

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the characterization results of the spent caustic obtained from the National Petrochemical Public Co., Ltd. will be provided. The spent caustic was taken from the weak section of a caustic tower. The results would provide an insight on the cause of the fouling in the caustic tower. The aldol condensation of acetaldehyde, which is believed to be the cause of the fouling, will be discussed followed by discussing the effects of temperature, concentration of antipolymerants and type of antipolymerants on the reaction.

4.1 Characterization of the Spent Caustic

The caustic sample was analyzed for its pH, concentration of NaOH, and amount of organic acid. pH of the spent caustic is 13.13 ± 0.03 . This result shows that the spent caustic at the weak section of the caustic tower is in the basic condition. Concentration of NaOH in the caustic sample is 1.723 ± 0.008 wt%. This result confirms that the concentration of NaOH is in the range of the NaOH concentration specification in the weak section of the caustic tower (1-2wt%). Last, concentration of the organic acid in the spent caustic is 8.85 ± 0.05 mM.

FT-IR spectra of the spent caustic, yellow oil, and aldol product synthesized from the aldol condensation were compared. FT-IR spectra of the spent caustic and yellow oil are shown in Figures 4.1 and 4.2. They show that the broad band near 3434 cm^{-1} represents the hydrogen bonded O-H stretch. The band at 3049 cm^{-1} represents the olefinic C-H stretch. C-H stretching vibration, in which the carbon atom is present in the alkene linkage. Two

distinct bands occur at 2961 cm^{-1} and 2854 cm^{-1} . The results from the asymmetrical stretching mode, in which 2 C-H bonds of the methyl group are extending while the third one is contracting ($\gamma_{\text{as}}\text{CH}_3$). The latter arises from the symmetrical stretching ($\gamma_{\text{s}}\text{CH}_3$). The presence of several methyl groups in a molecule results in strong absorption at this position (Silverstein, 1991). The asymmetrical stretching ($\gamma_{\text{as}}\text{CH}_3$) and symmetrical stretching ($\gamma_{\text{s}}\text{CH}_3$) of methyl groups occur near 2925 cm^{-1} and 2854 cm^{-1} , respectively. The symmetrical bending vibration of methyl group ($\delta_{\text{s}}\text{CH}_3$) occurs near 1373 cm^{-1} with the asymmetrical bending vibration ($\delta_{\text{as}}\text{CH}_3$) near 1448 cm^{-1} . The band near 700 cm^{-1} shows the methyl rocking vibration.

Some differences among each spectrum in Figures 4.1 and 4.2 are observed. They are quite different especially in the fingerprint region ($<1250\text{ cm}^{-1}$). The spent caustic, yellow oil, and aldol product synthesized primarily have CH_3 and CH_2 groups. Their ratios are slightly different, with the peak at 2961 cm^{-1} higher than the peak at 2925 cm^{-1} . This difference indicates that in the spent caustic and the yellow oil samples, the CH_2/CH_3 ratios are higher than that of the aldol condensation product. The reason is that molecular weights of the spent caustic and yellow oil increase by the polymerization of carbon-carbon double bonds. This reason can be further supported by the result from Gel Permeation Chromatography (GPC). The GPC results show that a molecular weight of the polymers in the spent caustic is about 250-500. In addition, the spent caustic, yellow oil, and aldol product synthesized have a high absorbance C-H stretch at 3049 cm^{-1} . These are typically C-H stretches, when H is on a carbon that has double or triple bonds. The spectra of aldol product synthesized for the carbonyl region are very sharp at 1673 and 1573 cm^{-1} .

The above results show that although the ratio of CH_2 to CH_3 of the aldol product is different to that of the spent caustic and yellow oil, their spectra are mostly the same wave number. Therefore, it can be concluded that

the aldol condensation is possibly to be one of the causes of the fouling. This conclusion also agrees with the work by Martin (1988).

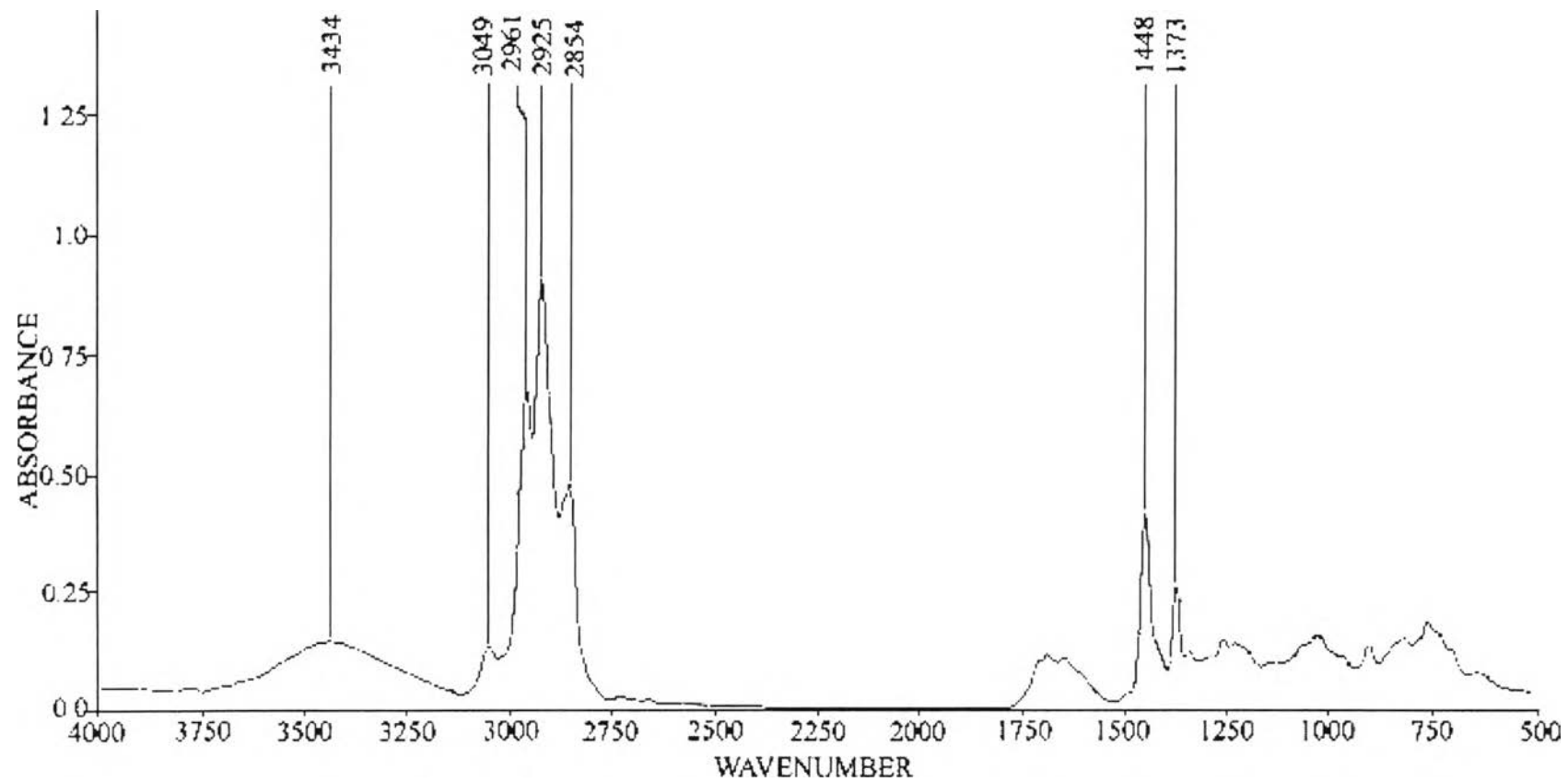


Figure 4.1 FT-IR spectrum of the spent caustic.

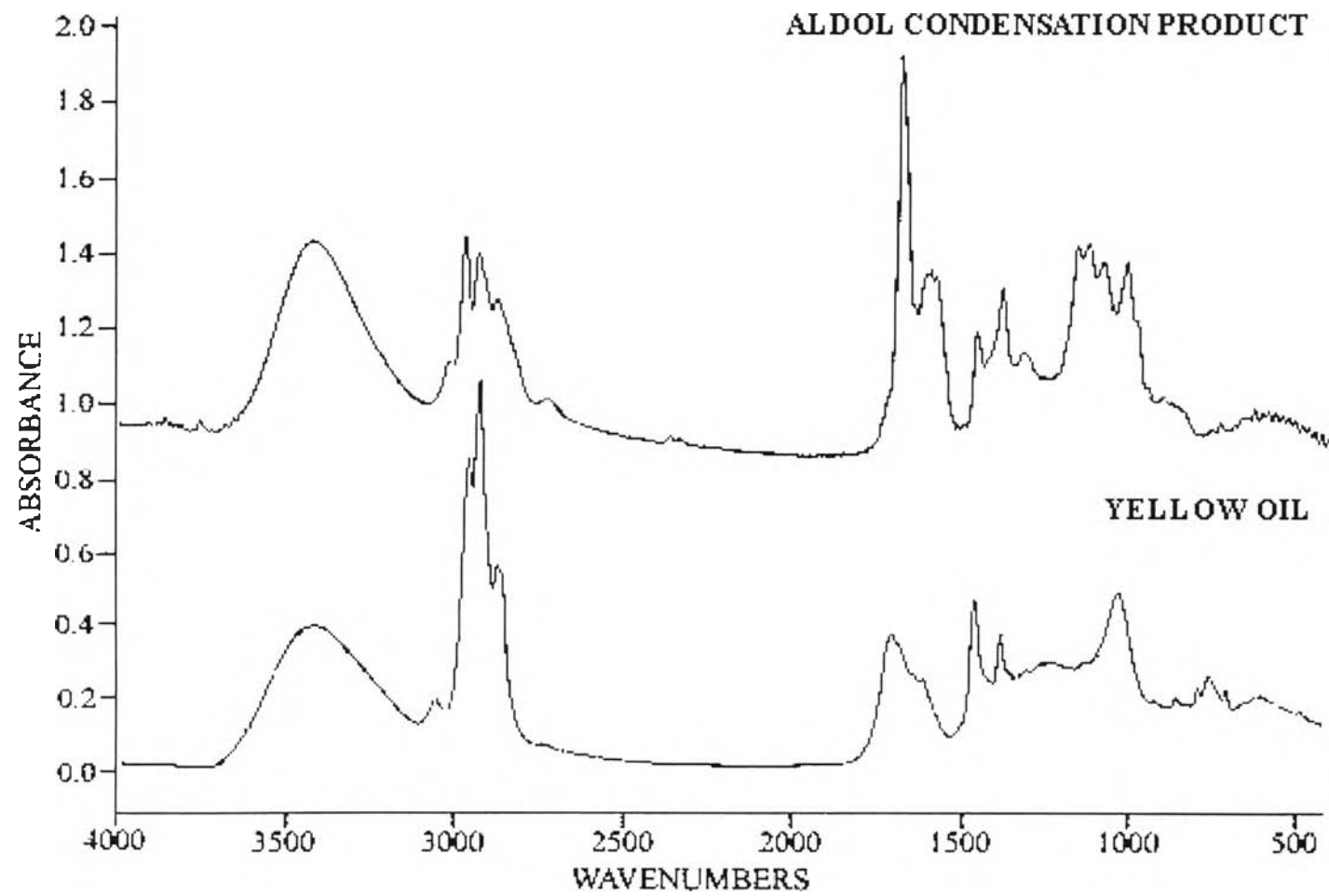


Figure 4.2 FT-IR spectrum of the yellow oil and the aldol condensation product.

4.2 Aldol Condensation of Acetaldehyde

As mentioned before, the aldol condensation is believed to be the cause of the fouling in caustic towers. Here, the aldol condensation of acetaldehyde was studied using a colorimeter. The reaction progress was observed by following the change of yellow color absorbance. Two variables, temperature and acetaldehyde concentration, were varied in this study.

Effects of acetaldehyde concentration to the aldol condensation at 25°C can be seen in Figure 4.3. The aldol condensation increases with time at all concentration ratios of acetaldehyde to sodium hydroxide. At any fixed reaction time, increasing acetaldehyde concentration results in higher aldol product. For example, at 60 minutes, the absorbance of the yellow color at the 1:1 acetaldehyde to sodium hydroxide concentration is 0.845. Then, the absorbance of the yellow color range decreases to 0.021, as the ratio of acetaldehyde to sodium hydroxide concentration decreases to 0.25:1. The same trend can also be observed at 35 and 50°C as shown in Figures 4.4 and 4.5.

Figure 4.6 shows effects of temperature to the aldol condensation at the 1:1 acetaldehyde to sodium hydroxide concentration. The aldol product increases as the temperature increases. For example, at 60 minutes, the absorbance of the yellow color changes from 0.035 to 1.595 as the temperature increases from 25 to 50°C. The same trend is also observed at the ratio of acetaldehyde to sodium hydroxide concentration 0.25:1, 0.5:1, and 0.75:1 as shown in Figures 4.7, 4.8, and 4.9.

For the range of the temperature studied, it can be concluded that the aldol condensation of acetaldehyde increases when the temperature increases. In addition, the absorbance of the yellow color can be used as an indicator for the fouling formation in the caustic tower.

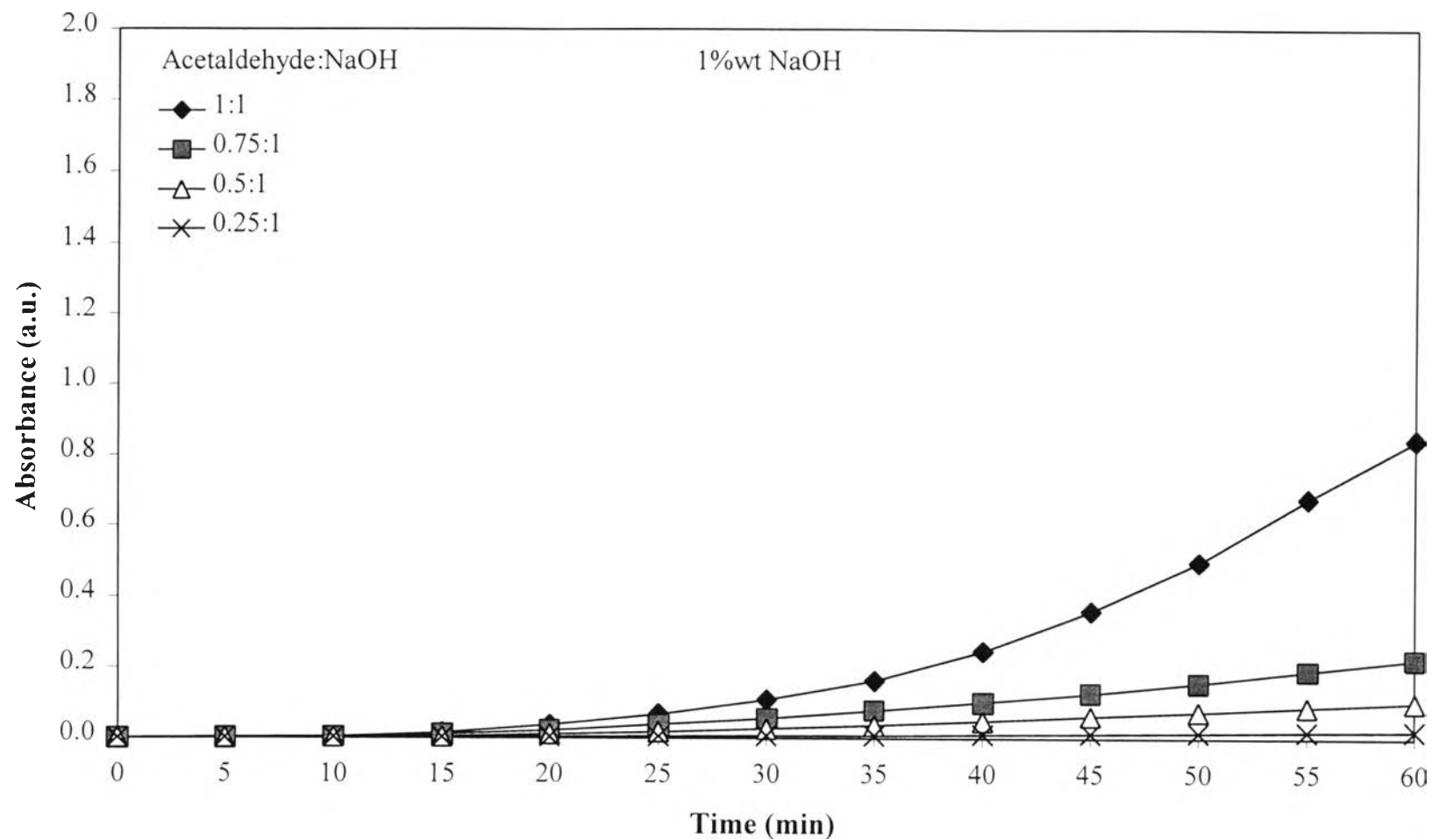


Figure 4.3 Relationship between the absorbance of the yellow color of the aldol product and time at 25°C.

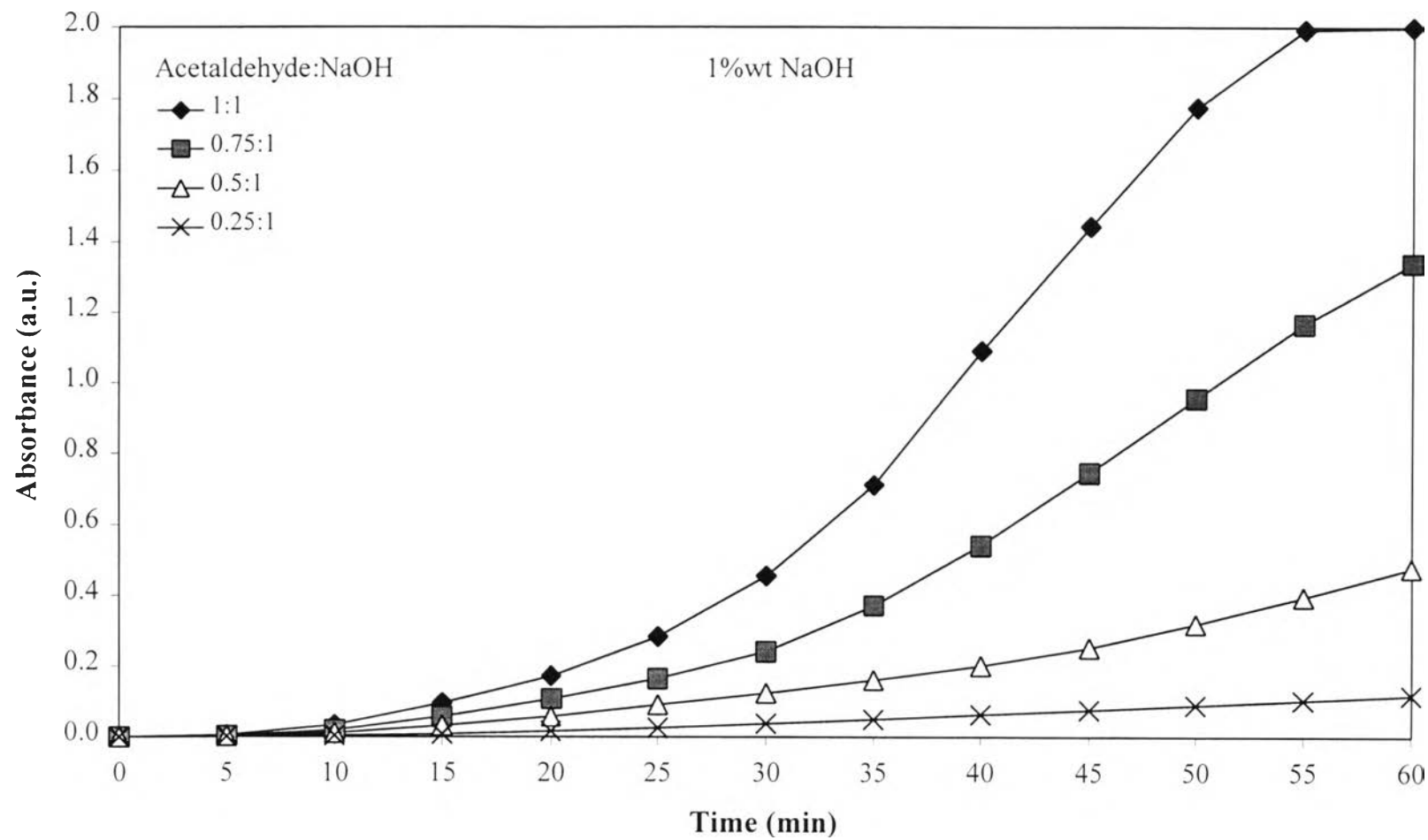


Figure 4.4 Relationship between the absorbance of the yellow color of the aldol product and time at 35°C.

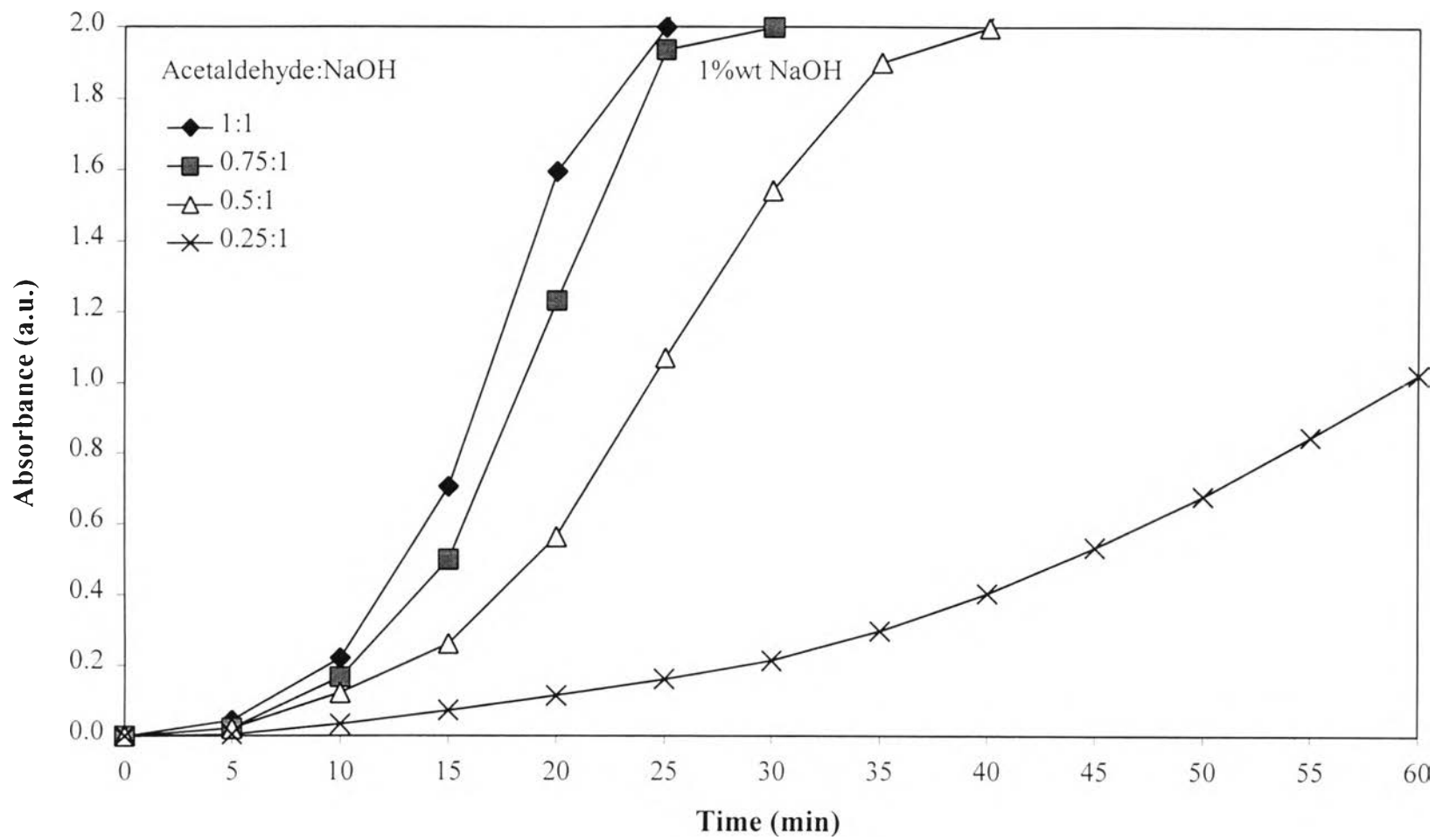


Figure 4.5 Relationship between the absorbance of the yellow color of the aldol product and time at 50°C.

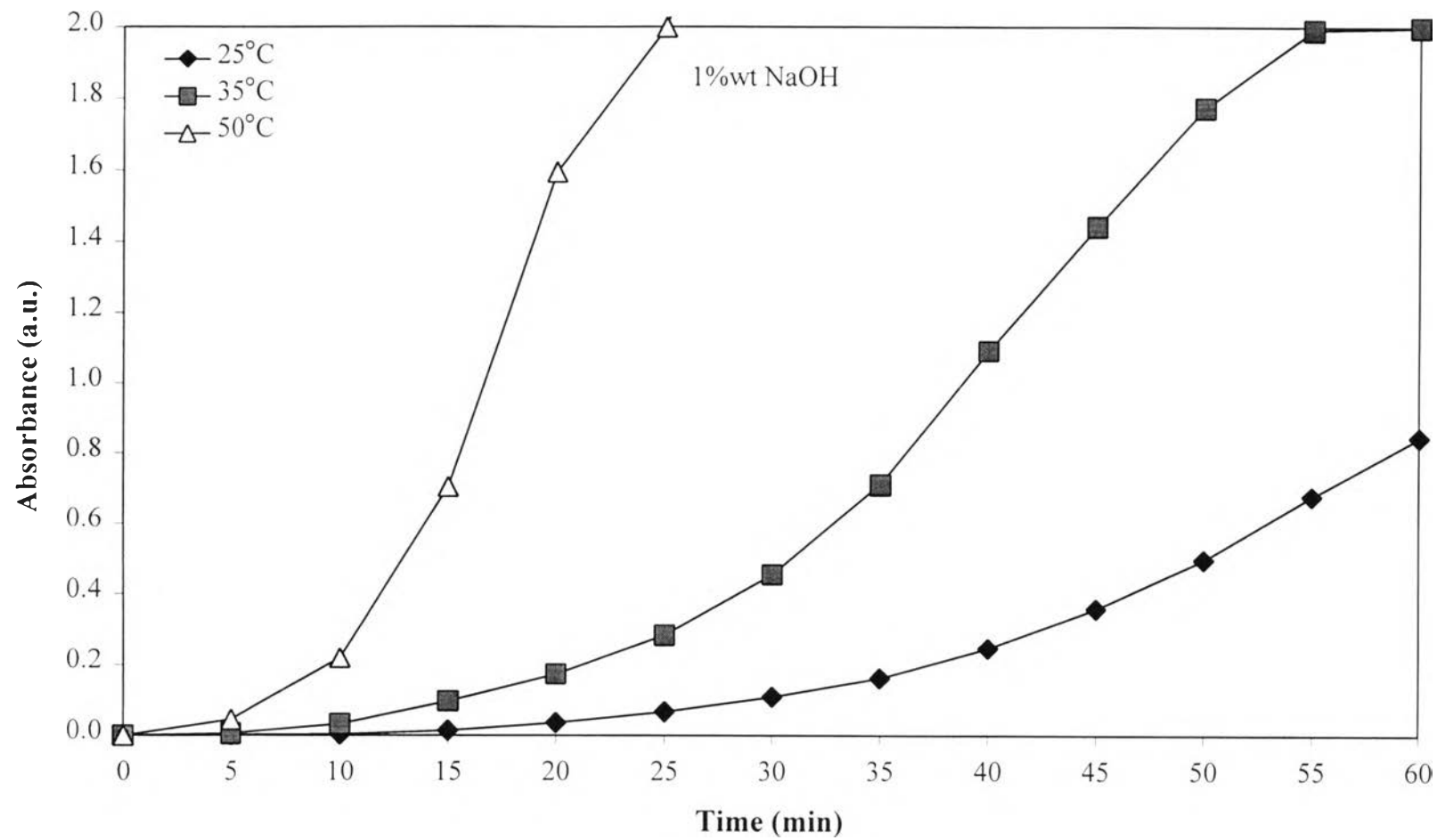


Figure 4.6 Relationship between the absorbance of the yellow color of the aldol product and time at the 1:1 acetaldehyde to sodium hydroxide concentration.

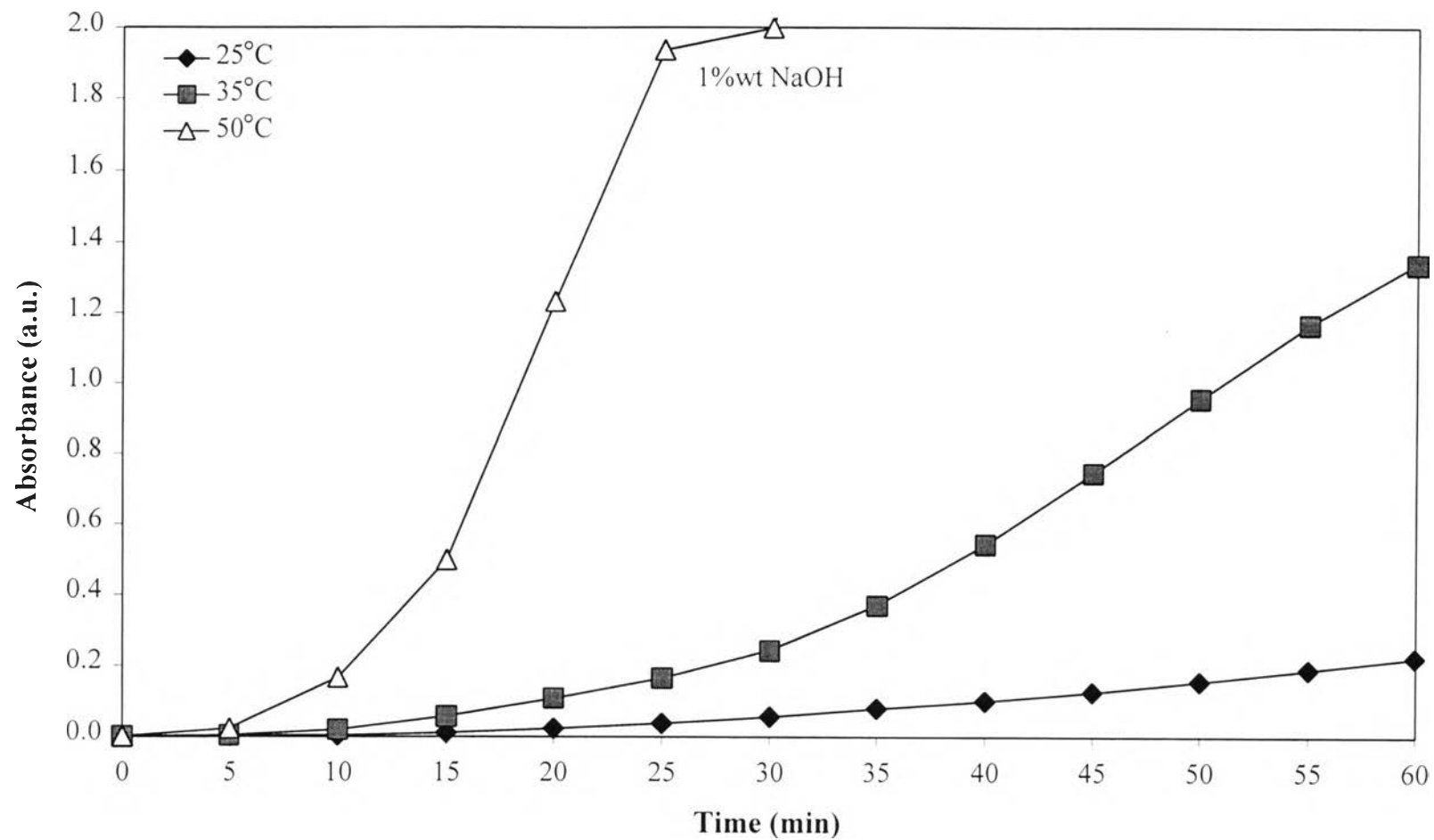


Figure 4.7 Relationship between the absorbance of the yellow color of the aldol product and time at the 0.75:1 acetaldehyde to sodium hydroxide concentration.

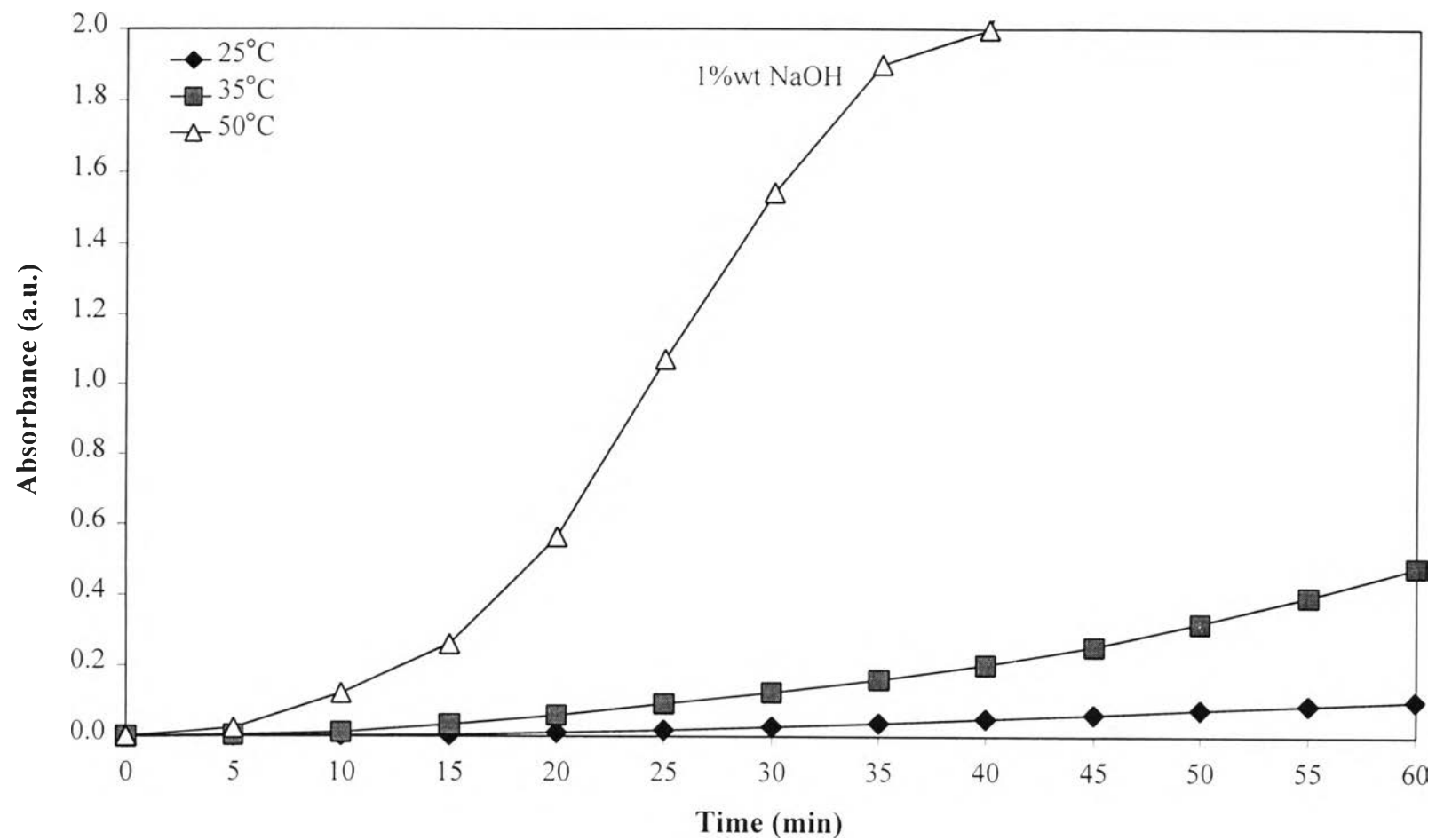


Figure 4.8 Relationship between the absorbance of the yellow color of the aldol product and time at the 0.5:1 acetaldehyde to sodium hydroxide concentration.

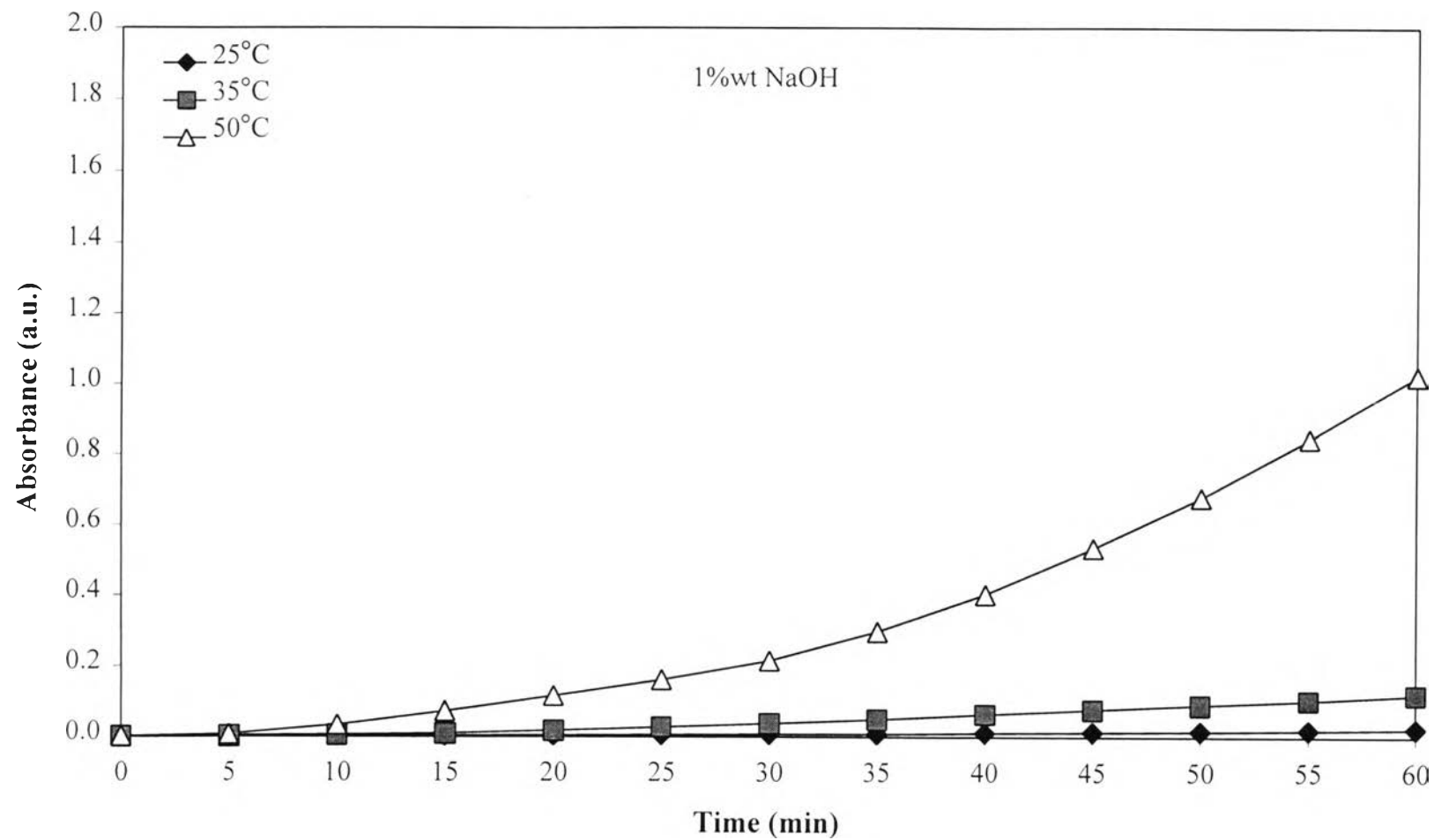
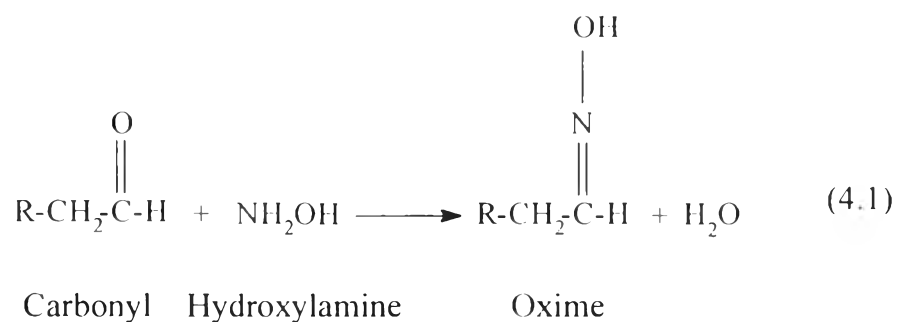


Figure 4.9 Relationship between the absorbance of the yellow color of the aldol product and time at the 0.25:1 acetaldehyde to sodium hydroxide concentration.

4.3 Reduction of the Fouling by Antipolymerants

Because of their inexpensive costs compared with other antipolymerants, two hydroxylamine salts, namely hydroxylamine hydrochloride and hydroxylamine sulfate, were used as a carbonyl stabilizer to interrupt the carbonyl polymerization from the aldol condensation reaction. Hydroxylamine, which was a product of the dissociation of a hydroxylamine salt, reacted with an active aldehyde group to form an inert oxime product. The reaction between acetaldehyde and hydroxylamine can be described below.



4.3.1 Hydroxylamine Hydrochloride as an Antipolymerant

For investigation at 25, 35, and 50°C with a fixed ratio of acetaldehyde to sodium hydroxide concentration 1:1 in the 1wt% sodium hydroxide solution, the ratios of hydroxylamine hydrochloride to acetaldehyde concentration were varied from 0.1:1 to 1:1. The results obtained are presented in graphical forms as follows:

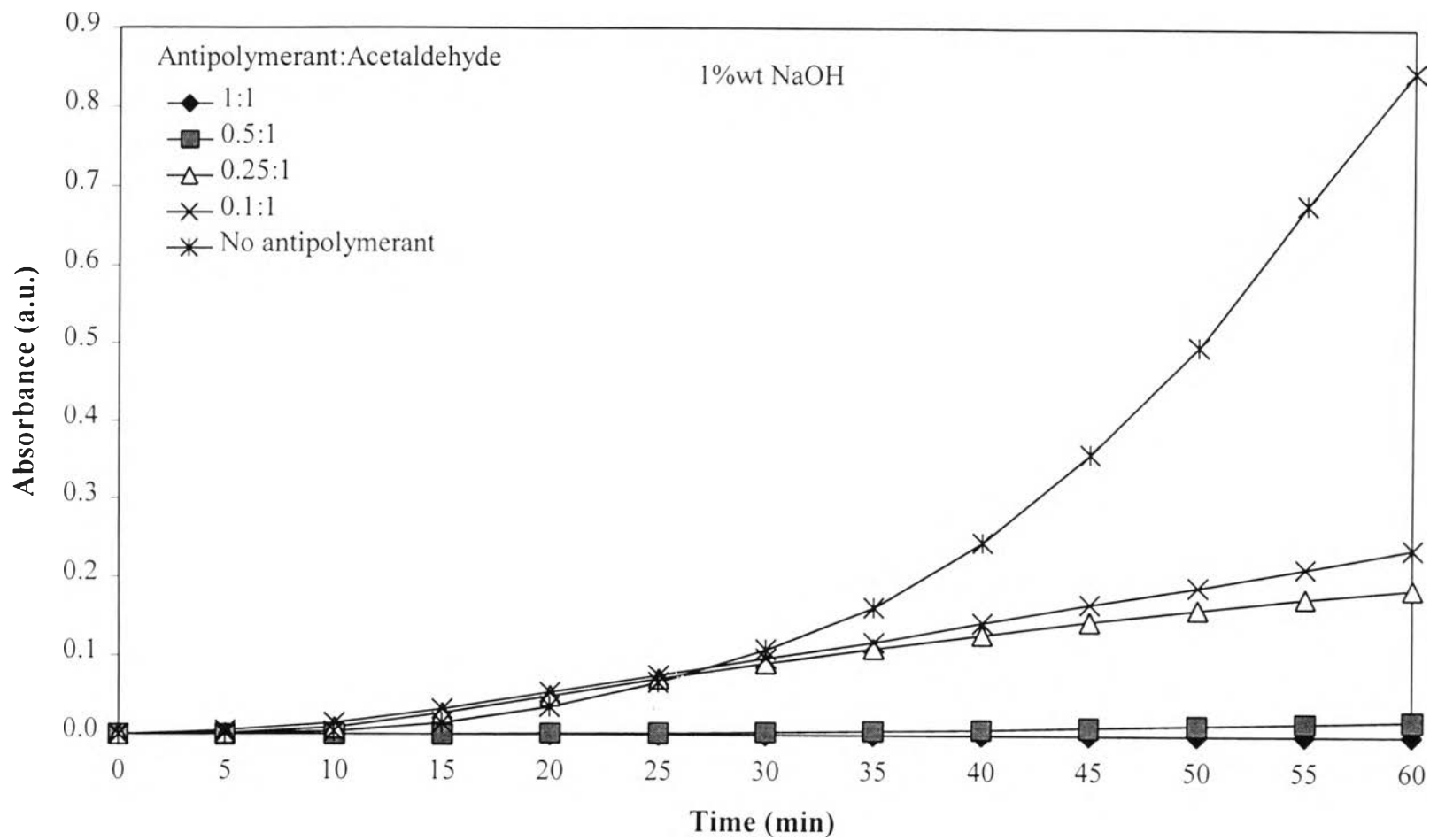


Figure 4.10 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine hydrochloride and time at 25°C.

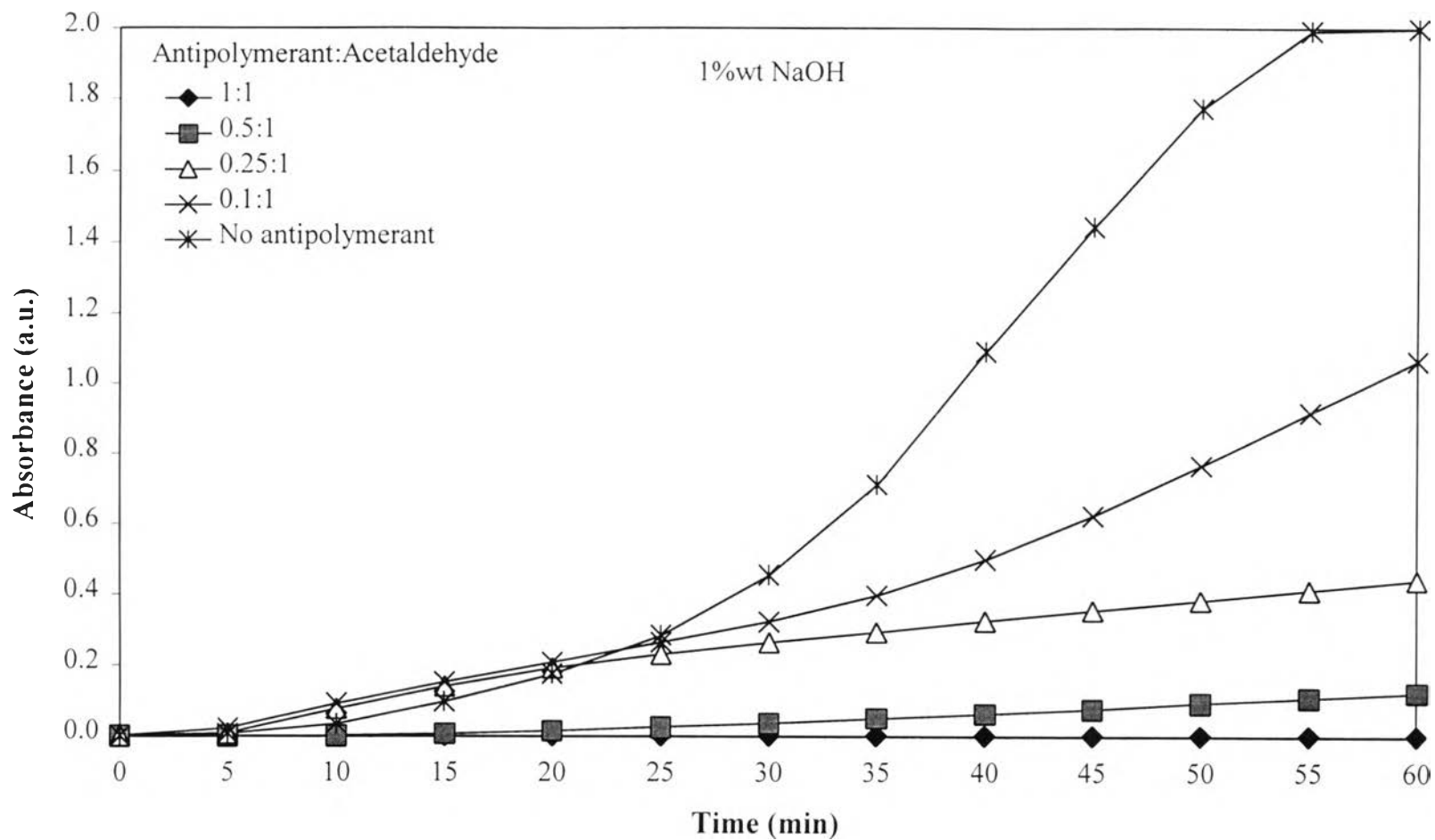


Figure 4.11 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine hydrochloride and time at 35°C.

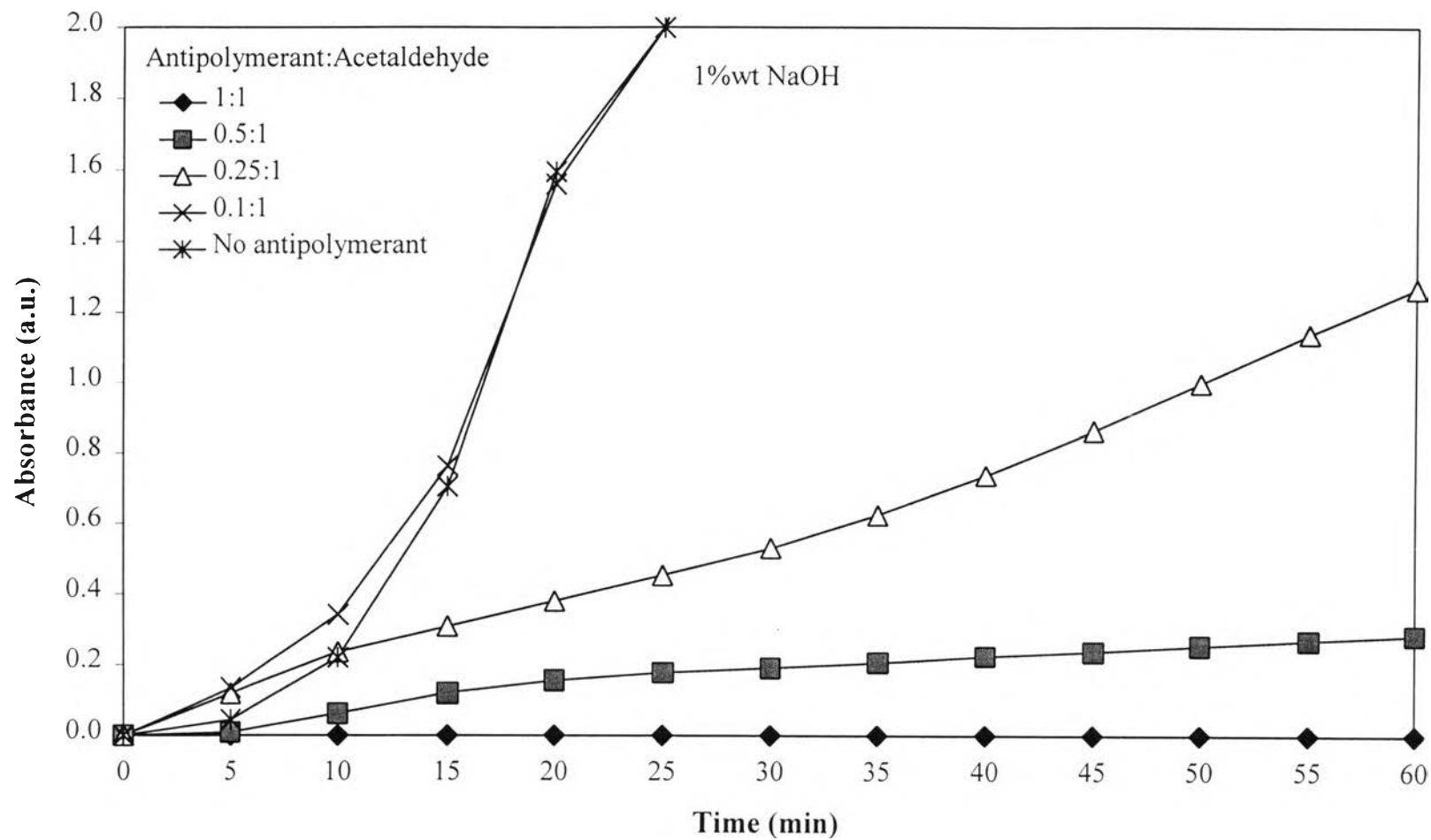


Figure 4.12 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine hydrochloride and time at 50°C.

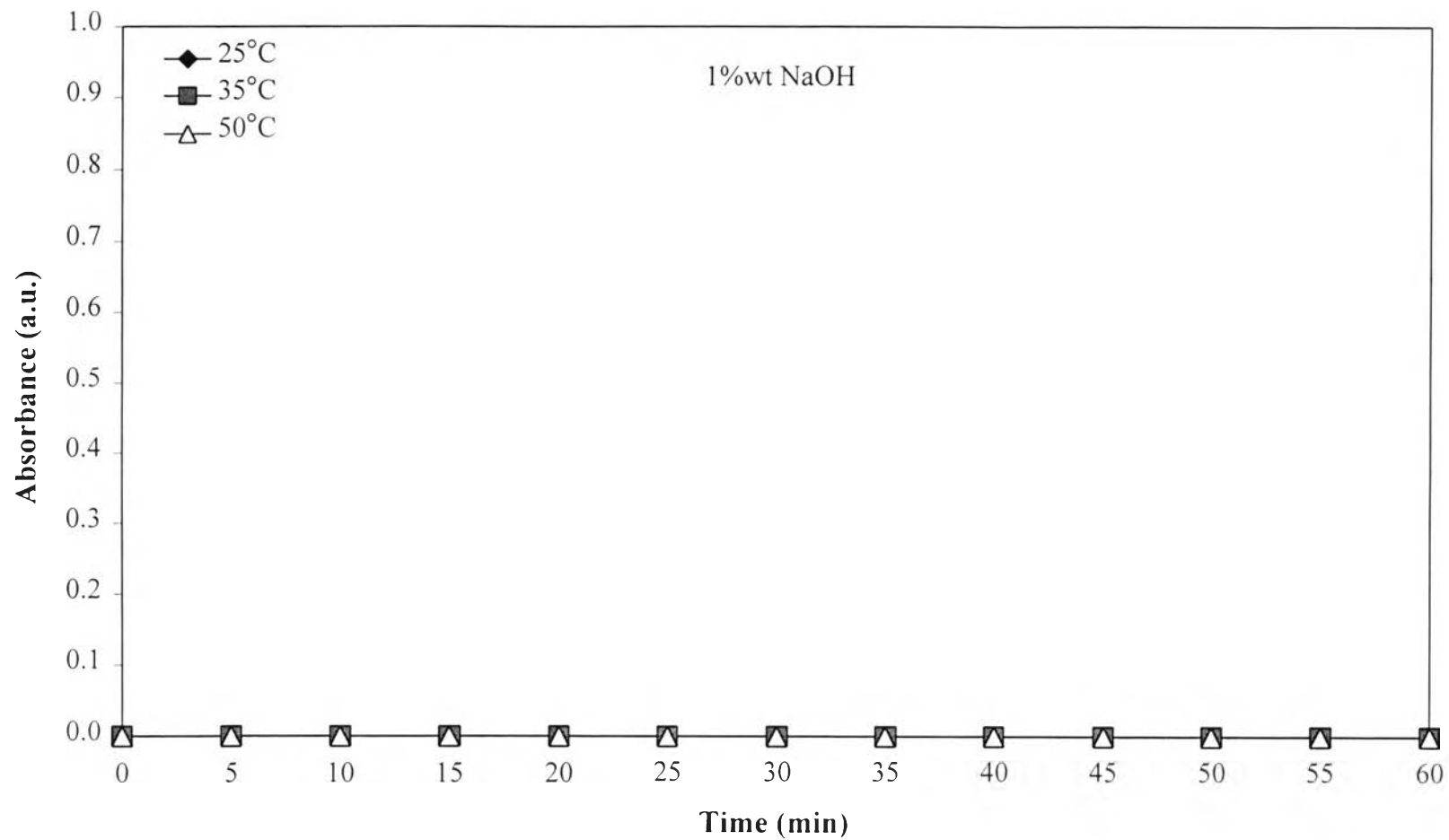


Figure 4.13 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine hydrochloride and time at the 1:1 hydroxylamine hydrochloride to acetaldehyde concentration.

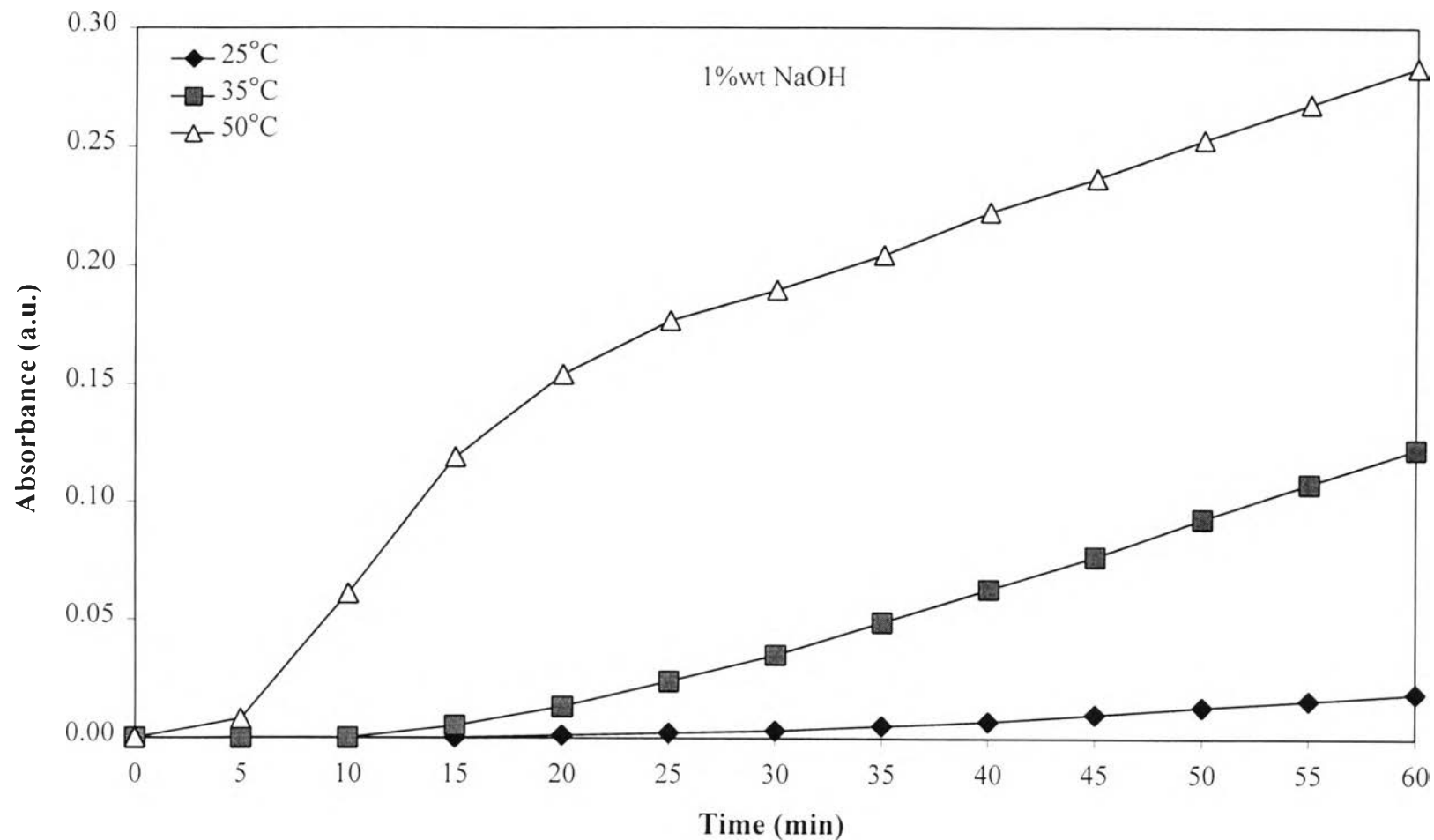


Figure 4.14 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine hydrochloride and time at the 0.5:1 hydroxylamine hydrochloride to acetaldehyde concentration.

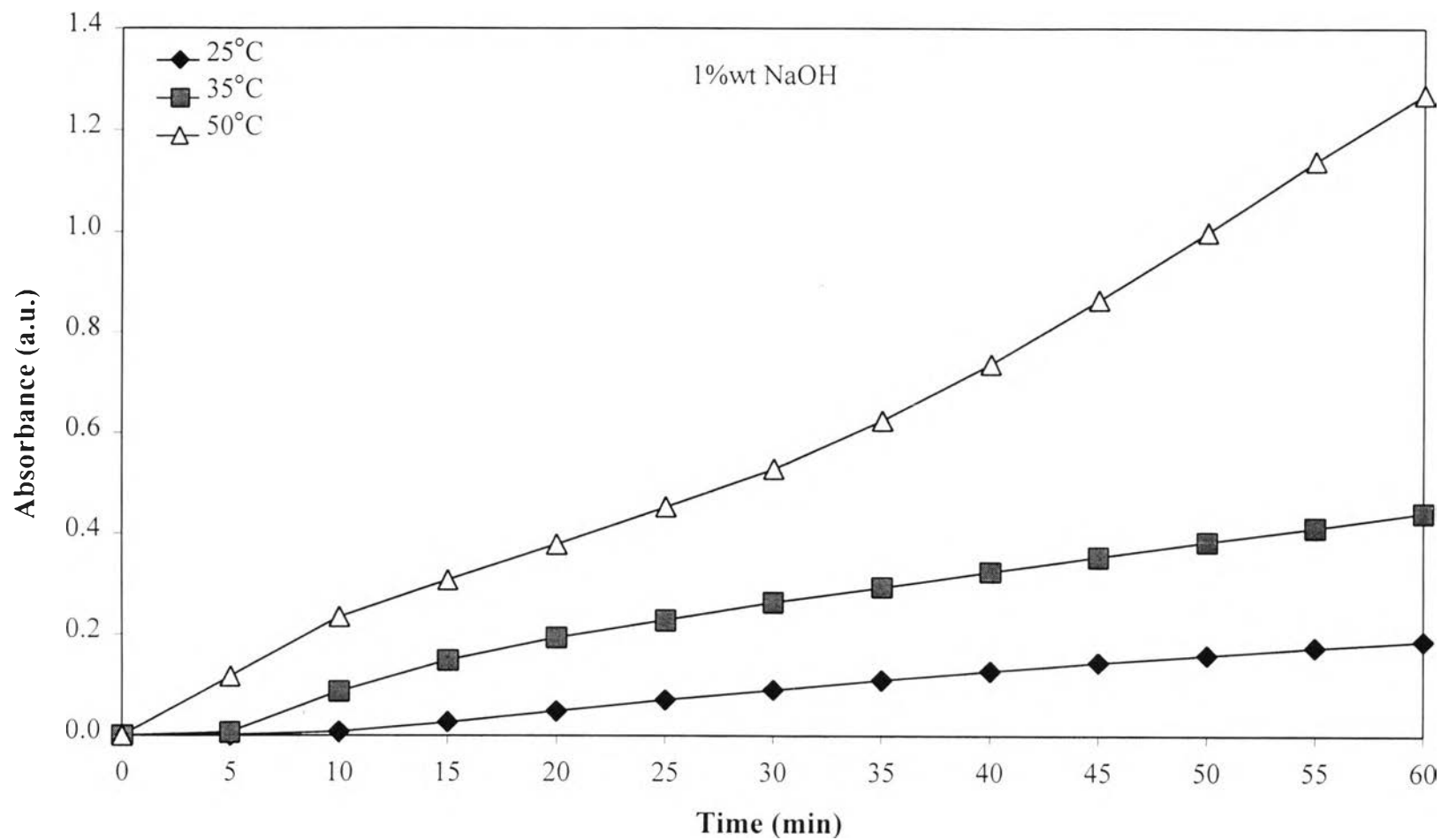


Figure 4.15 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine hydrochloride and time at the 0.25:1 hydroxylamine hydrochloride to acetaldehyde concentration.

119303026

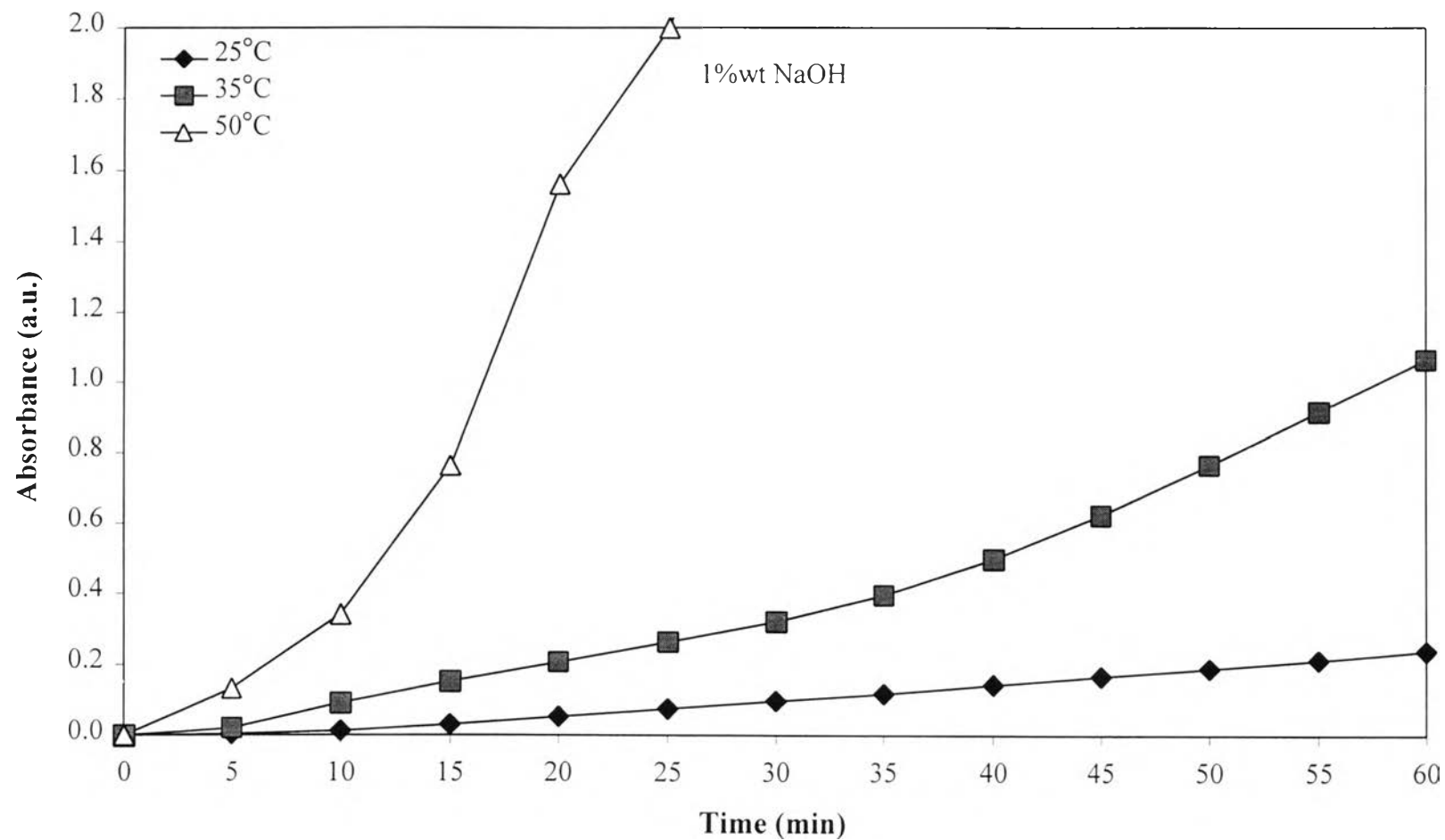


Figure 4.16 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine hydrochloride and time at the 0.1:1 hydroxylamine hydrochloride to acetaldehyde concentration.

Effects of the antipolymerant concentration on the aldol condensation can be seen in Figures 4.10 to 4.12. Figure 4.10 shows the absorbance of the yellow color in the presence of and in the absence of hydroxylamine hydrochloride at 25°C. The results indicate that hydroxylamine hydrochloride can reduce the yellow color, which is believed to be the cause of the fouling. At 60 minutes, the absorbances of the solution in the absence of the antipolymerant is 0.845 whereas the absorbance of the solution in the presence of the antipolymerant at the concentration ratios of 1:1, 0.5:1, and 0.25:1 are 0, 0.019, and 0.187, respectively. Ability of the antipolymerant to inhibit the aldol condensation increases with its concentration. The hydroxylamine can completely stop the aldol condensation at the ratio of 1:1. The complete stop of aldol condensation corresponds with the zero value of the absorbance. However, adding the antipolymerant at the concentration ratios of 0.1:1 and 0.25:1 promotes the aldol condensation before 30 minutes. The same effect can be observed at 35 and 50°C as seen in Figures 4.11 and 4.12.

Figures 4.13-4.16 show effects of temperature on the aldol condensation in the presence of the antipolymerant. At 25, 35, and 50°C, the concentration ratio of 1:1 can completely stop the aldol condensation, as shown in Figure 4.13. Figure 4.14 shows that although, at the concentration ratio of 0.5:1, the antipolymerant can not completely stop the aldol condensation, the aldol condensation can be inhibited to a certain extent. It is seen from Figures 4.13-4.16 that as the temperature increases, the aldol condensation reaction increases.

The results from both antipolymerants show that the hydroxylamine hydrochloride can inhibit or completely stop the aldol condensation because the reaction of hydroxylamine to acetaldehyde (reaction 4.1) consumes acetaldehyde much faster than the aldol condensation does. At time less than 30 minutes, the aldol condensation is promoted by the addition

of hydroxylamine hydrochloride, this antipolymerant is not suitable for the weak section in a caustic tower when the residence time in the section is less than 30 minutes, as shown in Figures 4.10-4.12.

4.3.2 Hydroxylamine Sulfate as an Antipolymerant

Results in this section were investigated at 25, 35, and 50°C with a fixed ratio of acetaldehyde to sodium hydroxide concentration at 1:1 in the 1%wt sodium hydroxide solution. The ratios of hydroxylamine sulfate to acetaldehyde concentration were varied from 0.1:1 to 1:1.

Effects of the antipolymerant concentration on the aldol condensation can be seen in Figures 4.17 to 4.19. Figure 4.17 shows the absorbance of the yellow color in the presence of and in the absence of hydroxylamine sulfate at 25°C. The results indicate that hydroxylamine hydrochloride can reduce the yellow color. At 60 minutes, the absorbance of the solution in the absence of antipolymerants is 0.845 whereas the absorbance of the solution in the presence of the antipolymerant at the concentration ratios of 1:1, 0.5:1, and 0.25:1 are 0, 0, and 0.042, respectively. Ability of the antipolymerant to inhibit the aldol condensation increases with its concentration. The hydroxylamine can completely stop the aldol condensation at the ratio of 1:1 and 0.5:1. The same effect can be observed at 35 and 50°C as seen in Figures 4.18 and 4.19.

Figures 4.20-4.22 show effects of temperature on the aldol condensation with the antipolymerant. At 25, 35, and 50°C, the concentration ratios of 1:1 and 0.5:1 can completely stop the aldol condensation, as shown in Figures 4.20 and 4.21. Figure 4.22 shows that at the concentration ratio of 0.25:1, although the antipolymerant cannot completely stop the aldol condensation, the aldol condensation can be inhibited to a certain extent. It is seen from Figures 4.20-4.22 that the aldol condensation reaction increases as an increase in temperature.

The results for both antipolymerants show that the hydroxylamine sulfate can inhibit or completely stop the aldol condensation. because the reaction of hydroxylamine to acetaldehyde (reaction 4.1) can consume the acetaldehyde much faster than the aldol condensation does.

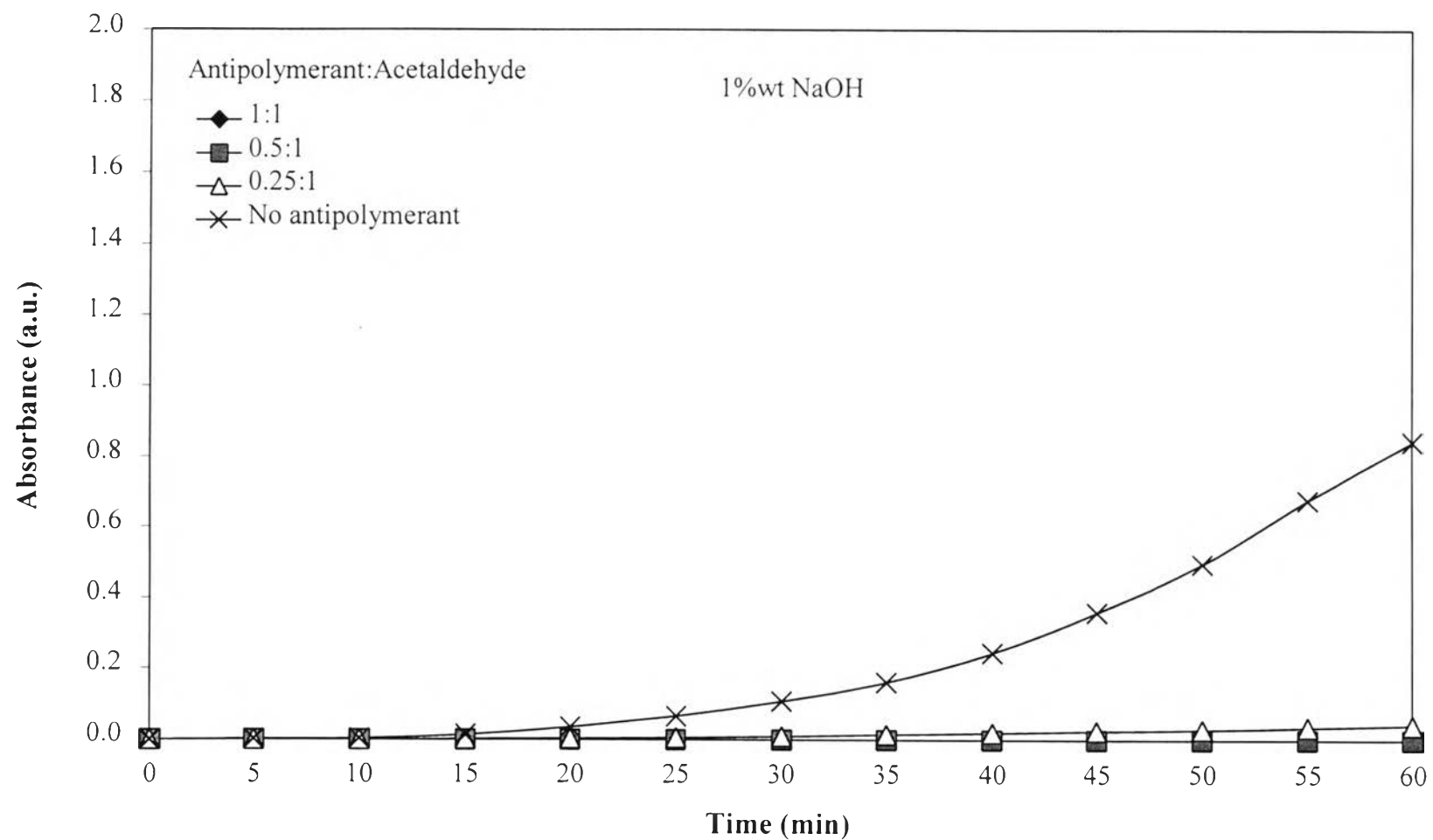


Figure 4.17 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine sulfate and time at 25°C.

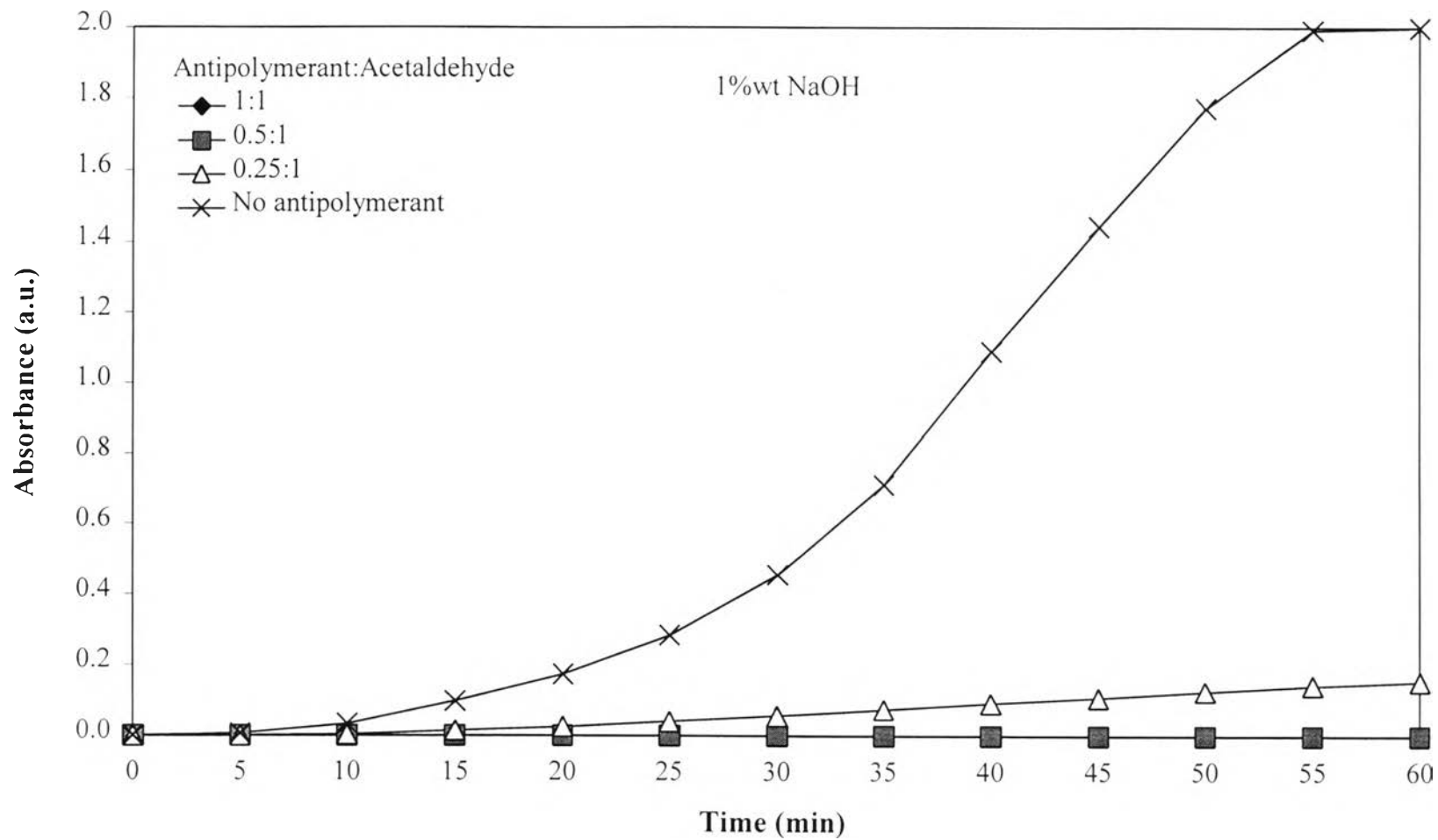


Figure 4.18 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine sulfate and time at 35°C.

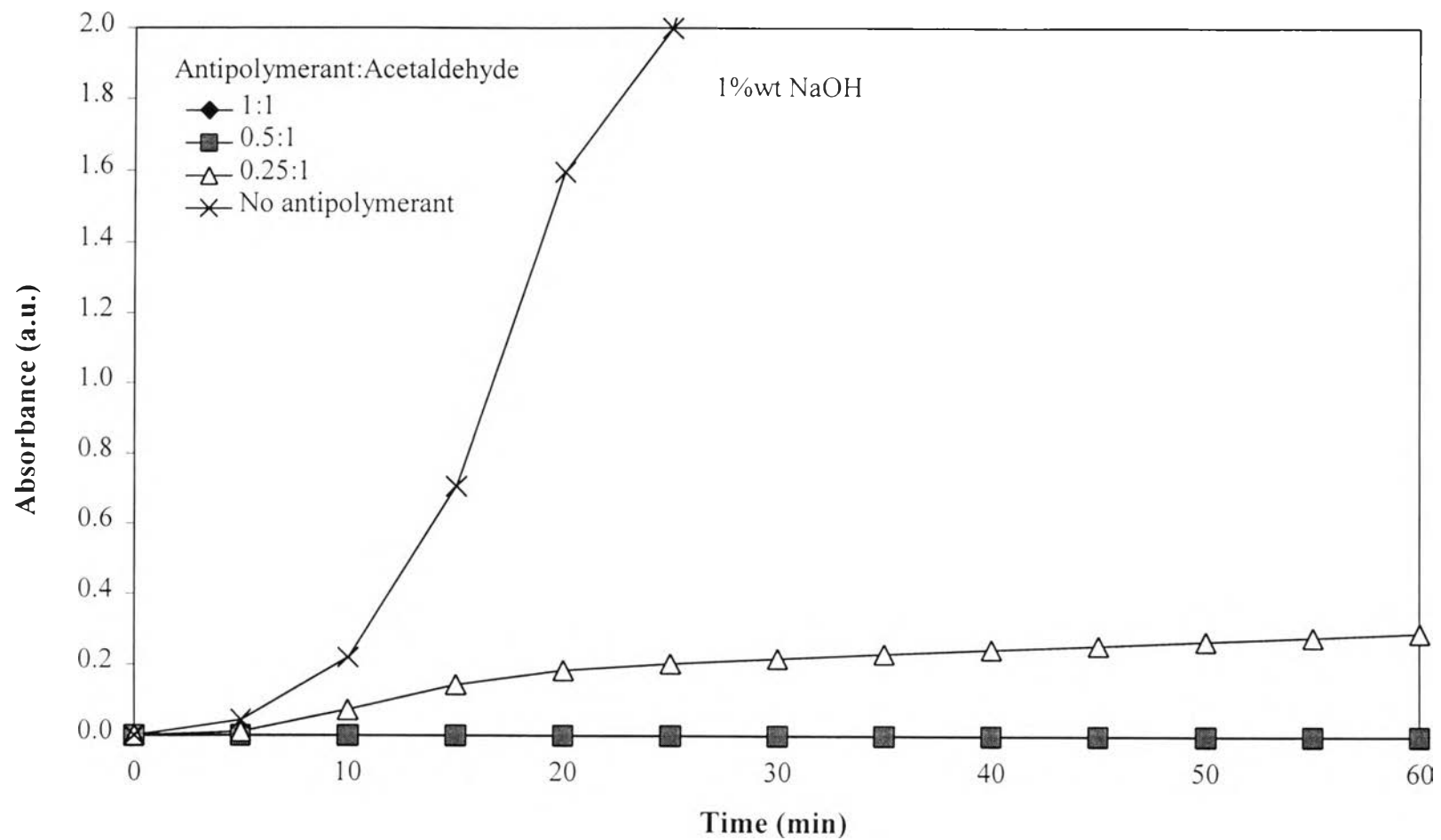


Figure 4.19 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine sulfate and time at 50°C.

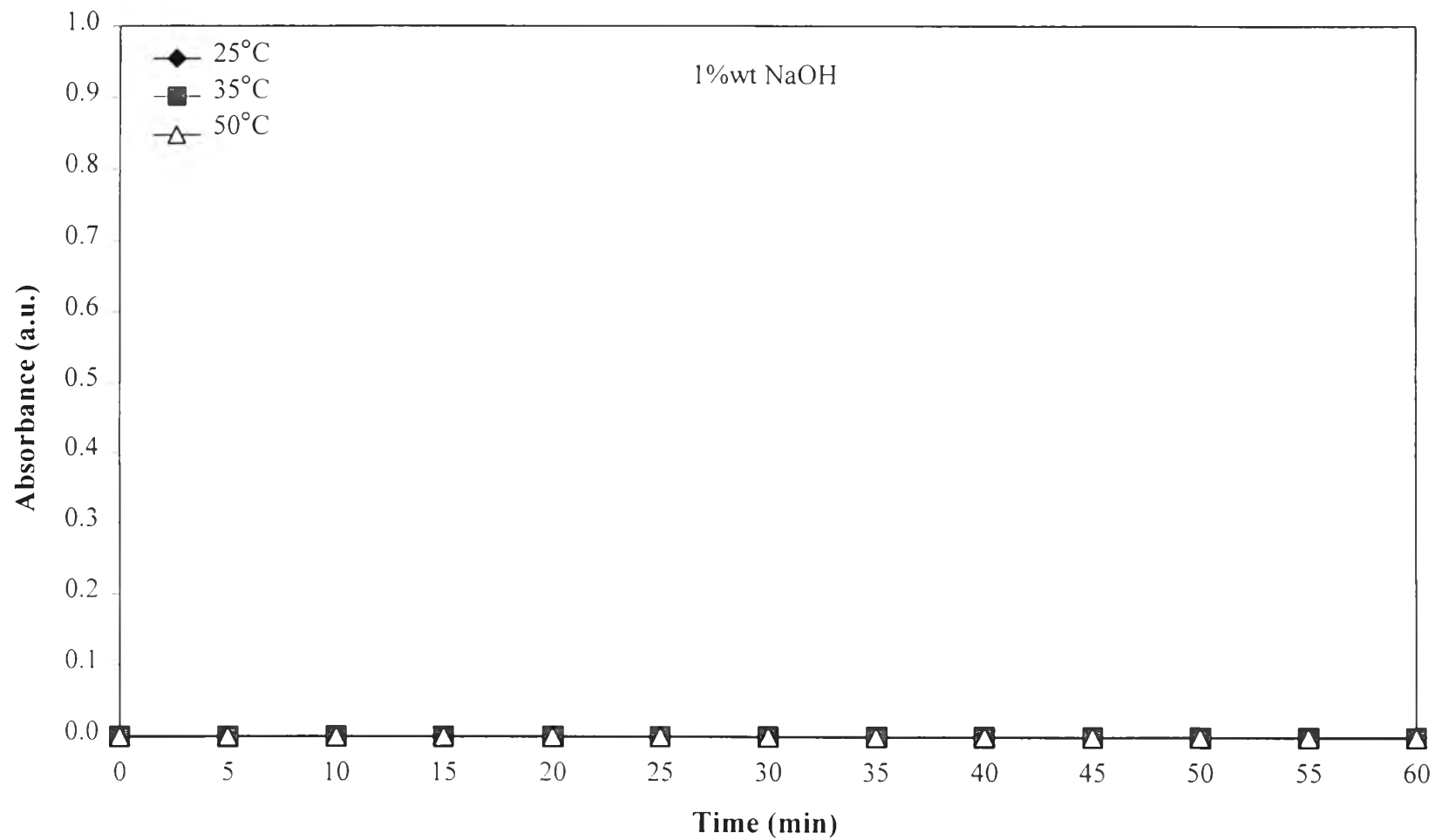


Figure 4.20 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine sulfate and time at the 1:1 hydroxylamine sulfate to acetaldehyde concentration.

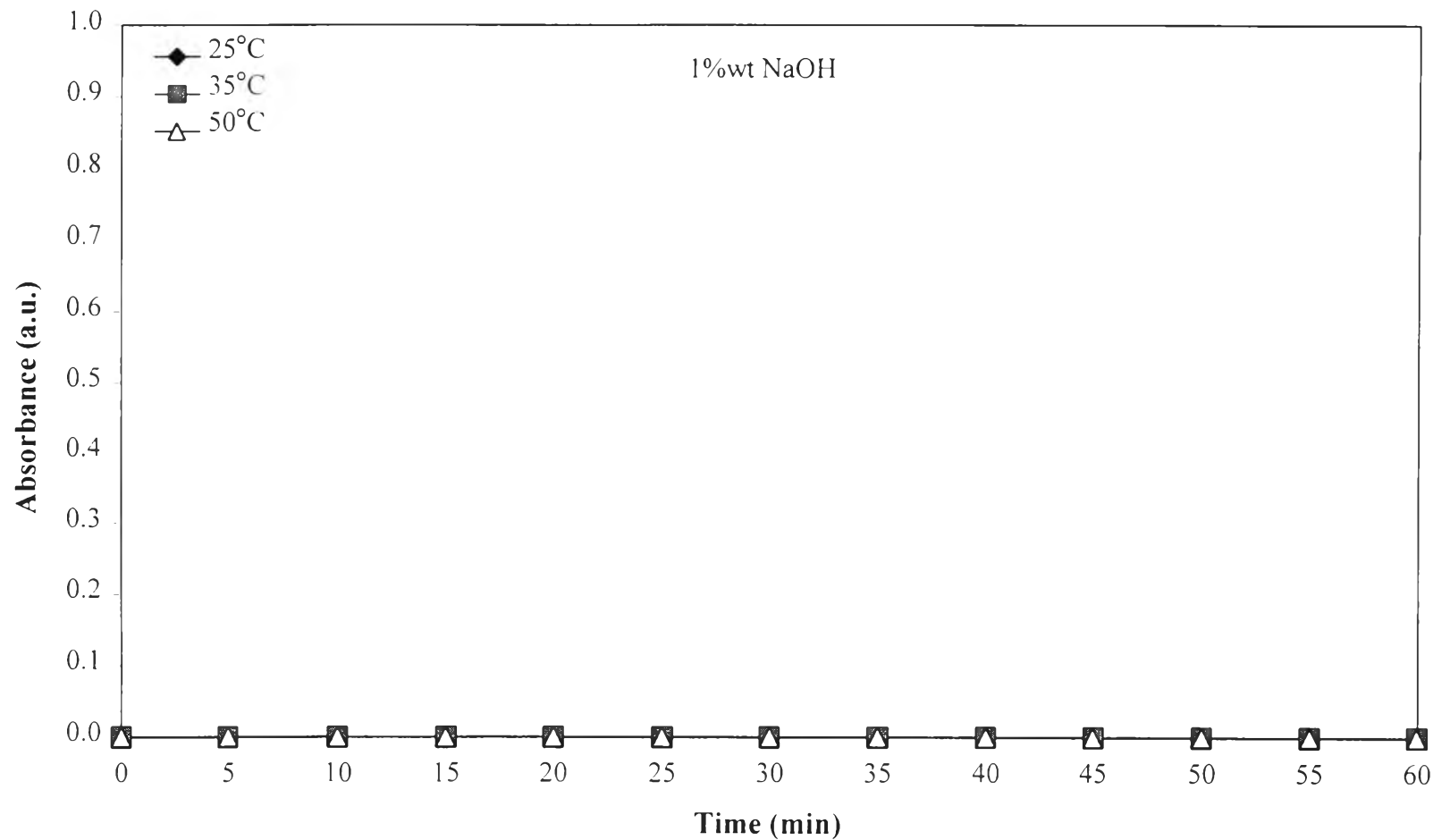


Figure 4.21 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine sulfate and time at the 0.5:1 hydroxylamine sulfate to acetaldehyde concentration.

4.3.3 Efficiency of Antipolymerants

Comparison of antipolymerant efficiency on the fouling reduction is essential for a user in terms of plant efficiency and economics. Experimental data from the antipolymerant concentration and temperature effect studied were made in this comparison.

Figure 4.23 shows the absorbance of the yellow color in the solution in the presence of two antipolymerants and in the absence of any antipolymerant. It can be reduced from the figure that hydroxylamine hydrochloride and hydroxylamine sulfate can substantially reduce the yellow color. For example at 60 minutes and the concentration ratio of 0.25:1, the absorbance of the solution in the presence of hydroxylamine hydrochloride is 0.019 and 0.043 in the presence of hydroxylamine sulfate. The hydroxylamine hydrochloride can completely stop the aldol condensation at the concentration ratio of 1:1; and 0.5:1 and 1:1 for hydroxylamine sulfate to completely stop the aldol condensation. The figure also indicates that the higher the hydroxylamine salts concentration, the more the aldol condensation can be inhibited. In addition, hydroxylamine sulfate can inhibit the aldol condensation more than hydroxylamine hydrochloride can because hydroxylamine sulfate required to completely stop the aldol condensation is less than what is needed for hydroxylamine hydrochloride to have the same effect. So hydroxylamine sulfate is the best antipolymerant in this system.

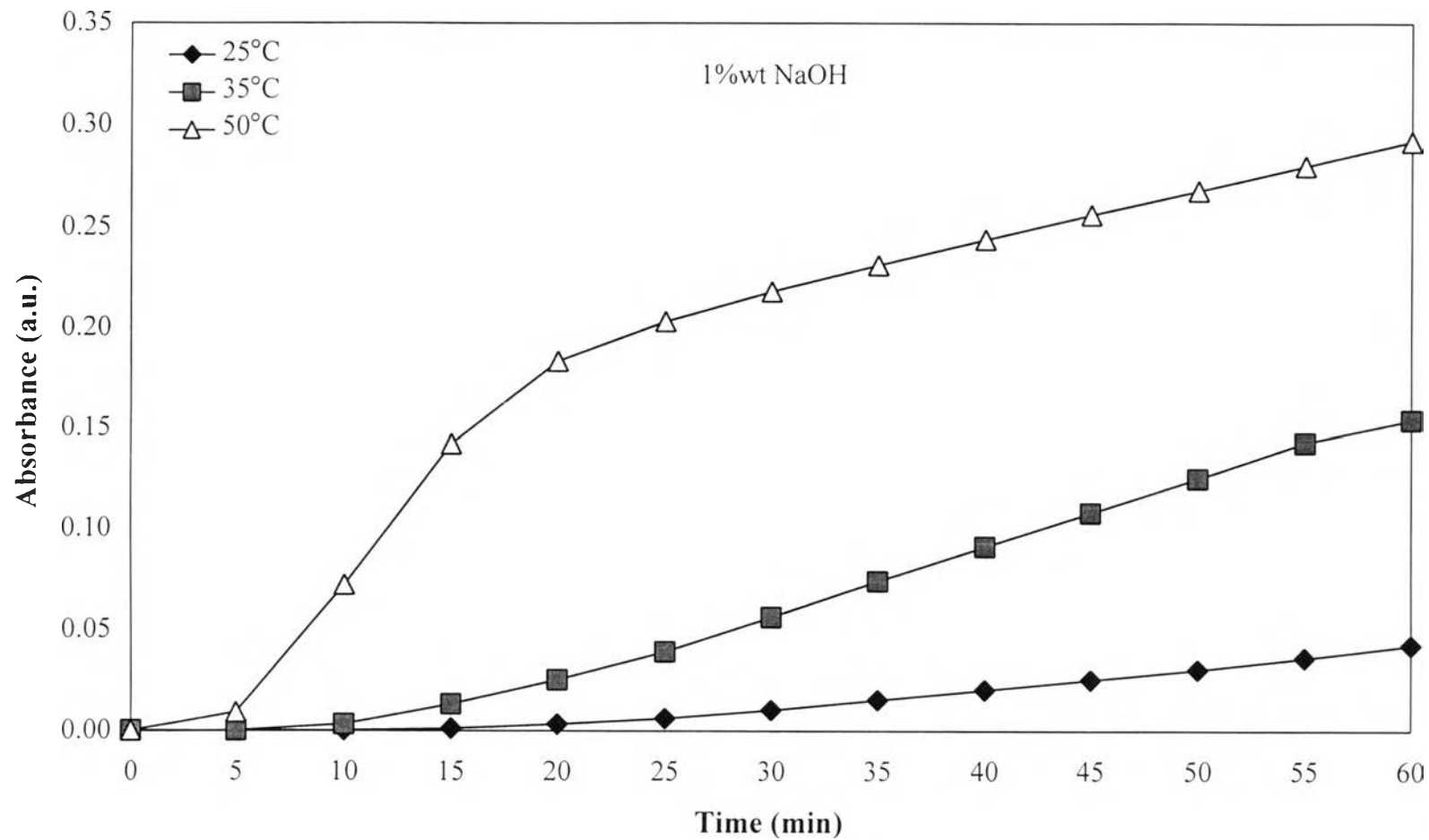


Figure 4.22 Relationship between the absorbance of the yellow color of the aldol product from the addition of hydroxylamine sulfate and time at the 0.25:1 hydroxylamine sulfate to acetaldehyde concentration.

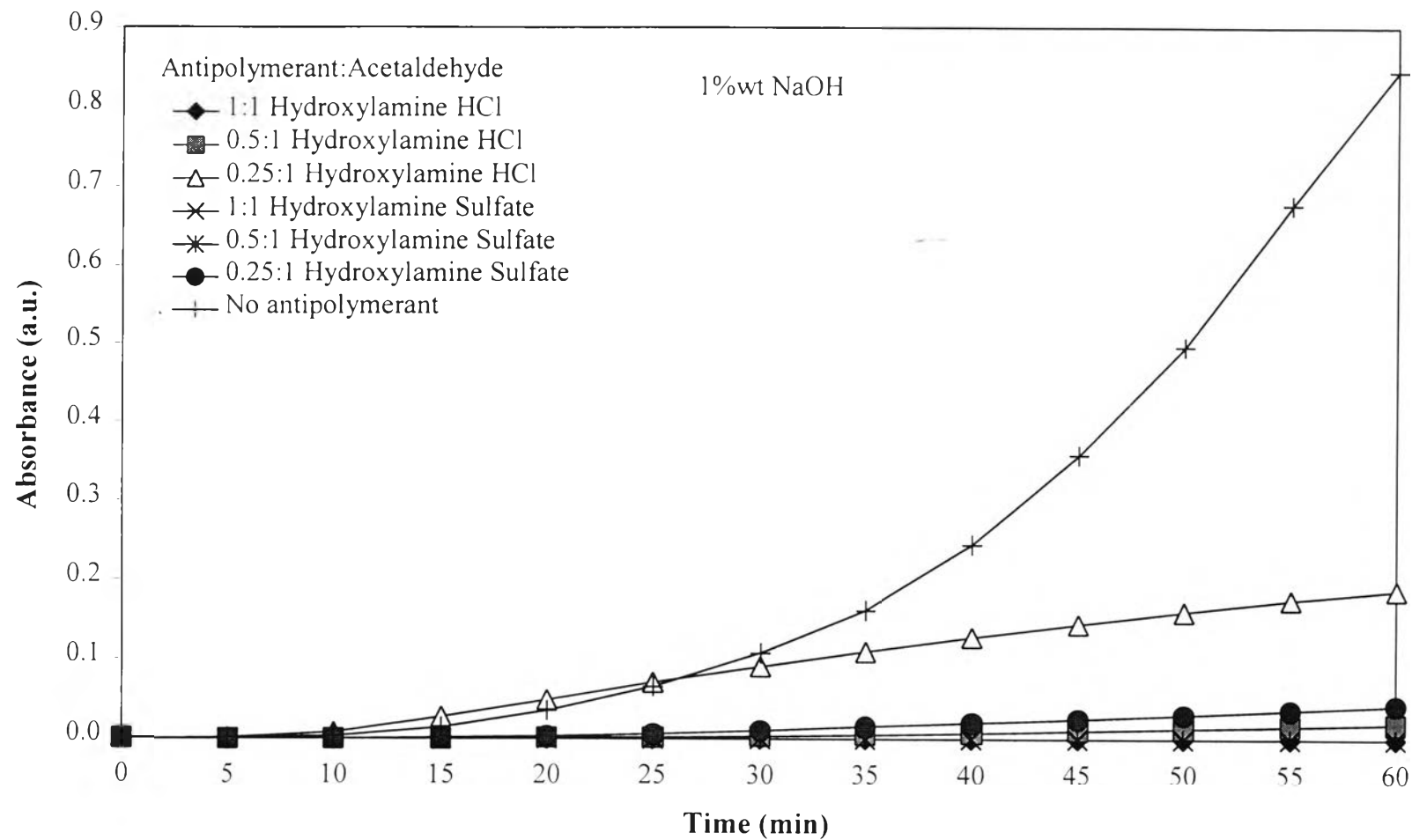


Figure 4.23 Comparison of the antipolymerant efficiency at 25°C.

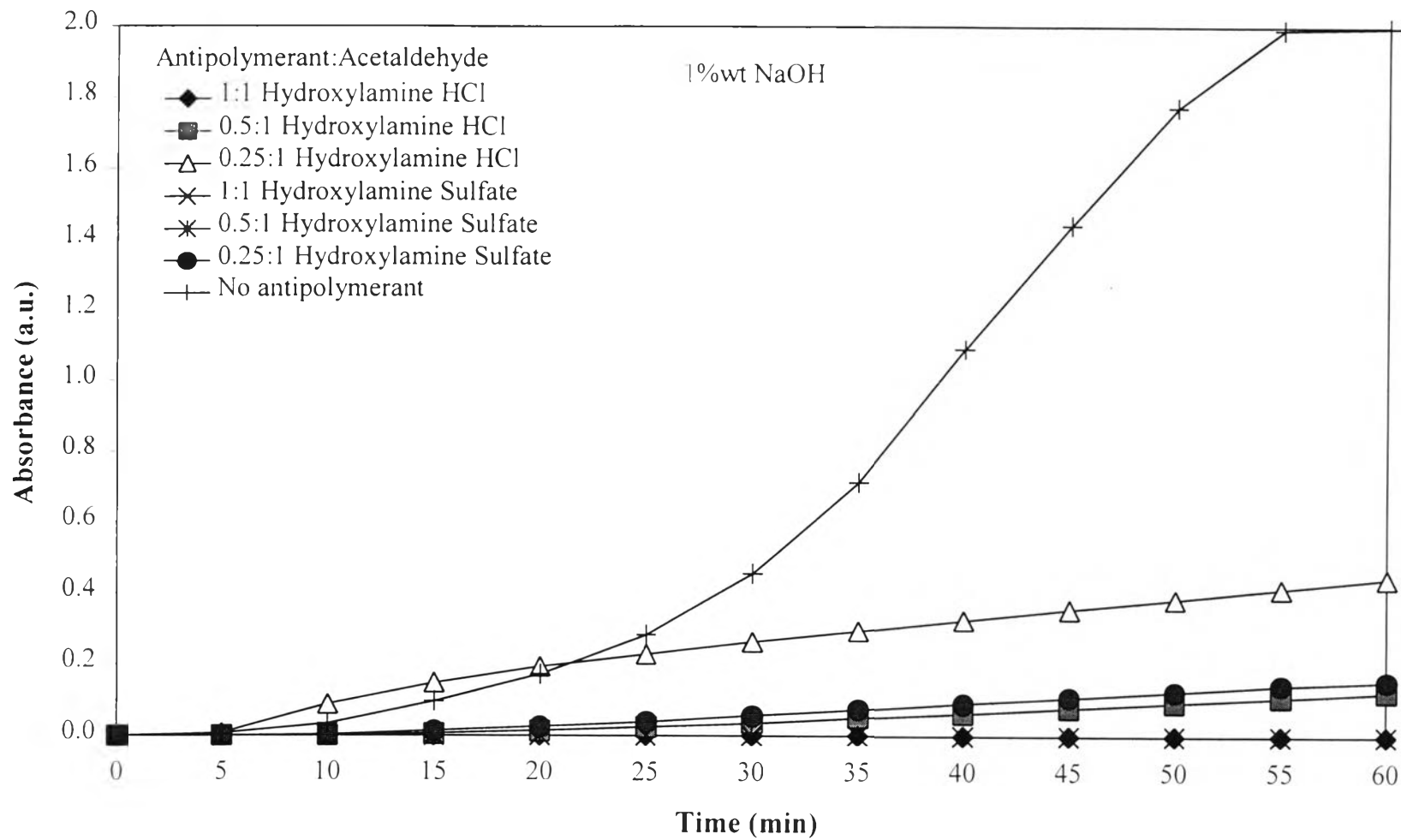


Figure 4.24 Comparison of the antipolymerant efficiency at 35°C.

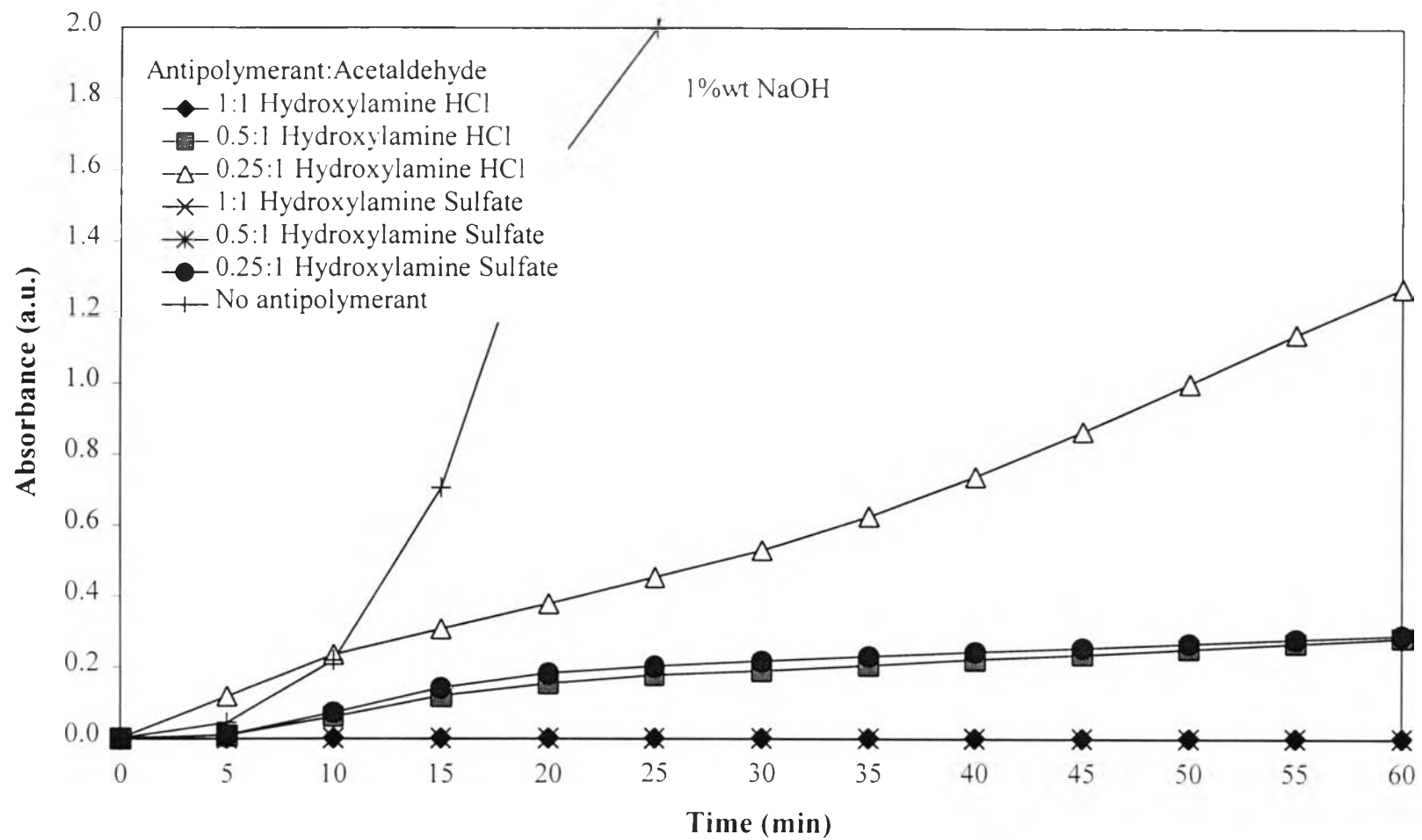


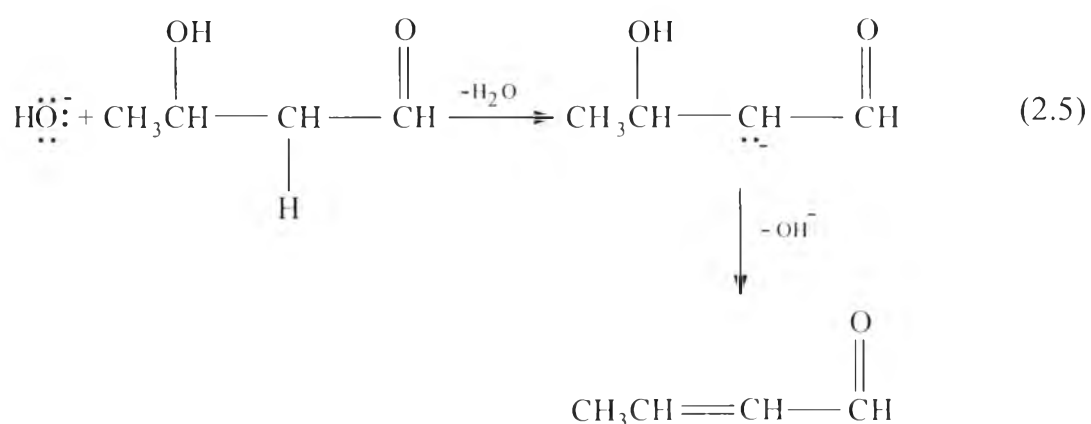
Figure 4.25 Comparison of the antipolymerant efficiency at 50°C.

4.4 Effects of Sodium Sulfate on the Aldol Condensation

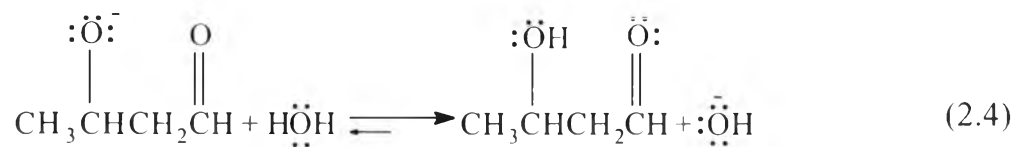
In an ethylene plant, fouling is not only found in the caustic tower but also found in the oxidation reactor, which is in the downstream of the caustic treater. The oxidation reactor is used to change sodium sulfide in the spent caustic to sodium sulfate prior to entering the biotreater for the final wastewater treatment. Sulfide is not allowed in the water effluent leaving the factory. In this reactor, the fouling was found as a red polymer. It was found in this work that sodium sulfate can promote the aldol condensation fouling in the oxidation reactor.

The results in Figures 4.25 and 4.26 show that sodium sulfate can promote the aldol condensation. At 60 minutes, the absorbance of the solution in the absence of sodium sulfate is 0.845 while the absorbance of the solution in the presence of sodium sulfate is 0.985 and 1.153 at the ratios of sodium sulfate to acetaldehyde 0.5:1 and 1:1, respectively.

Sodium sulfate promotes the aldol condensation because sodium sulfate removes water from the solution in the dehydration step in the aldol condensation mechanism (reaction 2.5).



When the dehydration reaction is not balance, the aldol products will be produced faster.



When the product from reaction (2.4) reaches the oxidation reactor, the production of the aldol products will be promoted.

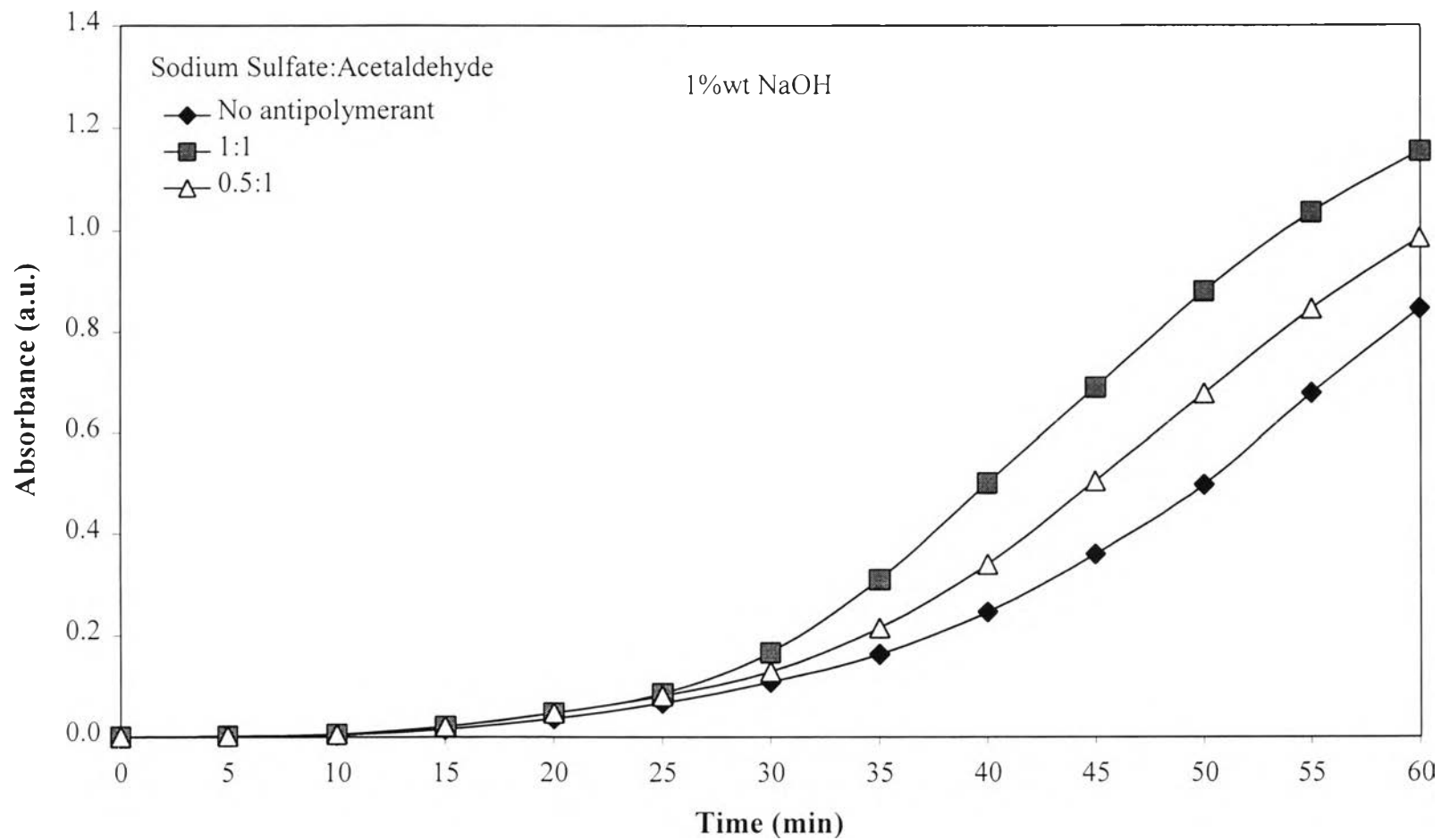


Figure 4.26 Relationship between the absorbance of the yellow color of the aldol product from the addition of sodium sulfate and time at 25°C.