.) in Figure 4.9. The pure yellow oil shows the  $\lambda$  absorption about 200-400 nm, absorption at  $\lambda$  300 nm of carbonyl group has high absorbance.

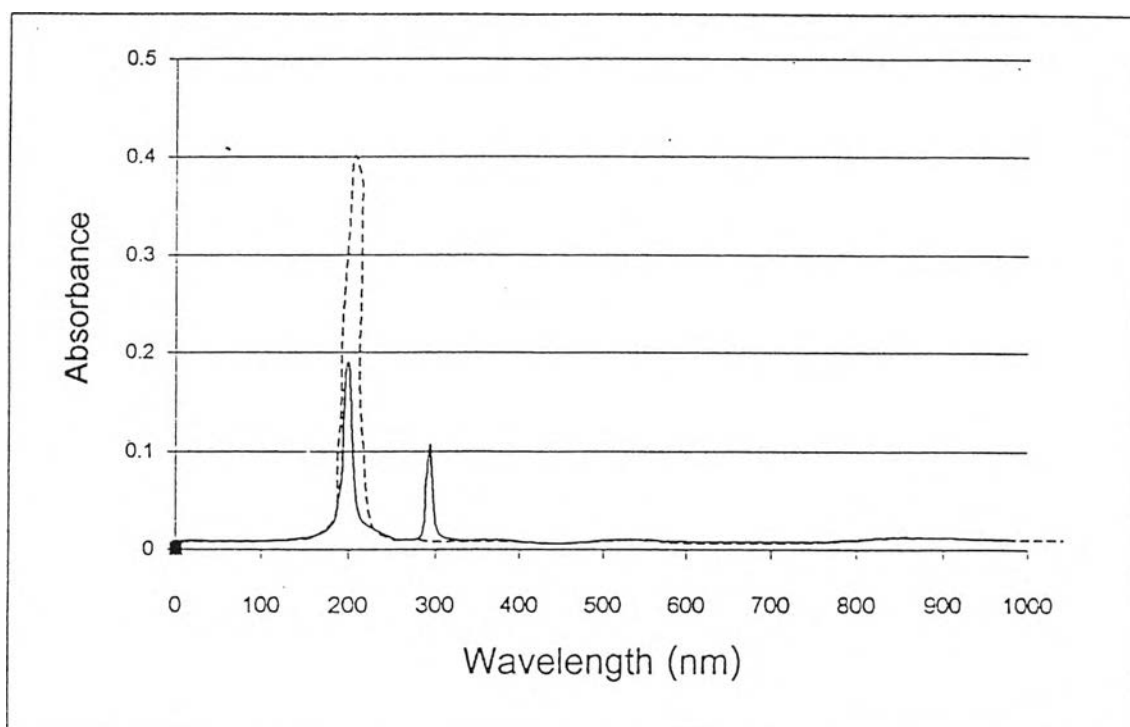


Figure 4.5: UV spectra of mixture of acetaldehyde in caustic solution and the presence of hydrazine at 25°C

— hydrazine 0.05 g  
- - - hydrazine 0.2, 0.3, 0.4 g

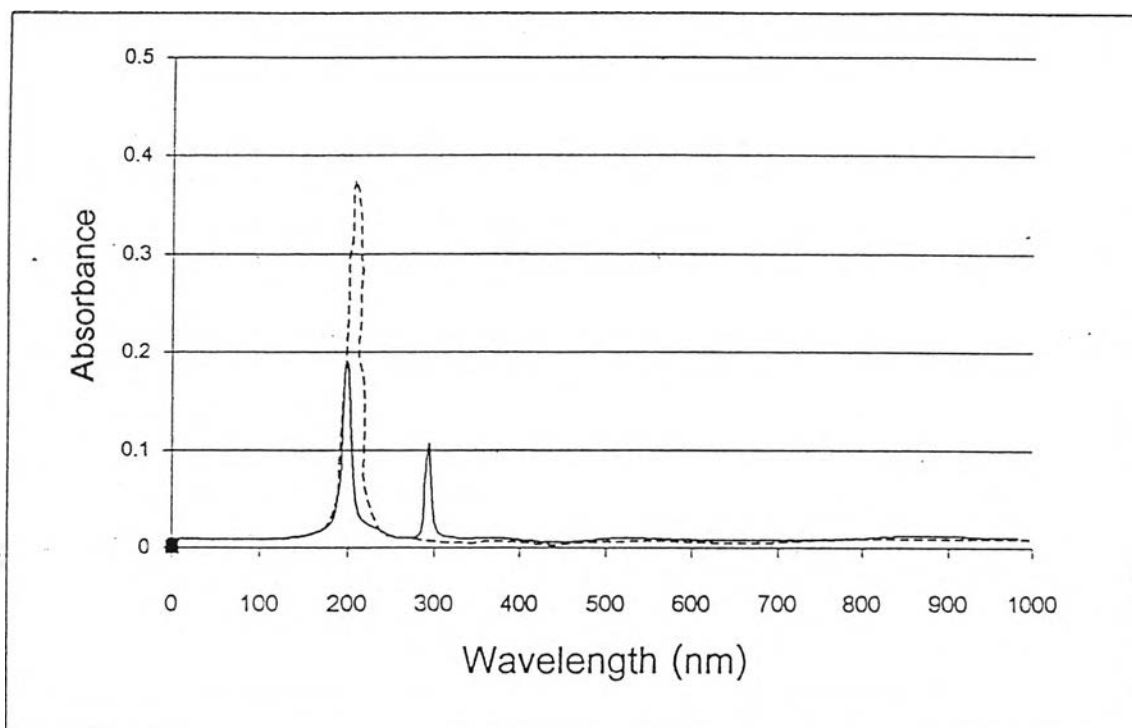


Figure 4.6: uv spectra of mixture of acetaldehyde in caustic solution and the presence of hydrazine at 50°C

— hydrazine 0.05 g  
- - - hydrazine 0.2, 0.3, 0.4 g

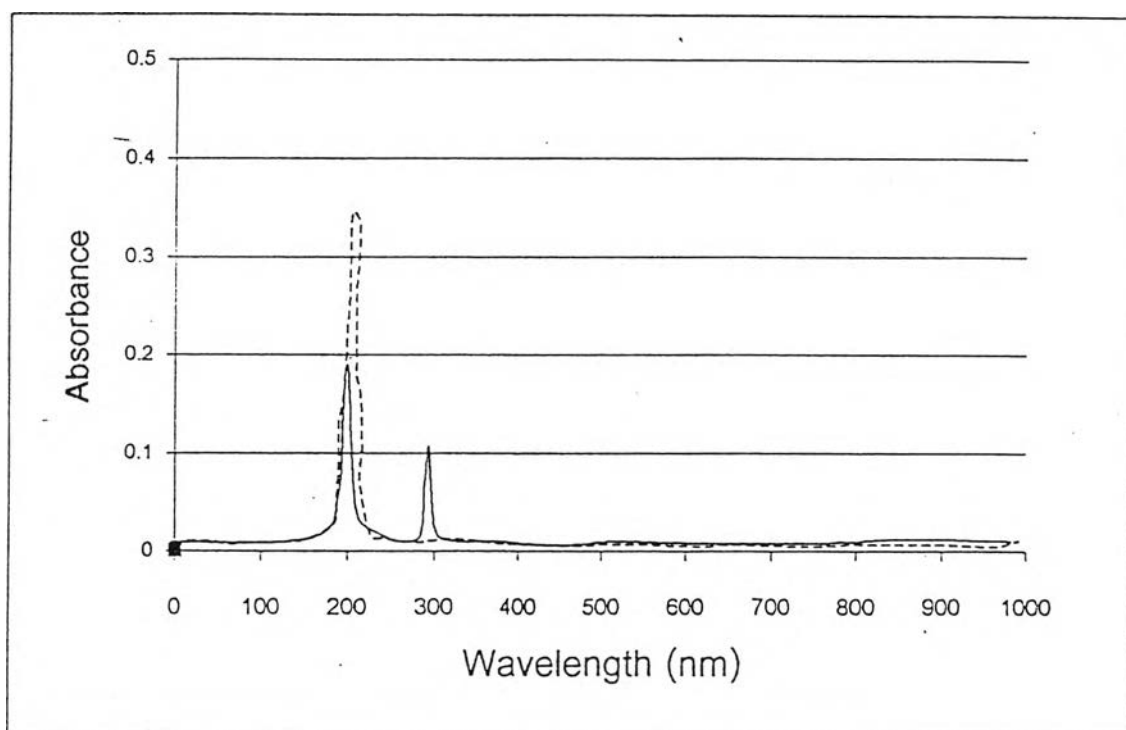


Figure 4.7: UV spectra of mixture of acetaldehyde in caustic solution and the presence of hydroxylamine at 25°C

— hydroxylamine 0.05 g  
- - - hydroxylamine 0.2, 0.3, 0.4 g

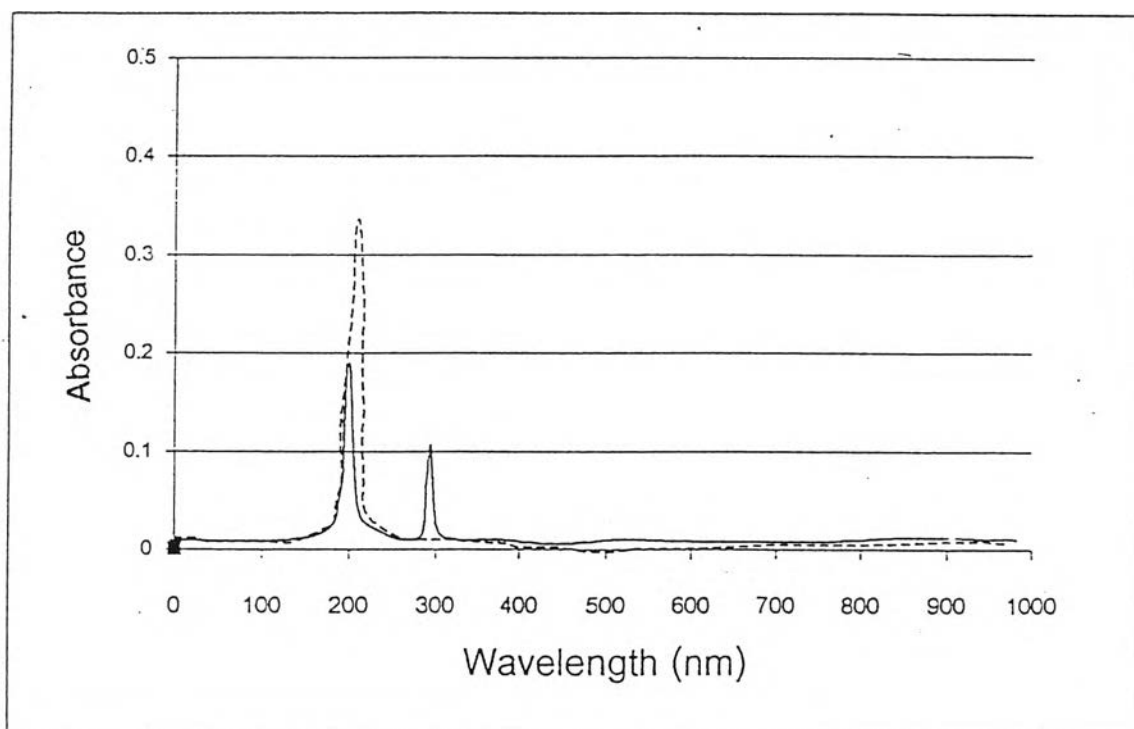


Figure 4.8: UV spectra of mixture of acetaldehyde in caustic solution and the presence of hydroxylamine at 50°C

— hydroxylamine 0.05 g  
- - - hydroxylamine 0.2, 0.3, 0.4 g

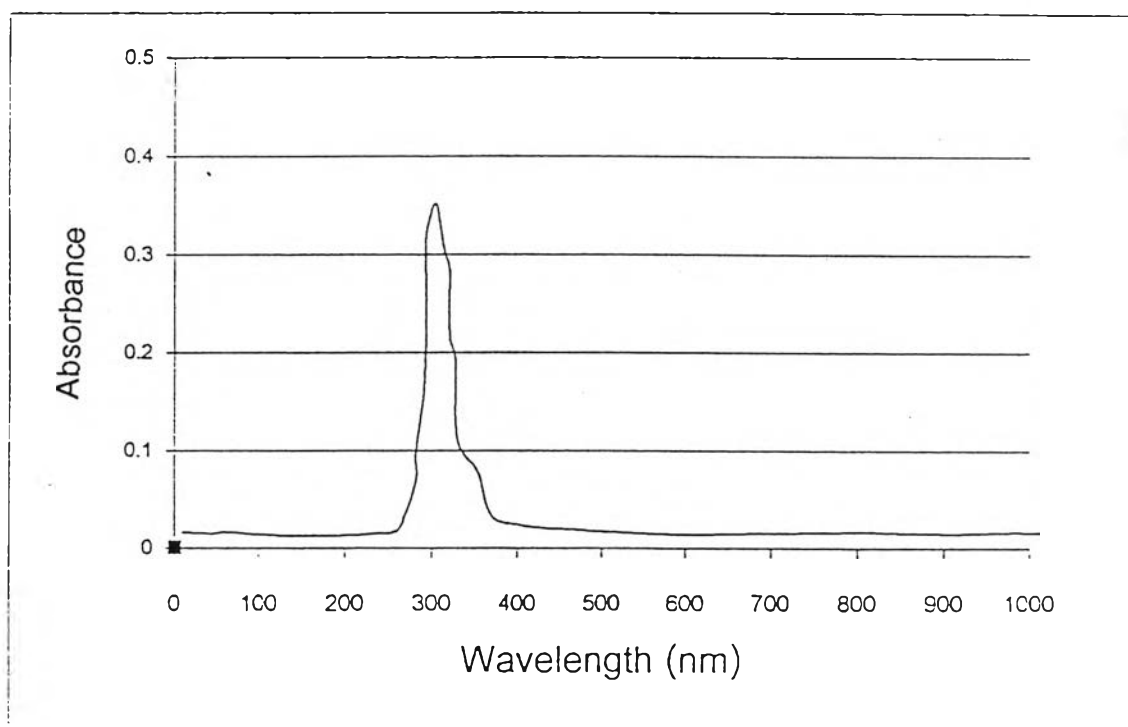


Figure 4.9: UV spectra of yellow oil dissolved in caustic solution



### 4.3 Impact of caustic soda and the amount of acetadehyde on yellow oil formation

Aldol condensation of acetaldehyde can be effected even in a weak caustic solution. Caustic solution simply acts as a catalyst. Acetaldehyde can change to enol form which is easy for abstraction by base and changes to enolate anion. Enolate anion can react with acetaldehyde and change to 2-butenol. Varying the strength of caustic solution has no impact on the polymer formation (Table 4.6). On the contrary varying the amount of acetaldehyde in the system has direct impact on the amount of polymer formed (Figure 4.10-4.12). The amount of polymer solid increased with the increase in the amount of acetaldehyde. In the reaction, acetaldehyde was reactant which reacted with caustic soda as a catalyst only. Solid product that occurred was carbonyl compound. Figure 4.13 shows the IR spectra of the yellow oil from olefins plant compared with spectra of aldol condensation product from reaction in laboratory. There are little difference in fingerprint region. Both samples have  $\text{CH}_3$  and  $\text{CH}_2$  groups. Their ratio is slightly different, with the 2956 peak higher than the 2924 peak. This difference simply shows that in the yellow oil sample the  $\text{CH}_2/\text{CH}_3$  ratio is higher than the aldol condensation product. This is not surprising if the molecular weight is increased by polymerization of the carbon-carbon double bond. In addition both samples have a high frequency C-H stretch at 3017 and 3048. These are typically C-H stretches when H is on a carbon that has double or triple bond. The peaks of aldol condensation product for the carbonyl region are very sharp at 1673 and 1573. In comparison the carbonyl region of the yellow oil sample is at 1698 and 1604. So the 1698 and 1673 peaks may belong to the same type of oxygen - carbon bond.

**Table 4.6: Amount of solid at 1, 5, 10% wt. caustic soda**

acetaldehyde %	amount of solid (mg / 100 ml solution )					
	1% wt. caustic solution		5% wt. caustic solution		10% wt. caustic solution	
	25°C	50°C	25°C	50°C	25°C	50°C
0.1	0.43	5.85	0.43	5.84	0.44	5.85
0.2	0.85	11.65	0.83	11.65	0.86	11.66
0.3	1.32	17.50	1.34	17.60	1.33	17.50
0.4	1.70	23.00	1.69	22.80	1.71	22.85

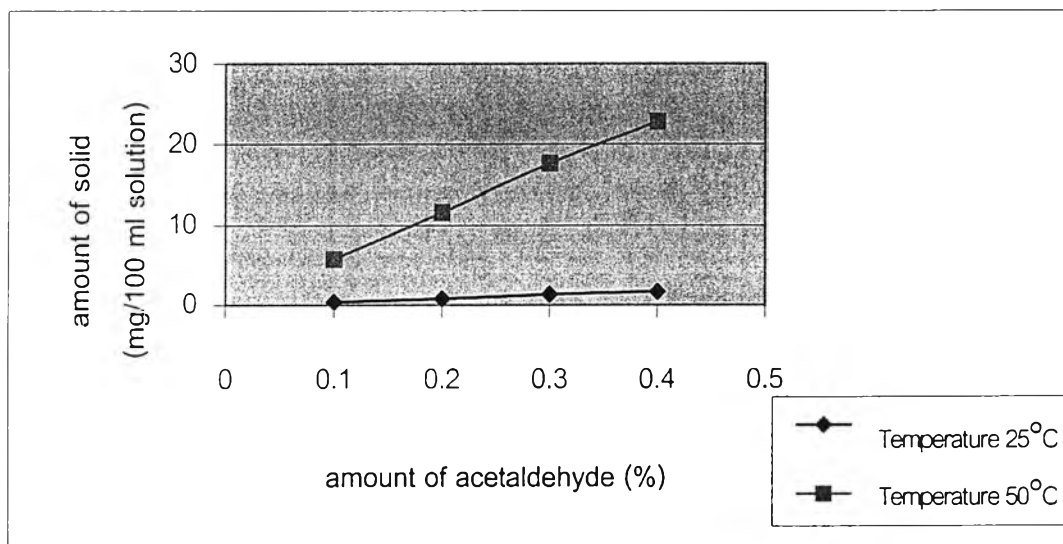


Figure 4.10: The acetaldehyde 1% wt. caustic solution  
at temperature 25°C and 50 °C

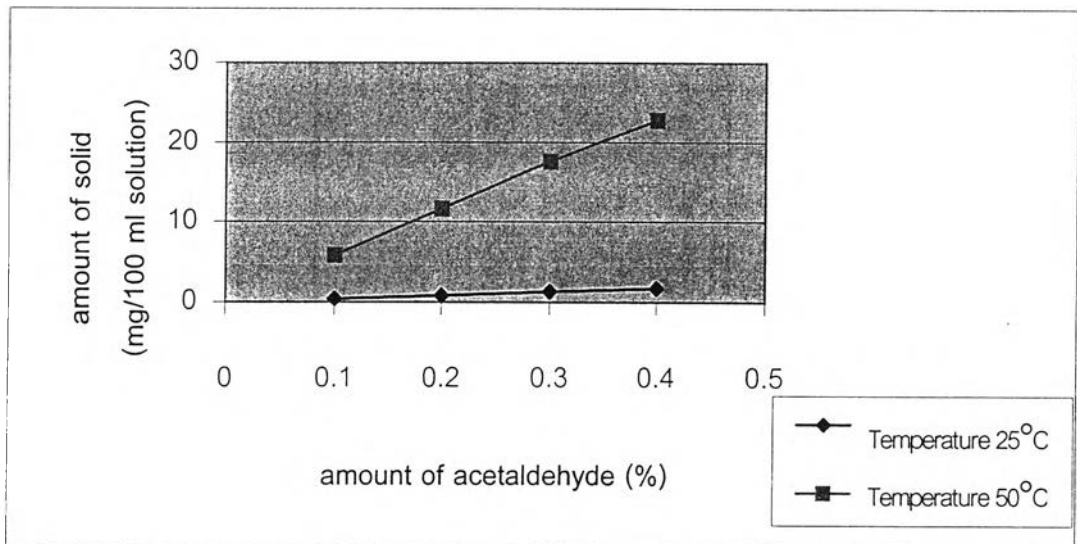


Figure 4.11: The acetaldehyde at 5% wt. caustic solution  
at temperature 25°C and 50°C

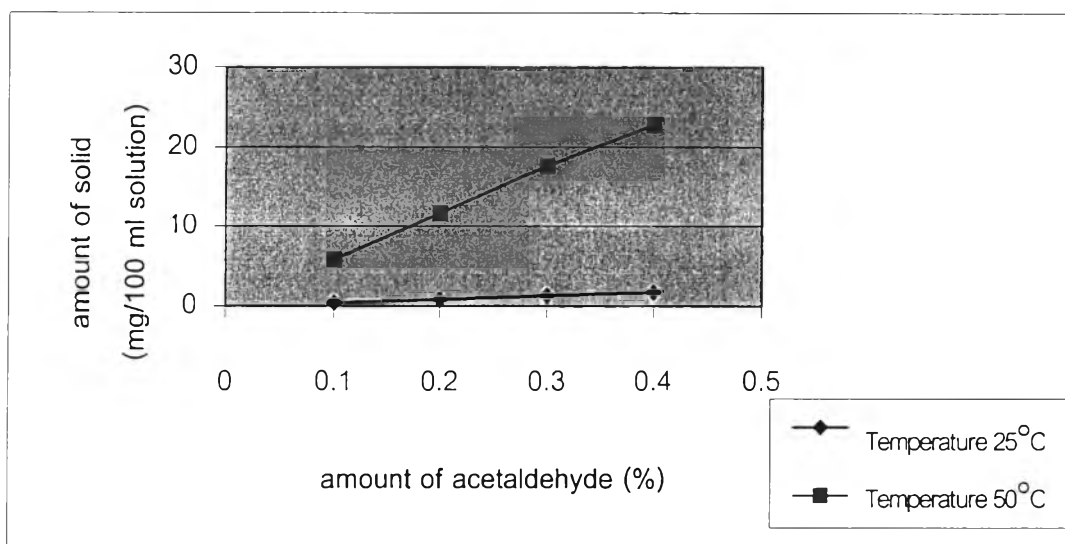


Figure 4.12: The acetaldehyde at 10% wt. caustic solution  
at temperature 25°C and 50°C

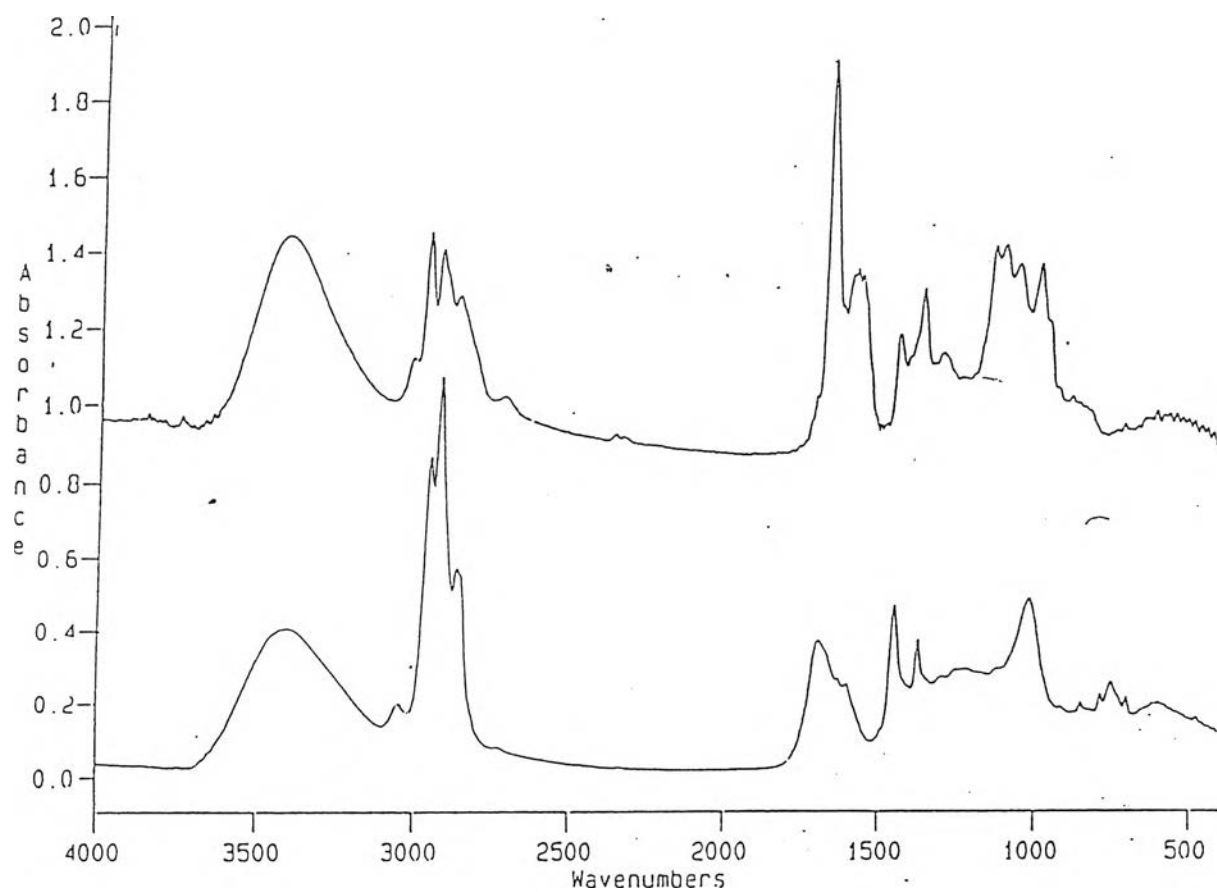


Figure 4.13: Comparison between IR spectra of yellow oil and the product from aldol condensation ( KBr)

upper: The product form aldol condensation

lower: yellow oil