CHAPTER III

RESULTS AND DISCUSSION

3.1   Gross Observations

Yellow oil, the fouling in internal caustic tower, found in both strong caustic section and weak caustic section, was collected at the drums. It possesses light yellow color owing to the presence of chromophoric groups but, at the top surface, it has darker color, red or red-brown, which is due to impurities frequently produced by air oxidation. So yellow oil may contain the usual chromophoric groups or functional groups that are easily oxidized.

Initially when yellow oil is drained from the caustic tower, it is a viscous liquid similar to a latex paint yet when the time increases it becomes more viscous. Finally yellow oil changes to a sticky solid which has dark color. These changes show that yellow oil increases in molecular weight with time.

3.2   Characterization of the Yellow Oil and Aldol Condensation Products

3.2.1   Elemental Analysis

The percentage of elements carbon, hydrogen, nitrogen, sulfur, and oxygen is reported by two operating mode, CHNS mode and O mode, so the sum of the percentages of elements C, H, N, S, O is not exactly 100 %. The

quantitative elemental analyses of yellow oil sample collected from the ethylene plant and the aldol condensation products at various reaction times are summarized in Table 3.1.

Table 3.1 Elemental analysis data of yellow oil and products from aldol condensation reaction

Sample	CHNS mode				O mode
	%C	%H	%N	%S	%O
yellow oil	70.95	7.54	2.38	6.95	13.32
2hr	67.76	7.74	2.29	1.27	19.88
3hr	68.92	7.99	2.54	1.3	19.64
4hr	70.25	8.08	2.28	1.35	17.79
5hr	69.5	7.94	1.83	1.26	18.33
6hr	70.34	8.1	2.72	1.28	19.16
7hr	70.97	8.12	2.83	1.25	19.21
8hr	70.2	8.12	2.33	1.32	22.09
9hr	64.38	7.48	1.49	1.21	24.93

* The number of hours indicates the reaction time of each sample in aldol condensation reaction

The CHNS analyzer is not good for sulfur and nitrogen determination because the starting materials in aldol condensation reaction do not have any nitrogen or sulfur. But the CHNS analyzer gives values of 1.5 % sulfur and 2 % nitrogen for the condensation products. This means that even for yellow oil sample the maximum sulfur may be about 4 % only and the values for nitrogen should be ignored completely.

For the conversion of elemental analysis data into an empirical formula, the first step is to divide the percentage of each element by its atomic weight, and the second is to divide the resulting numbers by the smallest one to determine the atomic ratios as shown in Table 3.2.

Table 3.2 The conversion of elemental data into an empirical formula of the yellow oil sample

Element	Percentage		Atomic Weight				Atomic ratio
C	70.95	÷	12.01	=	5.91		7.12
H	7.54	÷	1.01	=	7.47		9
N	0	÷	14.01	=	0	× 1/0.83	0
S	4.00	÷	32.06	=	0.12		0.14
O	13.32	÷	16.00	=	0.83		1

From the above results, the simplest empirical formula of the yellow oil can therefore be written as $C_7H_9O_1S_{0.14}$. The value of sulfur is very low. It shows that sulfur is not the main component in the chemical structure of the yellow oil and it may come from the impurities. The presence

of oxygen is important for the assumption that yellow oil forms polymer by ketone or aldehyde condensation polymerization.

Also, the simplest empirical formula of aldol condensation products can be calculated by the same method. The empirical formula is found to be $C_4H_6O_1$ for most samples. The ratio of hydrogen to carbon is 1.5 which indicates conjugated system of linear molecules.

Consider the aldol condensation of acetaldehyde in Figure 3.1, it is difficult to predict which one of the products will be obtained between aldol product and α, β unsaturated aldehyde.

$$2 \; H\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 \quad \xrightarrow{OH^-} \quad CH_3\text{-}\overset{\overset{\displaystyle OH}{|}}{C}H\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H$$

aldol product

$$H\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH\text{=}CH\text{-}CH_3 \quad \xleftarrow[\text{heat}]{OH^-}$$

α , β unsaturated aldehyde
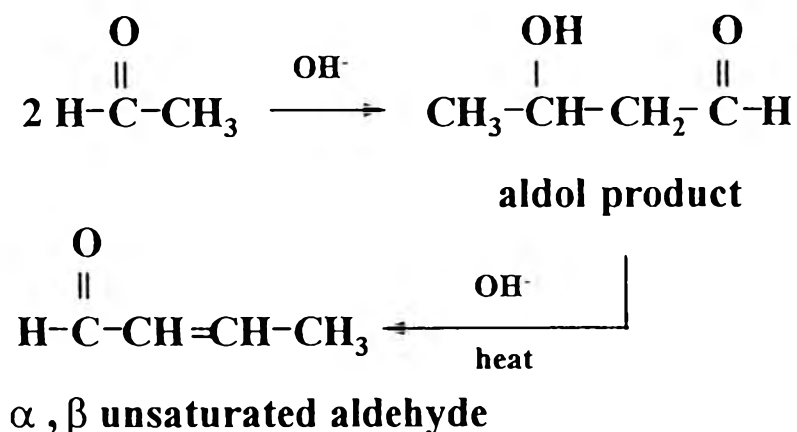
Figure 3.1 The aldol condensation of acetaldehyde under basic condition.

Aldol product represents the empirical formula $C_4H_8O_2$ and α, β unsaturated aldehyde represents $C_4H_6O_1$. The empirical formula of α, β unsaturated aldehyde is similar to that of iaboratory aldol condensation product.

3.2.2 Fourier Transform Infrared Spectroscopy

The infrared spectrum of yellow oil is shown in Figure 3.2 . The complete trace was taken of KBr pellet. Infrared absorption of yellow oil molecule is summarized in Table 3.3.

Table 3.3 Band assignments of yellow oil spectrum

Functional Groups	Wave Number (cm^{-1})
H-bonded, -OH	3410
= C-H	3048
Alkyl absorption	
γ_{as} CH_3	2956
γ_{as} CH_2	2924
γ_s CH_3	2868
γ_s CH_2	2856
δ_{as} CH_3	1453
δ_{as} CH_2	1375
aldehydic C-H stretch	2731
Carbonyl absorption	
C=O α, β - unsaturated	1698
conjugated C=C with C=O	1604
inplane and out-of-plane bending	near 1000
of the alkene C-H bonds	
methylene rock	near 700

The intense, broad band near 3410 cm^{-1} represents the hydrogen bonded O-H stretch. The bond at 3048 cm^{-1} represents the olefinic C-H stretch, C-H stretching vibration in which the carbon atom is present in the alkene lingkage. Two distinct bands occur at 2956 cm^{-1} and 2868 cm^{-1}. The first of these results from the asymmetrical stretching mode in which 2 C-H bonds of the methyl group are extending while the third one is contracting ($\gamma_{as}CH_3$). The second arises from symmetrical stretching (γ_sCH_3). The presence of several methyl groups in a molecule results in strong absorption at this position. The asymmetrical stretching ($\gamma_{as}CH_2$) and symmetrical stretching (γ_sCH_2) of methylene groups occur near 2924 cm^{-1} and 2856 cm^{-1} respectively. The symmetrical bending vibration of methyl group (δ_sCH_3) occurs near 1375 cm^{-1} with the asymmetrical bending vibration ($\delta_{as}CH_3$) near 1450 cm^{-1}. The band near 700 cm^{-1} shows the methylene rocking vibration.

The C=O (α, β unsaturated aldehyde) stretching band appears at 1698 cm^{-1}. Conjugation lower the carbonyl stretching frequencies of ketone and aldehyde because the partial pi-bonding character of the single bond between the conjugated double bonds reduces the electron density of the carbonyl pi bond, lowering the stretching frequency to 1710 - 1685 cm^{-1}. The assignment of a carbonyl band to an aldehyde can be confirmed by the appearance of a band near 2720 cm^{-1}, arising from C-H stretching vibration of the aldehyde group. The band at 1604 cm^{-1} represents the conjugated C=C double-bond stretch with attaching C=O

The lack of strong absorption bands in the 909 - 650 cm^{-1} region generally indicates a nonaromatic structure of the yellow oil. The absorptions in fingerprint region are difficult to assignment but they can be used to confirm

the presence of functional groups such as in-plane and out-of-plane bending of the alkene C-H bond near 1000 cm^{-1} .

Figure 3.3 shows the spectrum of the yellow oil relative to the spectrum of aldol condensation product. They are quite different espicially in fingerprint region. Both samples primarily have CH_3 and CH_2 groups. Their ratio is slightly different, with the 2956 peak higher than the 2924 peak and the reverse is true in laboratory sample. This difference simply shows that in the yellow oil sample the CH_2/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 1689 and 1673 peaks may belong to the same type of oxygen-carbon bond.
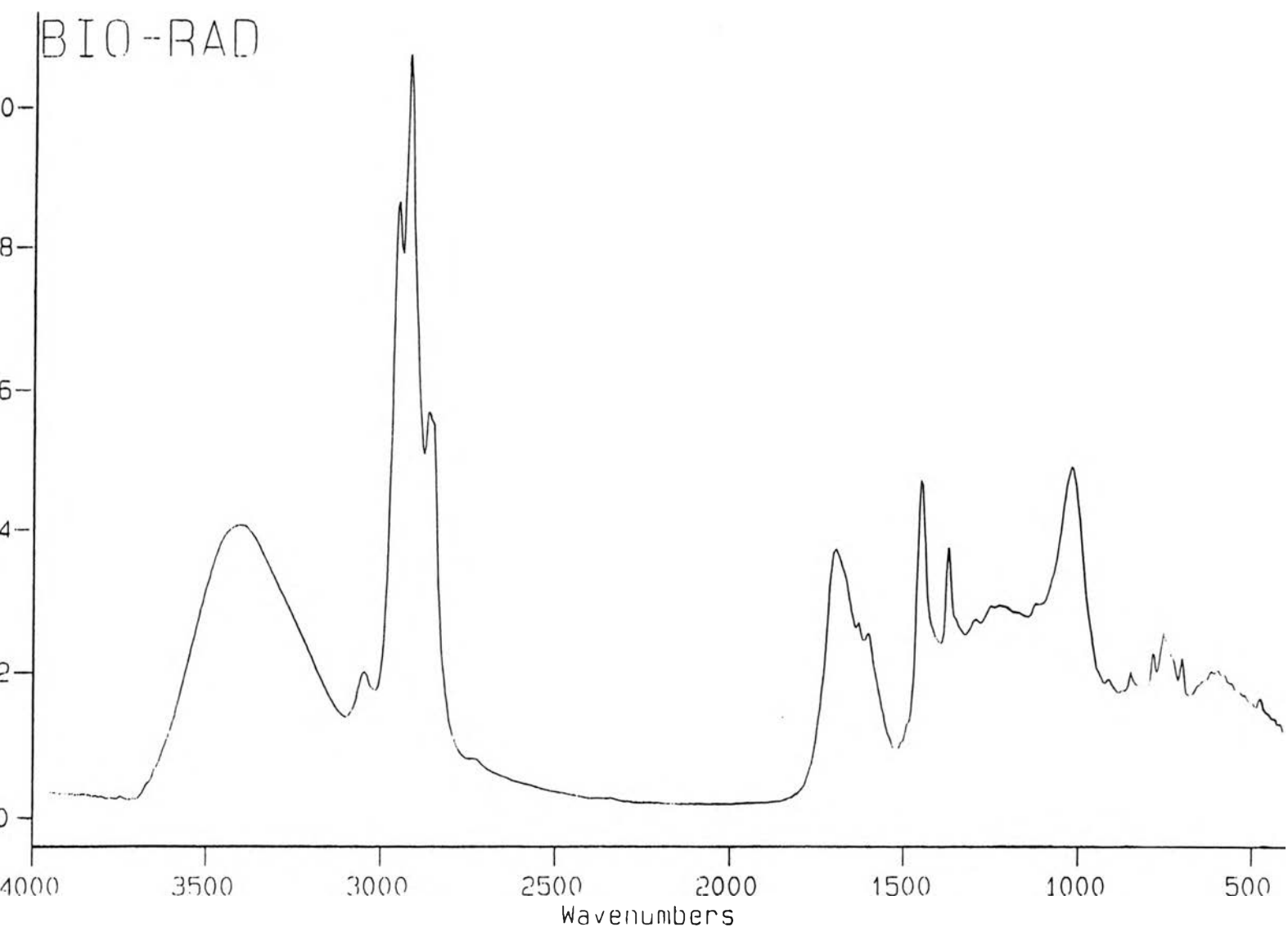
Figure 3.2 Spectrum of yellow oil (solid) prepared by KBr pellet technique.

ALDOL CONDENSATION PRODUCT
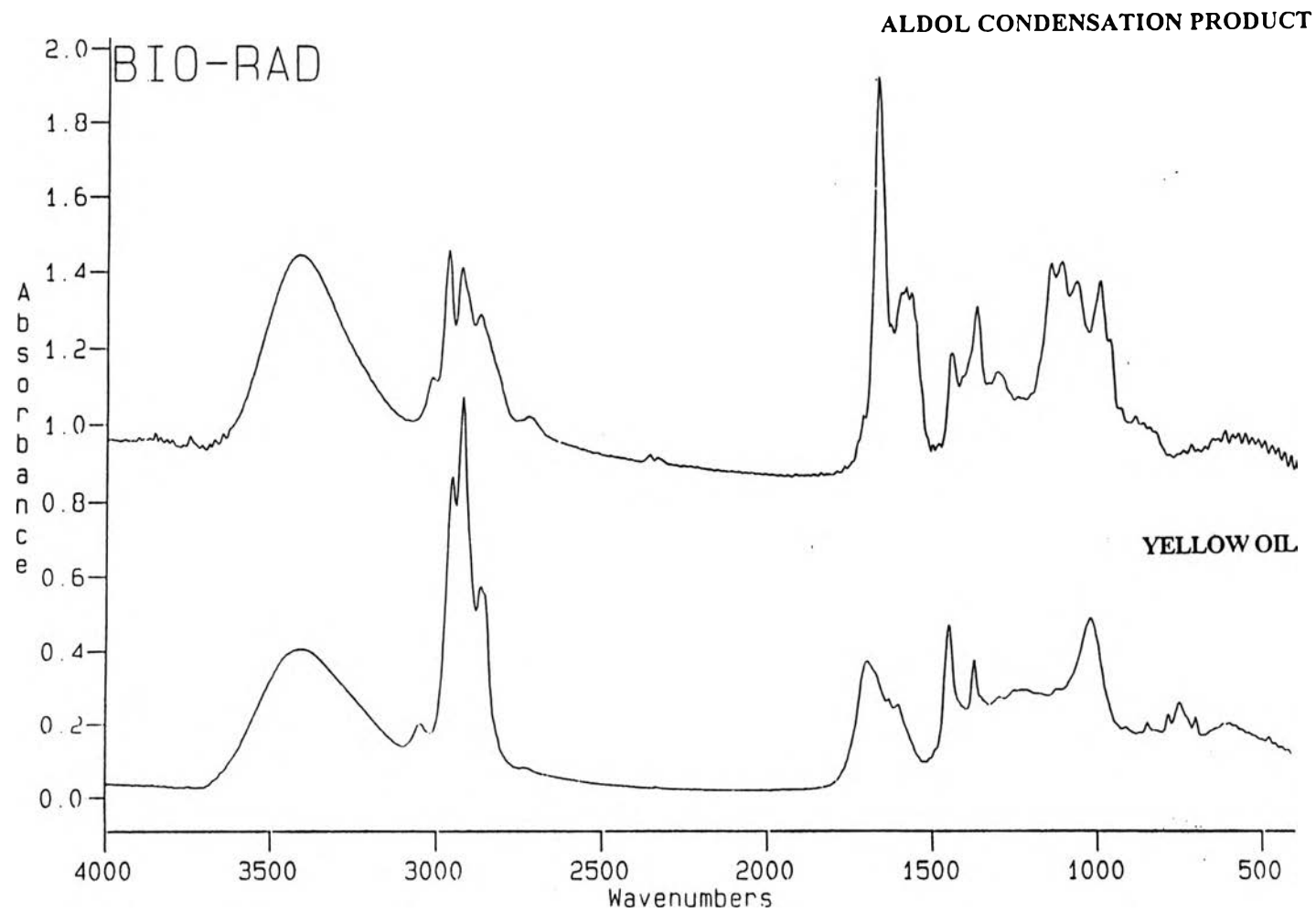
YELLOW OIL

Figure 3.3 Comparison between spectrum of yellow oil and spectrum of aldol condensation product.
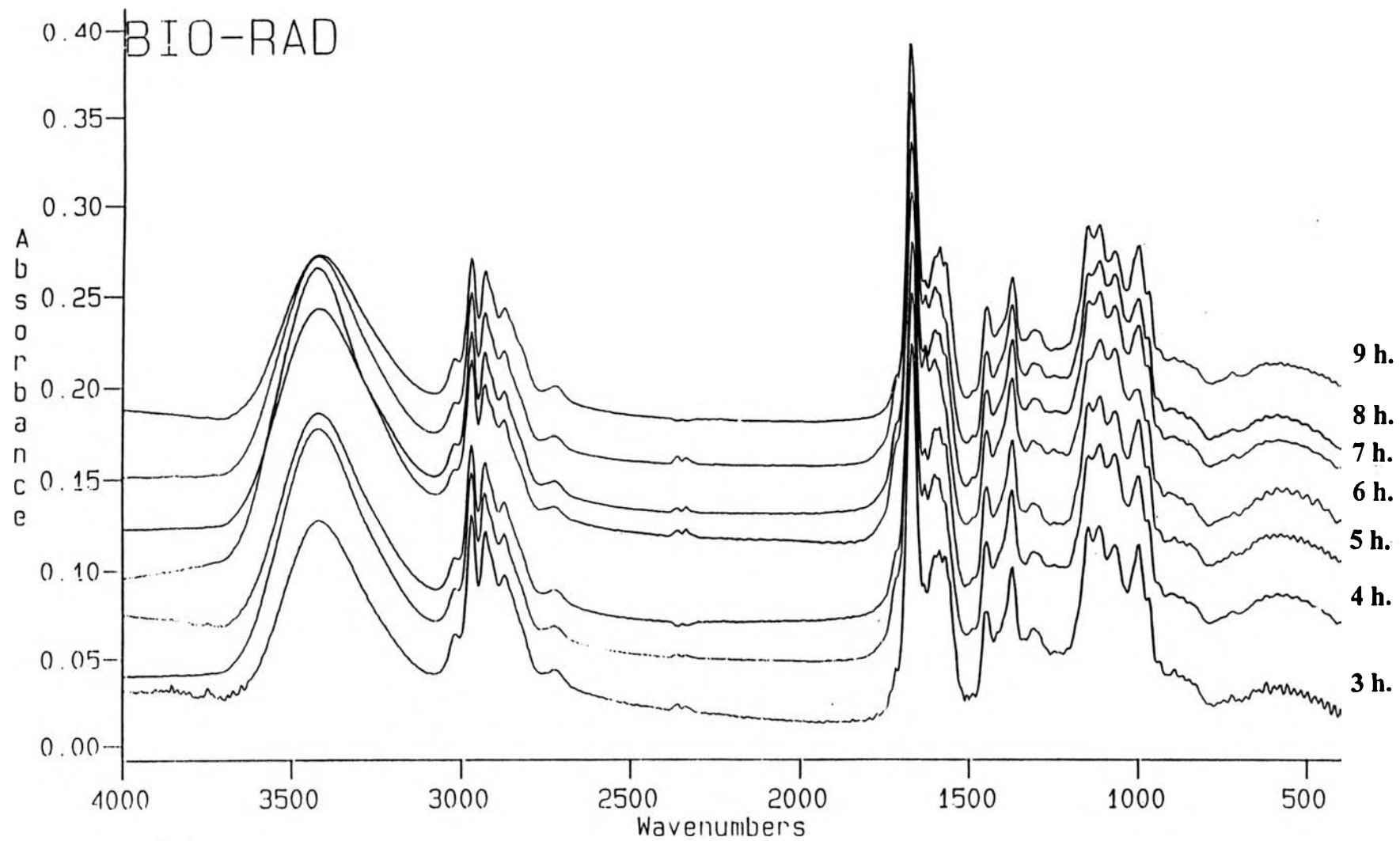
Figure 3.4 Spectra of aldol condensation products in various times.
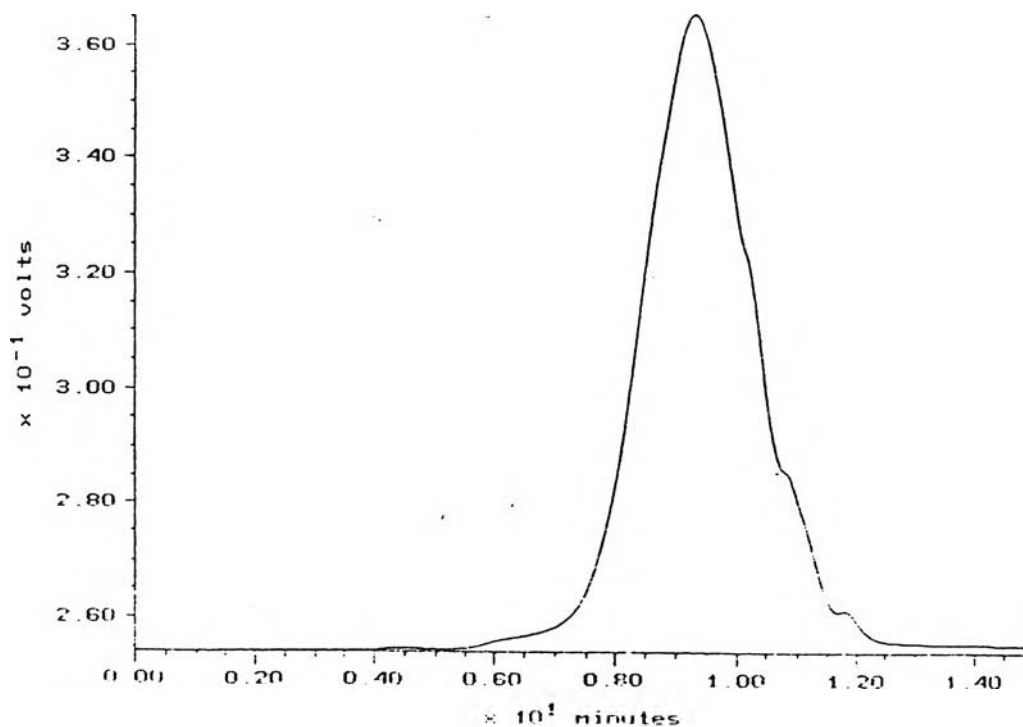
3.2.3 Size Exclusion Chromatography (SEC)

Figure 3.5 The molecular weight distribution of yellow oil.

As shown in Figure 3.5, the chromatogram of yellow oil is quite broad and the shoulder of the curve has distinct steps so the yellow oil may be composed of dimer, trimer, oligomer, and polymer. The weight average molecular weight of yellow oil was found to be 4,245. This leads to the conclusion that the components of yellow oil are mostly oligomers with low molecular weights.

Molecular weight distribution of yellow oil was found to be broader than molecular weight distribution of the aldol condensation product. It also has higher weight average molecular weight. These results are shown in Figure 3.6.

Size exclusion chromatography also showed that molecular weight increases with time in aldol condensation reaction. This indicates that aldol condensation reaction continues with time resulting in increasing molecular weight of products. The double bond of C=C or C=O may be responsible for the increase in the molecular weight through polymerization. Figure 3.7 shows the molecular weight distribution of aldol condensation products as a function of reaction time.
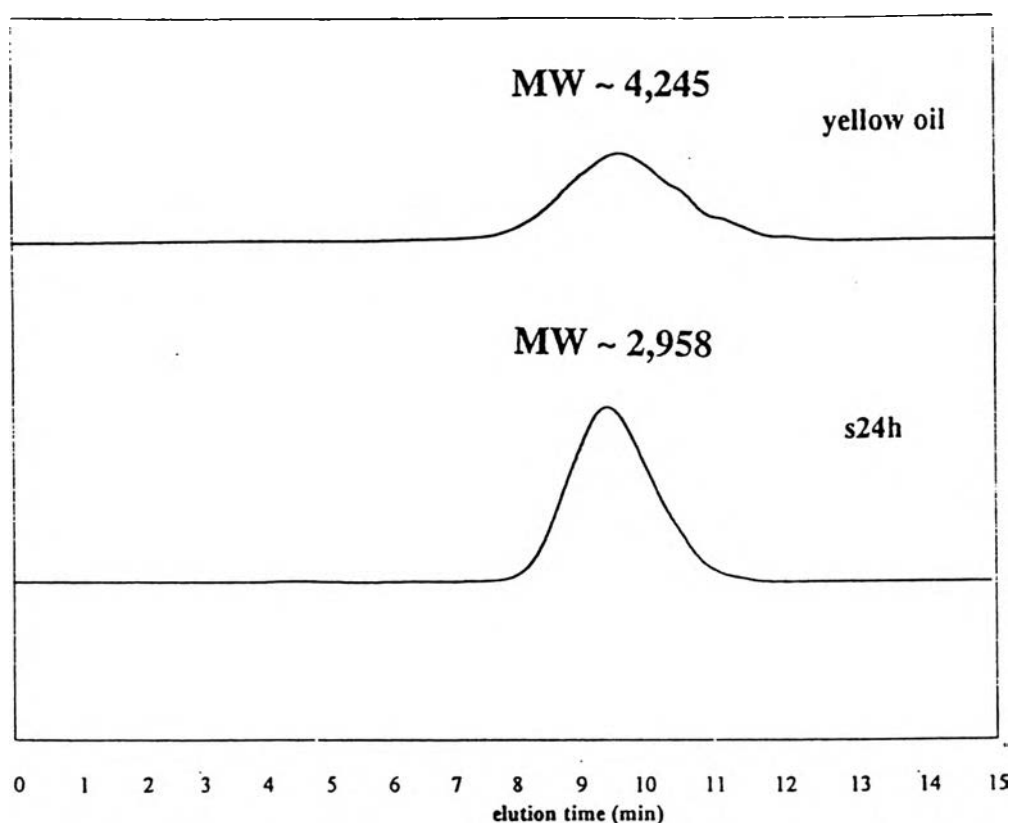

Figure 3.6 The molecular weight distributions of yellow oil sample and sample from aldol condensation, reaction time 24 hours.

Combination of the results shown in Figure 3.4 and 3.7 leads to the conclusion that there is very little change in the molecular structure with time, even though the molecular weight increases. This can happen if the

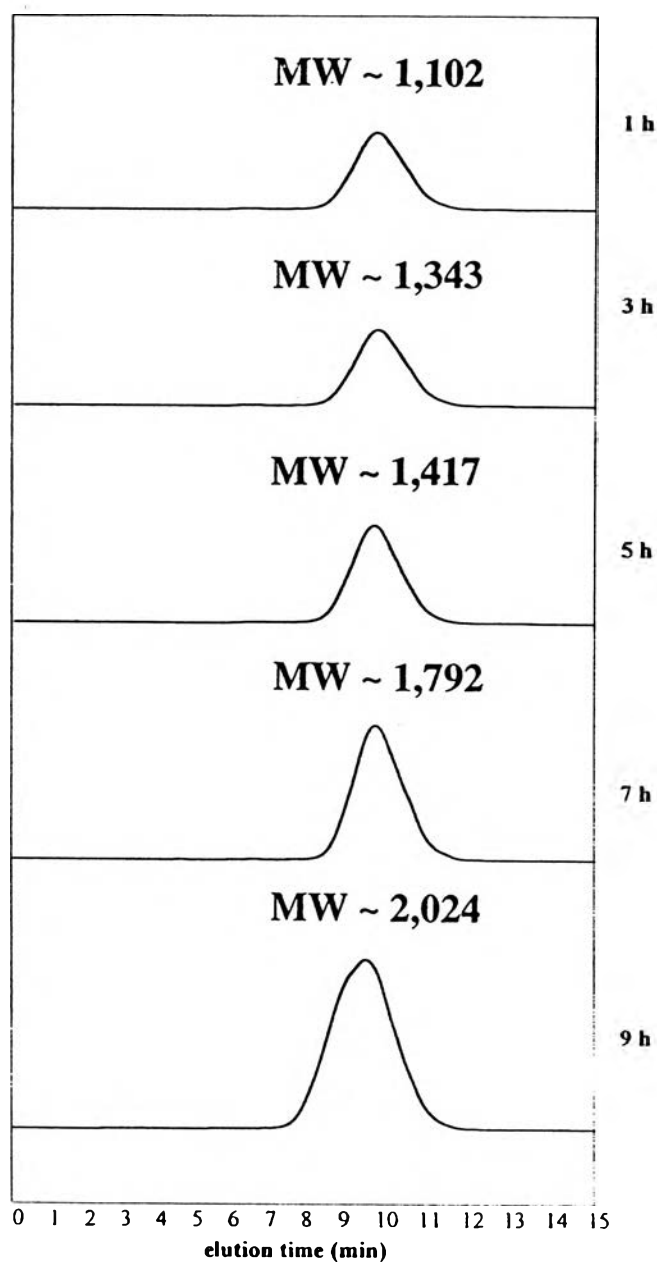primary polymerization after the formation of α, β unsaturated product is vinyl polymerization.

Figure 3.7 The changing of molecular weight distributions of products from aldol condensation at various times.

3.3 Carbonyl Polymerization and Stabilization

3.3.1 Carbonyl Stabilization by using Hydroxylamine as Stabilizer

In this work, laboratory simulation of yellow oil using acetaldehyde showed similar color transition and increase in molecular weight to the in-plant reaction. 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 polymerization reaction proceeds further and the molecular weight increases. Hydroxylamine hydrochloride was utilized to act as carbonyl stabilizer interupting the carbonyl polymerization from aldol condensation reaction. Hydroxylamine can react with the active aldehyde group to form an inert oxime product. The chemical reaction between acetaldehyde (a carbonyl species) and hydroxylamine is shown below:
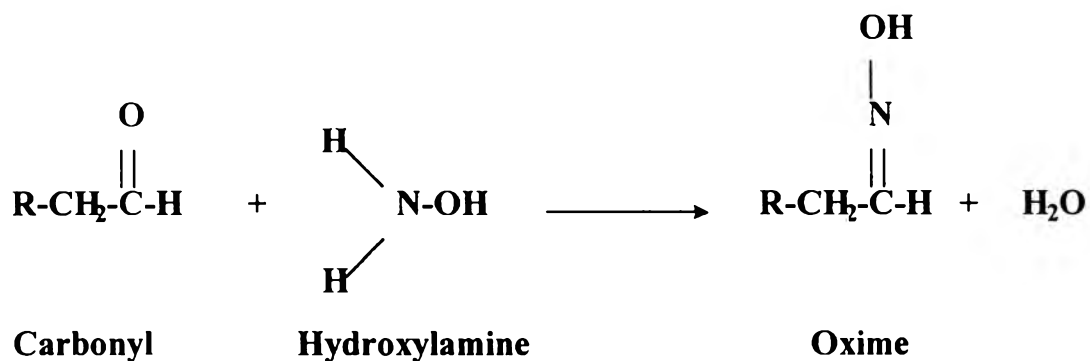
$$
\begin{array}{ccc}
\overset{\displaystyle O}{\underset{\displaystyle \|}{R\text{-}CH_2\text{-}C\text{-}H}} + \underset{H}{\overset{H}{\diagdown}}N\text{-}OH & \longrightarrow & \overset{\displaystyle OH}{\underset{\displaystyle \|}{\underset{\displaystyle N}{R\text{-}CH_2\text{-}C\text{-}H}}} + H_2O \\
\text{Carbonyl} \qquad \text{Hydroxylamine} & & \text{Oxime}
\end{array}
$$

Figure 3.8 The chemical reaction between acetaldehyde and hydroxylamine.

Results of the use of hydroxylamine hydrochloride as stabilizer in aldol condensation polymerzation are shown in Table 3.4.

Table 3.4 The carbonyl stabilization by using hydroxylamine as stabilizer

in 100 ml aldol condensation solution (varies weight of stabilizer)

Stabilizer (gram)	Aldol Condensation Reaction Time (hour)					
	0.5	1	1.5	2	2.5	3
0	+	++	++/ -	+++/ --	+++/ ---	++++/ ----
0.5	+	+	+	++	++	++/ -
0.8	clear	clear	+	+	+	+
1.0	clear	clear	clear	clear	clear	clear

+ the level of yellow color

- the amount of precipitation in reaction

When hydroxylamine was not use in reaction, the reaction changed as mention above. Increase in the amount of hydroxylamine led to reduction of the yellow color and the amount of precipitation. The use of 0.8 g hydroxtamine in 100 ml aldol condensation solution almost interrupted the reaction completely. The reaction product was clear in 1-2 hours but the reaction was not stable. At the reaction time of 3 hours, the reaction product became light yellow which indicates the presence of unsaturated aldehyde by aldol condensation reaction. The use of 1 g hydroxylamine in 100 ml solution has demonstrated that the application functions effectively. The reaction product was clear, stable and did not polymerize further even when heated for 24 hours.

This chemical treatment may be applied in plant by feeding with the fresh caustic. The oxime formed is soluble in water and in caustic solutions. Thus, the spent caustic blowdown can remove the oxime product.

3.3.2 Time Study of Aldol Condensation Reaction by UV-visible Spectrometer

1 g of hydroxylamine in 100 ml aldol condensation solution can stop the reaction completely so it was used to stop the reaction at specific time to detect the presence of conjugated system in the form of α,β unsaturated aldehyde. 1 g of hydroxylamine was added into the aldol condensation reaction to stop the polymerization at the reaction time of 5 min., 10 min., 30 min., 1 hour, 2 hours, 4 hours, 6 hours, 8 hours, and 10 hours. One evidence that can predict the increase of double bond was the transition of yellow color from light yellow to dark red. Ultraviolet spectroscopy was employed to prove the presence of conjugated system in aldol condensation reaction. The sample solution was diluted in 100 ml of water.

Figure 3.9 to Figure 3.17 show UV spectra of 1 ml of aldol condensation product at various reaction times. All spectra show the λ_{max} near 190 nm. These peaks have high absorbance because of the interference from water which exists in large amount in the system. The absorption at the wavelength of more than 250 nm shows the presence of α,β unsaturated aldehyde.

When the time of reaction increases, the absorbance occurs at longer wavelength. This shows the increase in conjugated system as the aldol condensation polymerizes further.
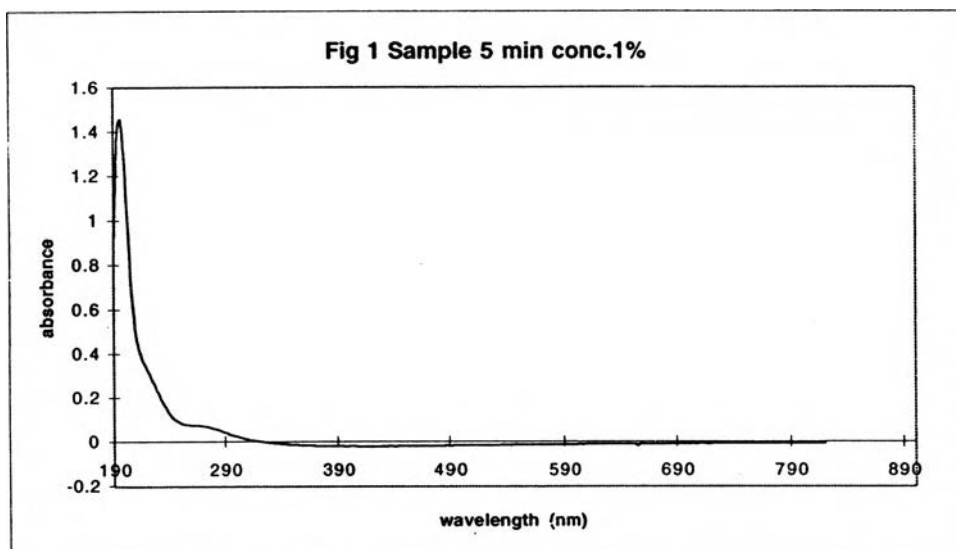
Fig 1 Sample 5 min conc.1%

Figure 3.9 UV spectrum of aldol condensation product, reaction time 5min.

Fig2. sample10 min conc.1%
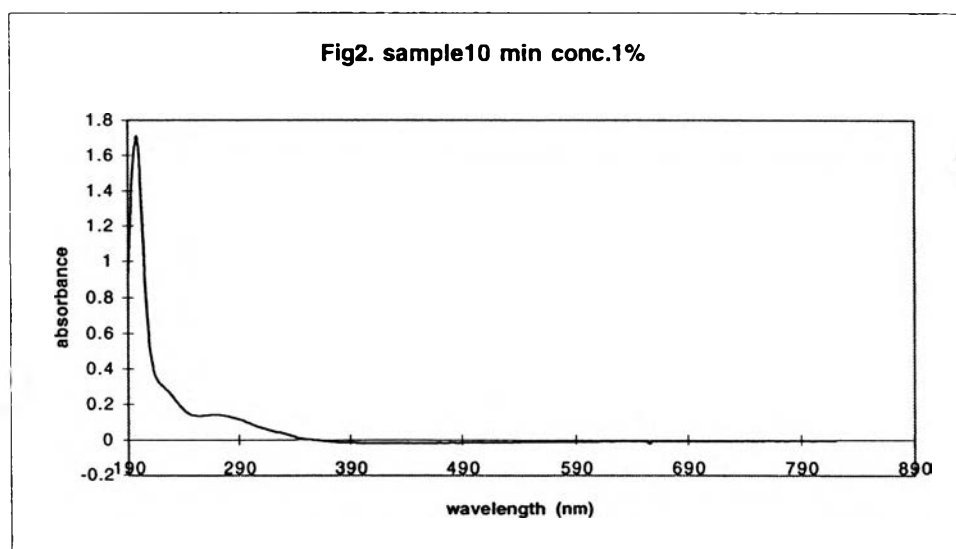
Figure 3.10   UV spectrum of aldol condensation product, reaction time 10 min.

Fig 3 sample 30 min conc.1%
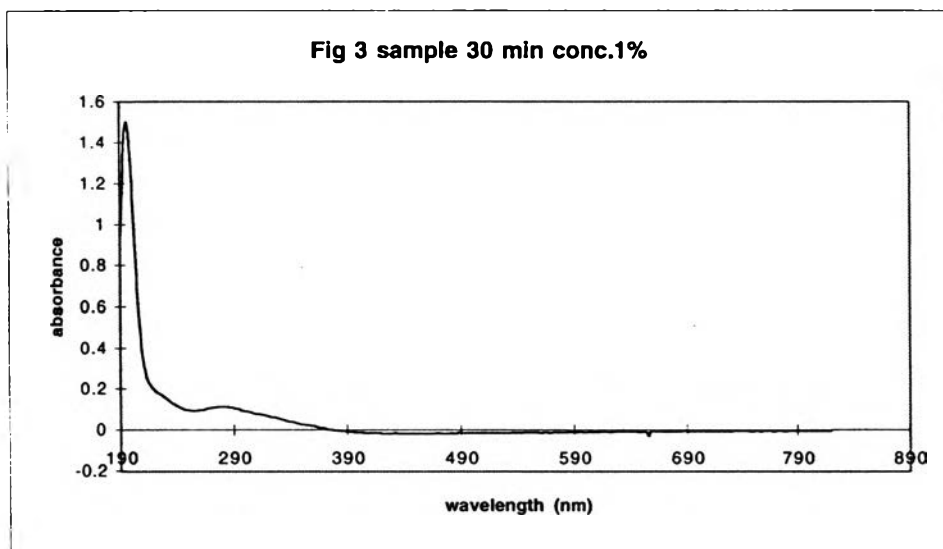
Figure 3.11   UV spectrum of aldol condensation product, reaction time 30 min.

Fig4 sample 1h conc.1%
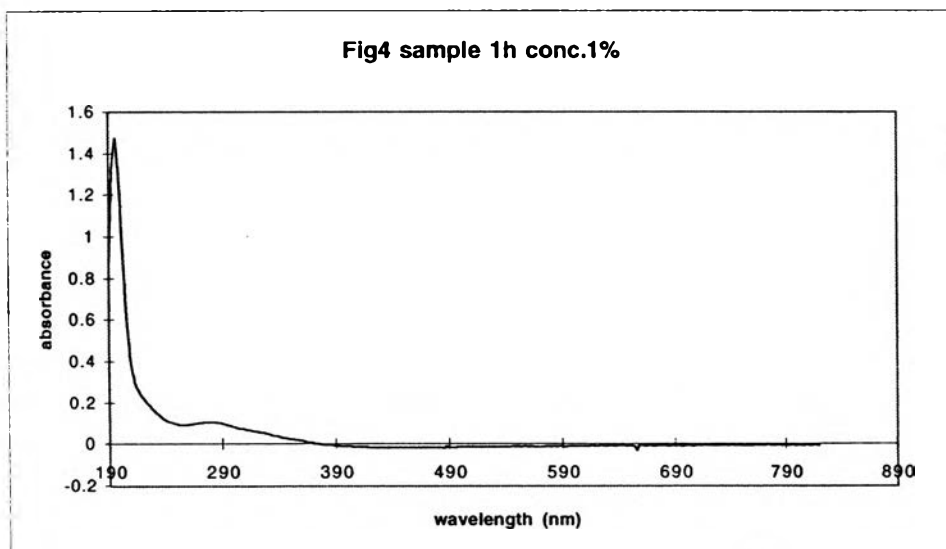
Figure 3.12 UV spectrum of aldol condensation product, reaction time 1 h.
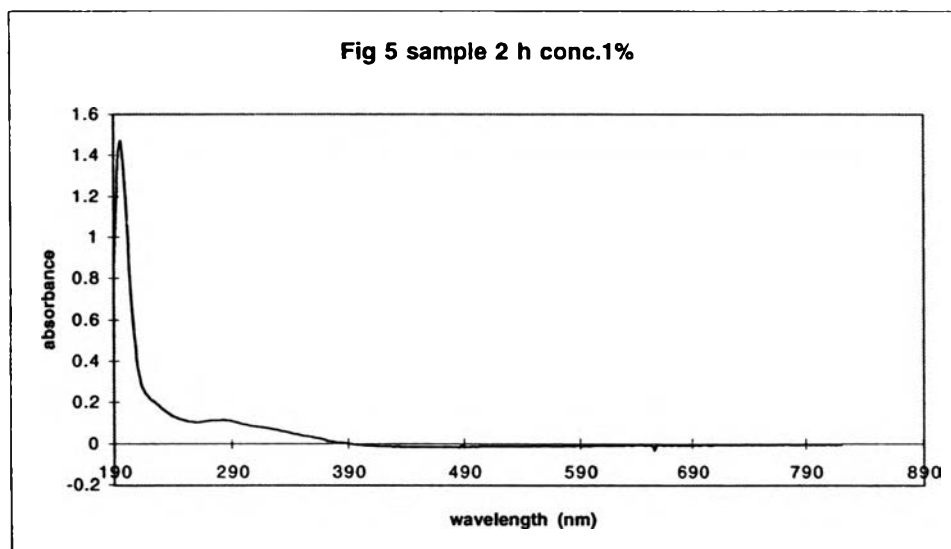
Figure 3.13 UV spectrum of aldol condensation product, reaction time 2 h.
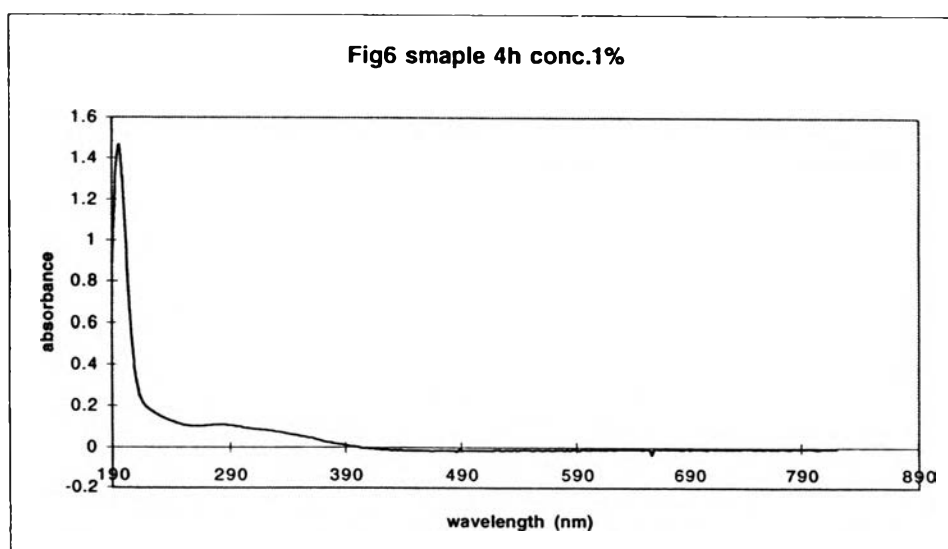
Figure 3.14 UV spectrum of aldol condensation product, reaction time 4 h.
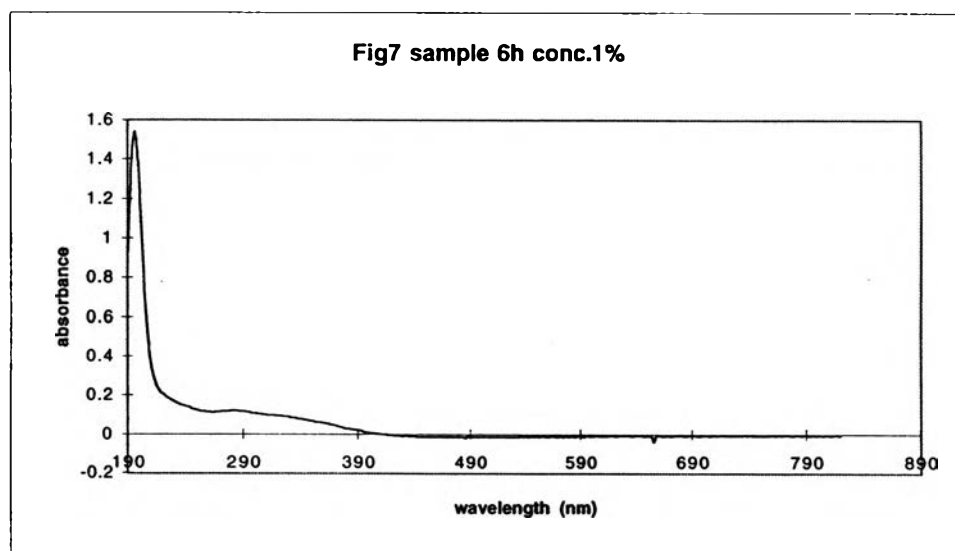
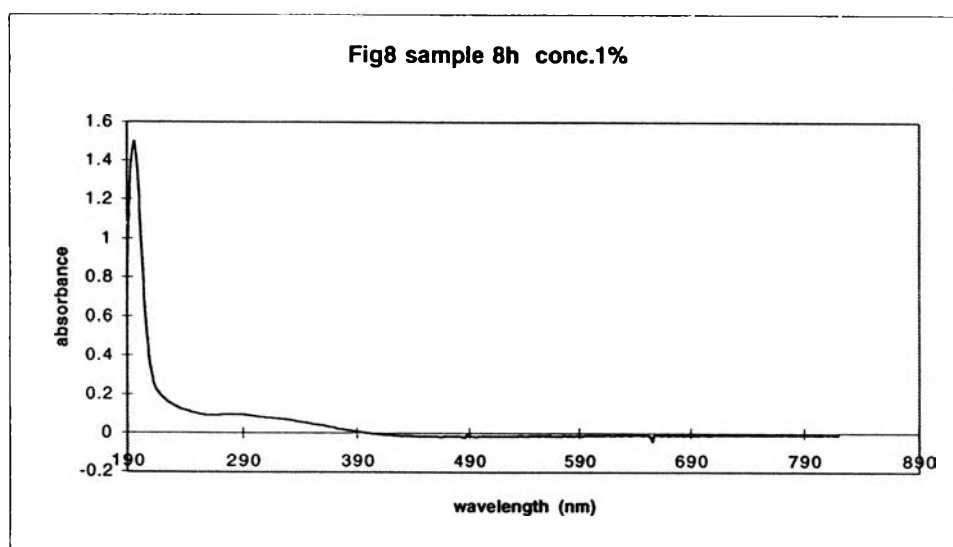**Figure 3.15 UV spectrum of aldol condensation product, reaction time 6 h.**

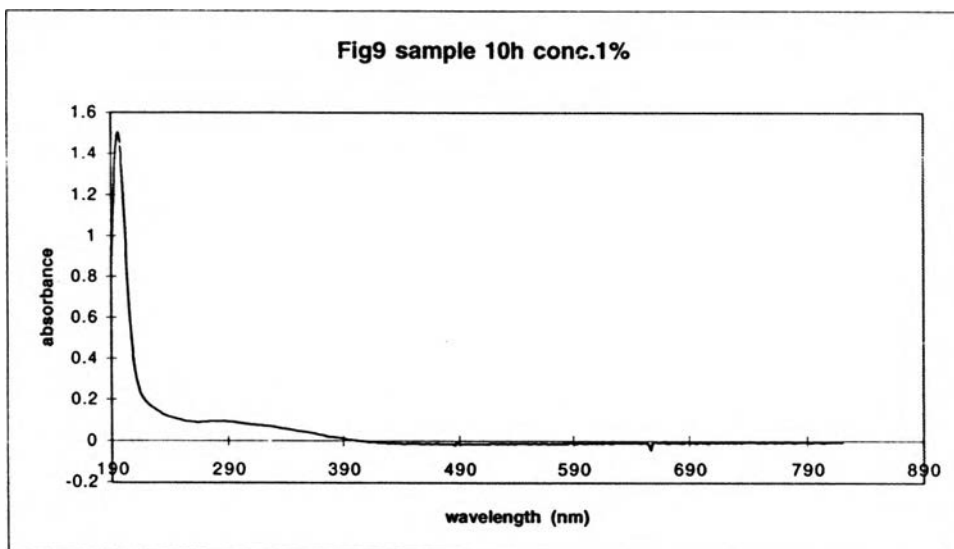**Figure 3.16 UV spectrum of aldol condensation product, reaction time 8 h.**

Figure 3.17 UV spectrum of aldol condensation product, reaction time 10h.