CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Acetaldehyde: C_2H_4O, 99.5% purity was purchased from J.T.Baker. It has a boiling range of 20.5-21.5^{o}C and has to be kept at the temperature lower than 15^{o}C.

Properties: Colorless liquid, fruity odor, density 0.783 (18/4^{o}C)

3.1.2 Sodium hydroxide (NaOH) was purchased from Merck chemical company.

Properties: White, deliquescent solid; density 2.13, mp 318^{o}C soluble in water, alcohol

3.1.3 Standard iron solution: was purchased from Merck chemical company. Concentration is 1000 mg/lit (ppm.) $FeCl_3$ in nitric acid.

3.1.4 Hydroxylamine hydrochloride ($NH_2OH.HCl$): was purchased from J.T.Baker. It is air and moisture sensitive and has to be stored with careful exclusion of moisture and air.

Properties: Colorless, hygroscopic crystals; density 1.67 (17 ^{o}C) soluble in water, alcohol, mp 152^{o}C

3.1.5 Hydrazine hydrate ($N_2H_4.H_2O$): was purchased from Fluka.

Properties: Colorless, fuming liquid; density 1.032, bp 119.4^{o}C, mw 50.06, miscible with water and alcohol

3.1.6 Hydrochloric acid (HCl): was purchased from Merck chemical company.

Properties: Colorless or slightly yellow, fuming, pungent liquid, and density 1.19 soluble in water, alcohol.[19,20]

3.1.7 Instrument air: was clean dry air and can be used for instrument system.

3.1.8 Nitrogen gas: UHP purity 99.999% was purchased from Thai industrial gases public company limited.

3.2 Instruments and Apparatus

The intruments and apparatus used in this study are listed below:

a) Potentiomatic titrator, Metorhm 686

b) Water bath, temperature 30 – 150 ^{o}C

c) Glass ware apparatus for filtration and vacuum pump

d) Transfer pipeting, Merck

e) Drying oven, temperature 100 $\pm$ 5 ^{o}C

f) Analytical balance, shimadzu

g) UV-visible spectrophotometer, JASCO model 530

3.3 Study of Aldol Condensation Reaction

In olefins plant, yellow oil that occurred in caustic tower have many factors that may be problem. Of the two polymerization mechanism for the caustic tower fouling described in 2.2-2.3 above, it appears that the aldol condensation is more predominant in ethane cracker plants due to the relatively small quantities of dienes and higher acetylenes in the cracked gas stream. This is confirmed by comparing the spectrum of aldol condensation product to that of yellow oil in Figure 4.13. For the benefit of ethane cracker operators this study is directed towards the aldol condensation reaction only.

Apart from the effect of temperature on the reaction, the effects of oxygen and iron solution were also studied. Oxygen is believed to enter the tower through the caustic make-up stream.

Air dissolved in caustic solution in storage tank could lead to the presence of oxygen in caustic tower catalyzing the polymerization reaction. Moreover the yellow oil deposit in the plant is found to contain rust and ion compounds. The effect of iron on the reaction was therefore studied.

The strength of the caustic solution used in the study was guided by the actual caustic solutions employed in the caustic tower of the plant which are 5% wt. caustic soda in the weak caustic section and 10% wt. caustic soda in the strong caustic section.

3.3.1 Effect of oxygen

Vacuum round bottle flask with vacuum pump and equipped with stopcock closing was used for the experiment. Nitrogen gas was filled first to the round bottle flask with continuous flow about 3-5 ml/min at neck of flask. 200 ml of 5% wt. sodium hydroxide solution was transfer to the round bottle flask. Then 0.1 ml of acetaldehyde was added to the solution in the round bottle flask and mixed well at room temperature. The reaction was observed and recorded every 30 minutes for 5 hours. Repeat the experiment at the temperature 50^{o}C in a water bath. The next experiment involved purging the reaction system with air, by repeating the above test using air purge instead of nitrogen. The experiment was carried out at room temperature.

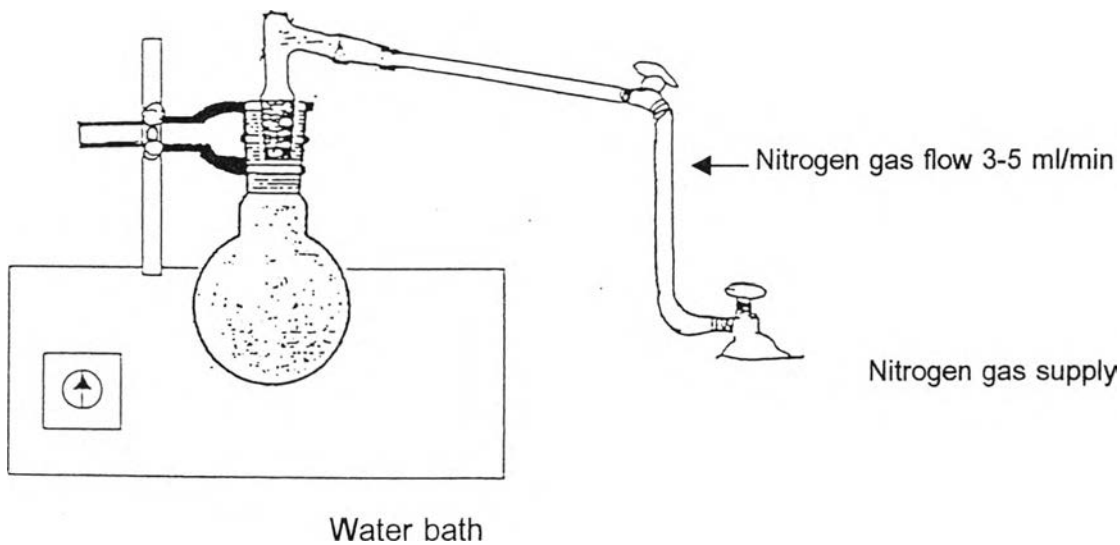

Figure 3.1: Equipment for oxygen effect testing

3.3.2 Effect of temperature

The 5% wt. sodium hydroxide solution was prepared in large amount and kept in plastic bottle. 100 ml of sodium hydroxide solution was poured into a 250-ml erlenmeyer flask followed by 0.1 ml of acetaldehyde. This mixture was then stirred at room temperature (25^{O}C), the experiment was repeated at 50^{O}C and 80^{O}C in water bath. The reaction time was 2 hours. The solid product was collected on microfiber filter 1.2 μM by suction filtration and washed on the filter funnel with water to remove the unreacted chemical as much as possible. The product was then dried at 100 $\pm$ 5^{O}C to remove water and it was cooled down to room temperature in dessiccator. They were weighed and the drying step was repeated again until the weight of the product was constant. The amount of solids in solution were then calculated. They were tabulated in Table 4.2 and plotted in Figure 4.1 of Chapter 4. Data is shown at appendix.

3.3.3 Effect of iron solution

The 5% wt. sodium hydroxide solution was prepared in large amount and kept in plastic bottle. 100 ml of sodium hydroxide solution was poured into a 250-ml erlenmeyer flask followed by 0.1 ml of acetaldehyde. Three more samples were prepared with the addition of Iron solution in varying quantities to make the final solutions having iron concentration of 0, 10, 50, 100, 500 ppm. respectively. These mixtures were then stirred at room temperature (25^{O}C). The test was repeated at 50^{O}C in a water bath. The reaction time was 2 hours.

The solid products were collected on microfiber filter 1.2 μM by suction filtration and washed on the filter funnel with water to remove the unreacted chemical as much as possible. The product was then dried at 100 ± 5 °C to remove water and was cooled down to room temperature. They were then weighed. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight was obtained or until the weight change was less than 4% of the previous weight or 0.5 mg, and amount of solids in solution were calculated. The experiment was repeated, however this time when solid product was collected on microfiber filter 1.2 μM by suction filtration it was washed on the filter funnel with acid solution 1:1 (hydrochloric: water) and water instead to remove the unreacted inorganic chemical as much as possible. The results were tabulated in Table 4.3 and plotted in Figure 4.2 of Chapter 4.

3.4 Impact of inhibitor on yellow oil formation

3.4.1 Hydrazine solution

The 5% wt. sodium hydroxide solution was prepared in large amount and kept in plastic bottle. 100 ml of sodium hydroxide solution was poured into a 250-ml erlenmeyer flask followed by 0.1 ml of acetaldehyde. Four more samples were prepared by adding hydrazine 0.05% (0.05g), 0.2%(0.2g), 0.3% (0.3g), 0.4% (0.4g) respectively to the base mixture. These mixtures were then stirred at room temperature (25°C). Another test was performed at 50°C in a water bath. The reaction time was 2 hours.

The solid products were collected on microfiber filter 1.2 μM by suction filtration and washed on the filter funnel with water to remove the unreacted chemical as much as possible. The product was then dried at

100 ± 5°C to remove water and was cooled down to room temperature. They were then weighed. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight was obtained or until the weight change was less than 4% of the previous weight or 0.5 mg, and amount of solids in solutions were calculated. The sample solutions were analyzed for reactive carbonyl species by UV-visible spectrophotometer. The results were tabulated in Table 4.4-4.5 and UV spectra plotted in Figure 4.5-4.6 of Chapter 4. They can be compared with the UV spectra of yellow oil in Figure 4.9 of Chapter 4.

3.4.2 Hydroxylamine hydrochloride solution

The 5% wt. sodium hydroxide solution was prepared in large amount and kept in plastic bottle. 100 ml of sodium hydroxide solution was poured into a 250-ml erlenmeyer flask followed by 0.1 ml of acetaldehyde. Four more samples were prepared adding hydroxylamine hydrochloride 0.05%, 0.2%, 0.3 %, 0.4% respectively to the base mixtures. These mixtures were then stirred at room temperature (25°C). The test was repeated at 50°C in a water bath. The reaction time was 2 hours. The solid product were collected on microfiber filter 1.2 μM by suction filtration and washed on the filter funnel with water to remove the unreacted chemical as much as possible. The product was then dried at 100 ± 5°C to remove water and was cooled down to room temperature. They were weighed. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight was obtained or until the weight change was less than 4% of the previous weight or 0.5 mg, and amount of solids in solutions were calculated. The sample solutions were analyzed by UV-

visible spectrophotometer. The results were tabulated in Table 4.4-4.5 and UV-spectra plotted in Figure 4.7-4.8 of Chapter 4. They can be compared with the UV spectra of yellow oil in Figure 4.9 of Chapter 4.

3.5 Impact of caustic soda and the amount of acetaldehyde on yellow oil formation

The 5% wt. sodium hydroxide solution was prepared in large amount and kept in plastic bottle. 100 ml of 5% wt. sodium hydroxide solution was transferred into each of four 250-ml erlenmeyer flasks followed by 0.1, 0.2, 0.3, 0.4 ml of acetaldehyde in each flask. These mixtures were then stirred at room temperature ($25^{\circ}C$). Two other sets (1% wt., 10% wt. sodium hydroxide solution) of same mixtures were prepared and stirred at $50^{\circ}C$ in a water bath. The reaction time was 2 hours. The solid products were collected on microfiber filter 1.2 μM by suction filtration and washed on the filter funnel with water to remove the unreacted chemical. The product was then dried at $100 \pm 5^{\circ}C$ to remove water and cooled down to room temperature. They were weighed. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight was obtained or until the weight change was less than 4% of the previous weight or 0.5 mg, and amount of solids in solutions were calculated. The experiment was repeated but used 100 ml 1% wt. and 10% wt. sodium hydroxide solution. The results were tabulated in Table 4.6 and plotted in Figure 4.10-4.12 of Chapter 4.