

## CHAPTER II

### EXPERIMENTAL SECTION

#### 2.1 Materials

Yellow oil sample used in the work was collected from the acid gas removal unit (caustic tower) in an olefin plant. It was found to compose of a solid component and a liquid component. The liquid component was drained off before the sample was tested.

Organic solvents, namely tetrahydrofuran (THF, 99.9% purity) and diethyl ether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ , 99.9% purity) used as solvents for yellow oil were purchased from Baker Analyzed Company and purified by standard techniques.

Sodium hydroxide (NaOH) was purchased from Merck Chemical Company. Acetaldehyde ( $\text{C}_2\text{H}_4\text{O}$ , 99.5% purity) was purchased from Riedel de Haen. It has a boiling range of 20.5-21.5 °C so has to be kept in the temperature lower than 15 °C. These chemicals were utilized in the aldol condensation reaction.

Hydroxylamine hydrochloride ( $\text{H}_2\text{NOH.HCl}$ , 99% purity) was purchased from Aldrich Chemical Company. It is air and moisture sensitive and has to be stored with careful exclusion of moisture and air.

The glassware was cleaned by soaking in a cleaning solution bath, followed by rinsing with water and acetone respectively, then dried in oven at 100°C prior to use.

## 2.2 Instrumentation and Characterization Techniques

### 2.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy has been used in this study to provide information of functional groups in yellow oil and the simulated condensation products.

**Instrument:** Fourier Transform Infrared (FTIR) spectra were obtained on a FT-45A Biorad spectrometer with a resolution of  $\pm 8 \text{ cm}^{-1}$  by using 16 scans.

**Preparation of the sample:** Solid samples were run as a solid dispersion in potassium bromide (KBr, oven dried at 105 °C for 24 hr.) with approximately 1% by weight in KBr. Samples were prepared by carefully grinding a mixture of the sample and KBr until it composed of very finely ground particles. The finely ground mixture was then pressed into a transparent disk under 8 tons of pressure. The disk was mounted on a holder, and the spectrum was then recorded. Liquid samples were run either as a pure liquid sample or in solution. One or two small drops of solution was smeared on a KBr plate. The KBr plate with the thin film of sample was then placed in a holder and its spectrum was taken.

### 2.2.2 Gel Permeation Chromatography

Gel permeation chromatography has been used to study molecular weight and molecular weight distribution of the samples and the aldol condensation polymerization reaction.

**Instrument:** Gel permeation chromatography consisting of a Waters 600 E system controller, one packed column, and ultraviolet detector at 254 nm (Waters Associates, Turnable Absorbance Detector model 486) was used to measure the molecular weight distribution. Column calibration Water styragel HR 4E 7.8×300 nm which has molecular weight range 50-100,000 was used as separation column. Tetrahydrofuran (HPLC grade) was used as the mobile phase at the elution rate of 1 ml/min. The molecular weight distribution of the samples was measured relative to linear monodisperse polystyrene standard (TOSOH Corporation).

**Preparation of the sample:** Tetrahydrofuran (HPLC grade) which was filtered by membrane filter (pore size 0.45  $\mu\text{m}$ ) was used as the solvent for dissolving the solid sample. This solution was filtered again by using NYPOR membrane filter (pore size 0.45  $\mu\text{m}$ ). Finally the filtrate was injected into the GPC.

### 2.2.3 Elemental Analysis

**Instrument:** The PE 2400 Series II CHNS/O Analyzer of Perkin Elmer was used to determined the following elements in the samples.

- Carbon, hydrogen, nitrogen, and sulfur
- Oxygen

Two classical organic elemental analysis techniques are used for these determinations

- Combustion in a pure oxygen environment for carbon, hydrogen, nitrogen, and sulfur
- Pyrolysis in a helium/hydrogen mixture for oxygen

**Standard:**

Option	Standard	Theoretical weight percent				
		C	H	N	S	O
<b>CHNS Analysis</b>	<b>cystine</b>	29.99	5.03	11.66	26.69	-
<b>Oxygen Analysis</b>	<b>benzoic acid</b>	68.85	4.95	-	-	26.20

**Measurement:** The CHNS operating mode was selected to measure the percentage of carbon, hydrogen, nitrogen, and sulfur. The combustion furnace temperature and the reduction furnace temperature were set at 950 °C and 500 °C respectively. Then the theoretical weight percent was entered by using cystine as standard. The empty tin foil vials were used for running the blank sample then the standard was weighed to approximately 1 milligram in the vial for running the K-factor. Subsequently 1 milligram of the sample was placed in the tin foil vial and the tin foil vial was taped lightly to ensure that all the sample particles had reached the bottom of the vial. The tin foil vial was then folded in half. The vial was placed in the instrument and started running. When changing to Oxygen operating mode, the Column Switching Accessory knob was turned to the Column Oxygen position. The pyrolysis furnace temperature was set at 1000 °C and the reduction furnace temperature was set at 500 °C. Benzoic acid was used as the standard for

entering the theoretical weight percent and running the K-factor. Then steps similar to that of CHNS operating mode were followed.

## 2.3 Procedures

### 2.3.1 The Aldol Condensation of Acetaldehyde

Aliphatic aldehydes will usually undergo self-condensation under base-catalysis or acid-catalysis called aldol condensation reaction. This work has studied the aldol condensation of acetaldehyde under base-catalysis. This reaction was then used to predict the mechanism of formation of yellow oil and the aldol products were characterized comparing with yellow oil by FTIR, GPC, and elemental analyzer.

**Procedure:** The 3% sodium hydroxide solution was prepared in large amount and kept in plastic bottles. 200 ml of sodium hydroxide solution was poured into a 250-ml Erlenmeyer flask followed by 2 ml of acetaldehyde (~ 35 mmole). The mixture was then stirred in a 50 ° C ultrasonic bath. The reaction time was varied from 1 hour to 24 hours. The solid products were collected by suction filtration and washed on the filter funnel with water to remove the unreacted chemicals as much as possible. The products were then dried and recrystallized from ethanol using the minimum amount of hot solvent to dissolve the products. They were then vacuum dried at room temperature overnight and characterized by the various techniques.

The temperature of the reactions and the concentration of sodium hydroxide solution were also varied to study their effects on the aldol condensation reaction.

### 2.3.2 Carbonyl Stabilization Reaction

To inhibit the aldol condensation reaction, hydroxylamine hydrochloride was used as inhibitor. Hydroxylamine hydrochloride functions as an antipolymerant interrupting the carbonyl polymerization reaction. It reacts with the active aldehyde group to form an inert oxime product.

**Procedure:** The 200 ml of 3% sodium hydroxide solution was prepared in Erlenmeyer flask. Varying amount of hydroxylamine hydrochloride was mixed into the sodium hydroxide solution to find the minimum amount that would prevent the reaction completely. Then 2 ml of acetaldehyde was added in all the flasks and stirred in 50 °C ultrasonic bath. The reaction was observed and recorded every 30 minutes.