CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 API Separator Sludge

The API separator sludge was obtained from an API separator in a wastewater treatment plant of PTT Public Company Limited. The sludge consists of a mixture of solid, water and oil. Before each experiment, the sludge was stirred until a homogeneously mixed mixture was observed.

3.1.2 Surfactant

Two nonionic surfactants, Empilan KB-7 and Empilan NP-9, were obtained from V.S. General Chem Company Limited. Empilan KB-7 is lauryl alcohol with 7 moles of ethylene oxide and Empilan NP-9 is nonylphenol with 9 moles of ethylene oxide. Surfactant solution was prepared in both distilled water and electrolyte solution and stirred for 30 min.

3.1.3 Electrolyte

Commercial grade NaCl and $CaCl_2$ obtained from Tokuyama Corp., Japan, were used as electrolytes in this work. Both electrolytes ware used to compare the effect of cation charge on the light components recovery.

3.1.4 Coagulant

Analytical grade ferric chloride was obtained from Aldrich Chemical Company Inc. It was used as a coagulant. The solution was always freshly prepared before use.

3.1.5 Flocculant

Several types of polyelectrolyte, Permafloc 2628 (PF2628), Permafloc 2525 (PF2525), Wachem Floctex 2413 (FT2413), Wachem Floctex 2431 (FT2431) and Wachem Floctex 2602 (FT2602), were obtained from V.S. Treatment

Chemicals Company Limited. These polyelectrolytes are anionic polyacrylamide with different charges and molecular weights. They were used to flocculate oil droplets.

3.2 Instruments

3.2.1 Total Organic Carbon Analyzer (TOC)

A Shimadzu TOC-5000A total organic carbon analyzer was used to determine the amount of surfactant in the solution for quantitative analysis.

### 3.2.2 Thermogravimetric Analyzer (TGA)

The pyrolysis of API separator sludge was carried out by using a DuPont TG-1000 thermogravimetric analyzer. The data of the sludge weight loss during pyrolysis was collected and used to study the pyrolysis behavior of the sludge.

3.2.3 Distillation Apparatus

The apparatus comprises a glass or metal still, a heater, a reflux condenser and a graduated glass trap. The still, trap and condenser may be connect by any suitable method that produces a leakproof joint. Typical assembly is illustrated in Figure 3.1.

3.2.4 Capillary Viscometer

The viscosity-average molecular weight of polyelectrolyte was determined by using Cannon Ubbelohde-type viscometer number 50 as seen in Figure 3.2.
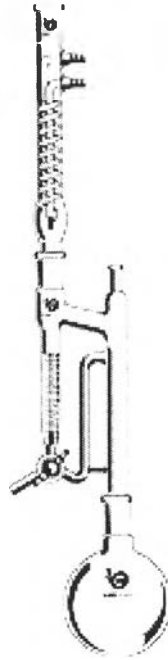
Figure 3.1 Distillation apparatus. (http://www.wilmad-labglass.com)

Figure 3.2 Ubbelohde viscometer. (http://www.paragon-sci.com)

3.3 Experimental

3.3.1 Sludge Composition

Water content in the sludge was determined by distillation followed ASTM D95-83. The sludge to be treated was heated under reflux with a water-immiscible solvent, which co-distilled with the water in the sludge. Condensed solvent and water were continuously separated in the trap, the water settled in the graduated section of the trap and the solvent returned to the still. Solid content was determined by extraction with toluene. The sludge was put in a cloth bag and extracted by toluene 3 times. The extracted oil was removed and the sludge was then distilled by using toluene as a solvent. The oil content could be calculated by the subtraction from 100.

3.3.2 Viscosity-Average Molecular Weight of Polyelectrolyte

The molecular weight of polyelectrolyte was determined by viscometric method. Polyelectrolyte solutions of different concentrations were prepared. An Ubbelohde viscometer was filled with polyelectrolyte solution, which was dipped vertically in the water bath, regulated to $30 \pm 0.1°C$ and left to equilibrate for 15 min. the solution was passed through the capillary once before the running timed were measured. The times were used to calculate the following:

$$\text{Relative viscosity} \quad (\eta_{rel}) \ = \ \frac{t}{t_s} \tag{3.1}$$

$$\text{Specific viscosity} \quad (\eta_{sp}) \ = \ \left(\frac{t}{t_s}\right) - 1 \tag{3.2}$$

$$\text{Reduced viscosity} \quad (\eta_{red}) \ = \ \frac{\eta_{sp}}{C} \tag{3.3}$$

$$\text{Inherent viscosity} \quad (\eta_{inh}) \ = \ \frac{(\ln \eta_{rel})}{C} \tag{3.4}$$

$$\text{Intrinsic viscosity} \quad [\eta] \ = \ (\eta_{red})_{C \to 0} \ = \ (\eta_{inh})_{C \to 0} \tag{3.5}$$

where

$\quad$ t $\quad$ = $\quad$ flow time of polyelectrolyte solution (sec)

$\quad$ t_s $\quad$ = $\quad$ flow time of water (sec)

$\quad$ C = $\quad$ concentration of polyelectrolyte solution (g/ml)

The value of reduced viscosity and inherent viscosity were plotted against the concentration. The value of intrinsic viscosity was obtained from the y-interception of the graph. Then, it was used to calculate the molecular weight based on the Mark-Houwink-Sakurada equation (shown as Equation 3.6).

$$[\eta] \quad = \quad KM^a \tag{3.6}$$

where $[\eta]$ is intrinsic viscosity, M is viscosity-average molecular weight, K and a are constants. For polyacrylamind:

$\quad$ K $\quad$ = $\quad$ 6.5×10^{-3} ml/g

$\quad$ a $\quad$ = $\quad$ 0.82

3.3.3 Recovery of Light Components by Using Surfactant and Electrolyte Solution

The sludge was weighed for 40 g and mixed with 320 ml of surfactant solution. The mixture was stirred at 200 rpm for 30 min. It was left at room temperature until the solid, aqueous solution and light components were separated completely. This step typically took at least 12 hr to be completed and we did not observe any increment of oil yield after 12 hr. Then, the volume of light components was measured in term of light components yield. To study the effect of temperature, water bath was used to control the operating temperature, ranging from 40 to 80°C. The mixture was stirred and left at the operating temperature for 1 hr.

3.3.4 Recovery of Light Components by Using Coagulant, Flocculant and Flotation Technique

40 g of a sludge sample and 320 ml of coagulant or flocculant solution were mixed. The mixture was stirred at 200 rpm for 30 min and the air

bubble was induced to the system simultaneously. Light components were floated to the surface of the solution. They were skimmed off and the volume was measured as the light components yield. In case of using surfactant together with coagulant solution, 100 ml of surfactant solution was mixed with the sludge and the mixture was stirred for 15 min to promote detergency process and create emulsion droplets. Then, 320 ml of coagulant solution was added into the system.

3.3.5 Pyrolysis Behavior

The pyrolysis behaviors of the original and treated sludge were studied under the N_2 atmosphere by using a DuPont TG-1000 thermogravimetric analyzer controlled by a PC compatible system. The N_2 was continuously flowed into the furnace at the flow rate of 20 ml/min. To avoid the heat and mass transfer limitations, approximately 10 to 15 mg of the sample was loaded in a platinum pan in the furnace of TGA. The temperature was increased from room temperature up to 700°C with the heating rate of 5, 10 and 20°C/min. A small thermocouple measured the temperature in the vicinity of the sample. The experiments were repeated at least twice. The sample weight loss data were continuously detected and recorded under these conditions. They were used to calculate the derivative weight loss. Thremogravimetric (TG) and derivative thermogravimetric (DTG) curves were plotted for study the pyrolysis behavior.