

## CHAPTER III

### EXPERIMENTAL SECTION

This experimental study of the aldol condensation reaction in the presence of and in the absence of antifoulants was performed at 25, 35, and 50°C. In addition, effects of sodium sulfate, which is present in the oxidation reactor, on the aldol condensation reaction were investigated. Characterization of the spent caustic from the National Petrochemical Public Co., Ltd. was also provided.

#### 3.1 Aldol Condensation of Acetaldehyde

1 wt% sodium hydroxide solution was prepared in a volumetric flask. The sodium hydroxide (NaOH) was purchased from Fluka Chemie AG.  $10 \pm 0.03$  ml of the sodium hydroxide solution was poured into each vial (6 dram). Then, acetaldehyde was added using a NICHIRYO digital micro pipette model 5000DG. The concentration of acetaldehyde used in this study was varied from 0.0625 to 0.25 M. The acetaldehyde ( $C_2H_4O$ , 99.5% purity) was purchased from Fluka Chemie AG. The temperatures set in the experiment were 25, 35, and 50°C and controlled in a water bath. The reaction time was varied from 5 to 60 minutes. The reaction progress was followed by observing the change of the solution absorbance with a colorimeter model 6061 with 0.001ABS resolution from the Jenway Ltd. The change was recorded every 5 minutes.

### 3.2 Reduction of the Fouling by Antipolymerants

$10 \pm 0.03$  ml of 1wt% sodium hydroxide solution was prepared in each vial (6 dram). Varying amount of two hydroxylamine salts, hydroxylamine hydrochloride and hydroxylamine sulfate, was mixed into the sodium hydroxide solution. Both hydroxylamine hydrochloride and hydroxylamine sulfate concentration were varied from 0.0625 to 0.25 M. The hydroxylamine hydrochloride ( $\text{H}_2\text{NOH}\cdot\text{HCl}$ , 99% purity) and hydroxylamine sulfate ( $(\text{H}_2\text{NO})_2\text{H}_2\text{SO}_4$ , 99% purity) were purchased from Fluka Chemie AG. Then, 0.25 M of acetaldehyde was added into each vial. The temperatures used in this experiment were set at 25, 35, and 50°C. They were controlled in a water bath. The reaction time was varied from 5 to 60 minutes. The reaction progress was followed by observing the change of the solution absorbance with a colorimeter model 6061 with 0.001ABS resolution from the Jenway Ltd. The change was recorded every 5 minutes.

### 3.3 Effects of Sodium Sulfate on the Aldol Condensation

$10 \pm 0.03$  ml of 1wt% sodium hydroxide solution was prepared in each vial (6 dram). Varying amount of sodium sulfate was mixed into the sodium hydroxide solution. Sodium sulfate concentration was varied from 0.125 to 0.25 M. Sodium sulfate anhydrous ( $\text{Na}_2\text{SO}_4$ , 99% ACS) was purchased from Scharlau Chemie SA. Then, 0.25 M of acetaldehyde was added into each vial. The temperatures used in this experiment were set at 25, 35, and 50°C. They were controlled in a water bath. The reaction time was varied from 5 to 60 minutes. The reaction progress was followed by observing the change of the solution absorbance with a colorimeter model 6061 with 0.001ABS resolution from the Jenway Ltd. The change was recorded every 5 minutes.

### 3.4 Characterization of the Organic Substance in the Spent Caustic from the Caustic Tower

First, the spent caustic from the caustic tower was filtered using Whatman No. 5 filter paper. pH of the filtered solution was measured with an ORION pH meter model 1420A. Next,  $50 \pm 0.09$  ml of the filtered solution was measured into a beaker. Then, pH of this 50 ml solution was adjusted to 3-4 by adding 2 N hydrochloric acid. The 37% hydrochloric acid (HCl) was purchased from the BDH Laboratory Supplies. The solution was extracted by 50 ml of n-hexane in a separatory funnel. The n-hexane ( $C_6H_{14}$ , 96%) was obtained from Scharlau Chemie SA. Then,  $40 \pm 0.12$  ml of the extracted phase was separated from the solution with a pipette and concentrated using a vacuum evaporator. The concentrated product was dissolved with  $10 \pm 0.03$  ml ethanol. The amount of the organic acid was determined by titrating the solution with 0.1 N sodium hydroxide, that was standardized by potassium hydrogen phthalate, and phenolphthalein used as an indicator. The absolute ethanol ( $C_2H_5OH$ , 99.8%) and potassium hydrogen phthalate ( $C_6H_4(COOK)(COOH)$ , 99.8-100.2%) were purchased from the Montedison Group and Nacalai Tesque.

The concentrated product was further characterized with a Fourier Transform Infrared Spectrometer (FT-IR). The FT-IR spectra were obtained from a Bruker Equinox 55 spectrometer with 16 scans at a resolution of  $4\text{ cm}^{-1}$ . A frequency range of  $400\text{-}4000\text{ cm}^{-1}$  was observed using the ZnSe technique.

The spent caustic was dissolved in tetrahydrofuran (THF) to measure its molecular weight distribution with a Gel Permeation Chromatography (GPC). The THF ( $C_4H_8O$ , 99.8%) was purchased from the Labscan Co., Ltd. Water GPC 600E with an UV detector (Water 486) was utilized to obtain the GPC chromatograms. The separating column in the GPC was HR 0.5, which

is capable to handle the molecular weight 0-1,000. Polytetrafluoroethylene (PTFE) membrane with 0.2  $\mu\text{m}$  pore size was used as the filter. The PTFE membrane filter was purchased from the Lida Manufacturing Co., Ltd.