

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

Single Walled Carbon Nanotubes used in this study was produced by the CoMoCAT[®] method. The carbon monoxide was used as the carbon source.

Silica gel was obtained from Aldrich Chemical Company, Inc. Its surface area is 500 m²/g and the size is about 70-230 mesh (63-210 μm).

Triethylenetetramine (TETA), which is commercial grade, was obtained from Huntsman Co., Ltd. The purity is about 97 wt%.

Sodium hydroxide (NaOH), which is analytical grade, was purchased from Labscan Asia Co., Ltd. It has the purity about 99.3 wt%.

Alcohol ethoxylate (Surfonic L24-7), which is nonionic surfactant, was received from Huntsman Co., Ltd. It has the seven-mole ethoxylate of linear, primary 12-14 carbon number alcohol. It is an industry grade.

Acetonitrile was obtained from LabScan Asia Co., Ltd. The purity is about 99.7 wt%.

Distilled water used throughout this work was purchased from the government pharmaceutical organization, Bangkok, Thailand.

All chemicals were used as received without any purification.

3.1.2 Gases

Air zero grade was obtained from Thai Industrial Gas Public Co., Ltd (Thailand). It used as the air generator in the froth flotation procedure.

3.2 Methodology

There were two parts of this study. The first part was the investigation of silica dissolution, which the effect of TETA volume, NaOH concentration, temperature and the reaction time were studied. The second part was the purification

experiment, which included the sonication study and froth flotation study. For the sonication study, the effects of sonication time, TETA volume and NaOH concentration were investigated. After that, the froth flotation experiment was conducted to investigate the effect of all operational parameters affecting concentration and purity of SWNTs.

3.2.1 Dissolution study of Silica by Triethylenetetramine

Samples of silica gel with surface area of $500\text{m}^2/\text{g}$ were used to establish the silica dissolution as a function of volume of amine base, temperature and reaction time. All experiments were repeated at least three times to ensure reproducibility. The average values of data were obtained.

3.2.1.1 *The Effect of Triethylenetetramine Volume*

A certain amount of silica gel about 1.5 g (25 mmol) was placed in a 500 mL three-necked round bottomed flask. Amine base was added at different volumes. Then, the mixture, the silica gel and amine bases, was stirred by a magnetic stirrer with mild heating until the mixture was homogeneous. After that, the bottomed flask was immersed in an oil bath pre-heated to $70 \pm 5^\circ\text{C}$ for a pre-set reaction time. The reaction time was started when a stirrer was turned on. For any fixed reaction time, the reactor was cooled quickly in an ice water box, in order to stop the reaction. The solid, which was washed with acetonitrile, was separated from the solution by filtering with a filter paper number 42 ($2.5\ \mu\text{m}$). After that, the filtered solid was then heated in a furnace at 550°C for more than 12 hours. The dried solid was weighed indicating the amount of silica undissolved. Blanks were also run for each set of dissolution experiment.

3.2.1.2 *The Effect of Reaction Temperature*

The experiment was also carried out by adding 1.5 g (25 mmol) of silica and 300 ml TETA into a 500 mL three-necked round bottomed flask. The temperature was varied from room temperature (26°C) to 50°C , 70°C , 100°C and 140°C with a constant reaction time of 1 hour. The same procedure as mentioned before was done.

3.2.1.3 The Effect of Reaction Time

To observe the effect of reaction time, the same amount of silica and TETA were placed in the 500 mL three-necked round bottomed flask and the reaction was fixed constant at 70°C. The reaction time was varied in the rang of 1 to 10 hours.

3.2.2 Dissolution study of Silica by Sodium Hydroxide

Samples of Silica gel with an initial surface area of 500m²/g were used to established the silica dissolution as a function of sodium hydroxide concentration and temperature. All experiments were triplicate times to ensure reproducibility. The experiment data were reported in average values.

3.2.2.1 The Effect of Sodium Hydroxide Concentration

A certain amount of silica gel of 1.5 g (25 mmol) was added in a 304 stainless steel beaker. Some of sodium hydroxide solution having different concentration was added. Then, the mixture, the silica gel and alkaline solution, was mixed by a magnetic stirrer and the beaker was immersed in an oil bath pre-heated to 70 ± 5°C. The reaction time was fixed at 1 hour. After that, the reactor was cooled quickly in the ice water box in order to stop the reaction. The analytical procedure was the same as mentioned before. Blanks were also run with pure water.

3.2.2.2 The Effect of Reaction Temperature

To determine the effect of reaction temperature, the same amount of silica gel and NaOH were placed in the beaker and the reaction temperature was varied at a constant reaction time of 1 hour.

3.2.3 Sonication and Froth Flotation Experiment

The SWNTs concentration of 0.2 mg/mL was fixed for the purification experiment, which was separated into two parts of sonication studies and froth flotation experiments. Prior to the removal of the silica, the AP-SWNTs was placed in an oven at 250°C for 12 hours to oxidize the Co and Mo species remaining in the products. At that point, the heater was turn off and the oven was allowed to cool by natural convention. The parameters of the sonication studies were TETA volume, NaOH concentration and sonication time, whereas, the froth flotation

experiments were to study the effect of pH solution. All experiments were at least duplicated to ensure reproducibility.

3.2.3.1 Sonication Studies

The AP-SWNT solution having 0.2 mg/mL (0.16 g) was mixed with TETA and NaOH solution. The TETA volume was varied from 50 to 250 mL while the NaOH concentration was varied from 1 to 10 molar in 30 mL. After that the mixture was sonicated in a sonication bath at different times. The temperature of solution was maintained at $70\pm 5^\circ\text{C}$. After sonication the mixture was filtered and the filtered solid was washed by acetonitrile and distilled water, respectively until the pH was neutral. The washed solid was then dried at 110°C for 12 hours. The carbon fraction in the dried solid was characterized by Laser Raman spectroscopy and the temperature programmed oxidation (TPO).

3.2.3.2 Froth Flotation Experiment

The AP-SWNT solution containing 0.2 mg/mL (0.16 g) was mixed with different amounts of TETA and NaOH. After that, the mixture was sonicated as described before. The surfactant solution of Surfonic L-24 and the AP-SWNT solution were to place into the froth flotation column. The initial solution volume in the froth flotation column was kept constant at 800 mL. The froth flotation experiment was run at a constant air flow rate of 150 cc/min. A schematic diagram of the froth flotation unit used in this study is shown in Figure 3.1. A glass cylindrical column with 3 cm internal diameter and 150 cm height was used as the froth flotation column (see in Figure 3.2). Air Zero was introduced into the column through a sintered glass disk, having pore size diameters about 16 - 40 μm . The sample, AP-SWNTs (that was sonicated) as well as the surfactant solution, were transferred to the froth flotation column (see Figure 3.3). The froth accumulated at the top of the column came out into a receiver. The experiment was terminated when no foam came out. The froth collected was broken by freezing. After that the overflow foam solution was filtered and washed with distilled water to remove the surfactant. The washed solid was dried at 110°C and taken to characterize by Laser Raman spectroscopy and the temperature programmed oxidation (TPO).

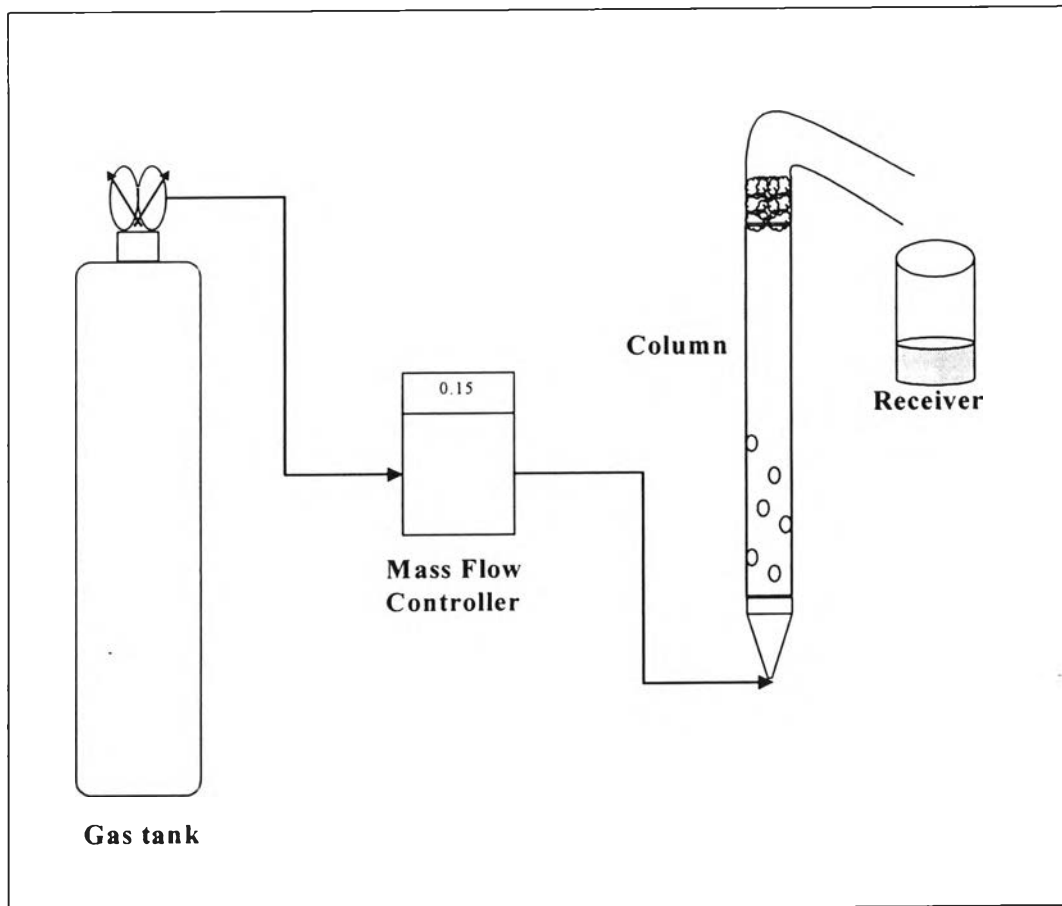


Figure 3.1 Experimental froth flotation apparatus.

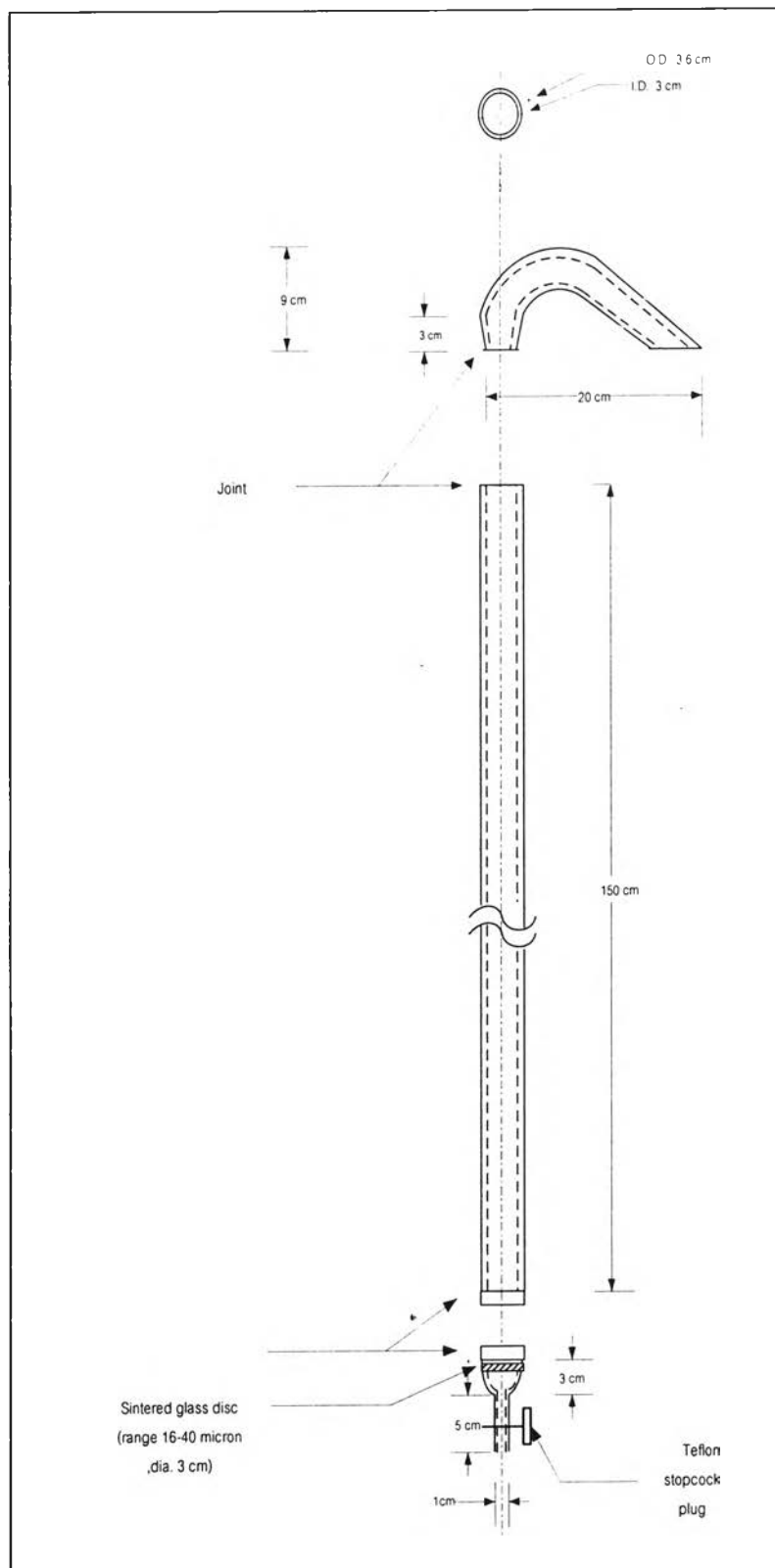


Figure 3.2 Schematic diagram of froth flotation column.

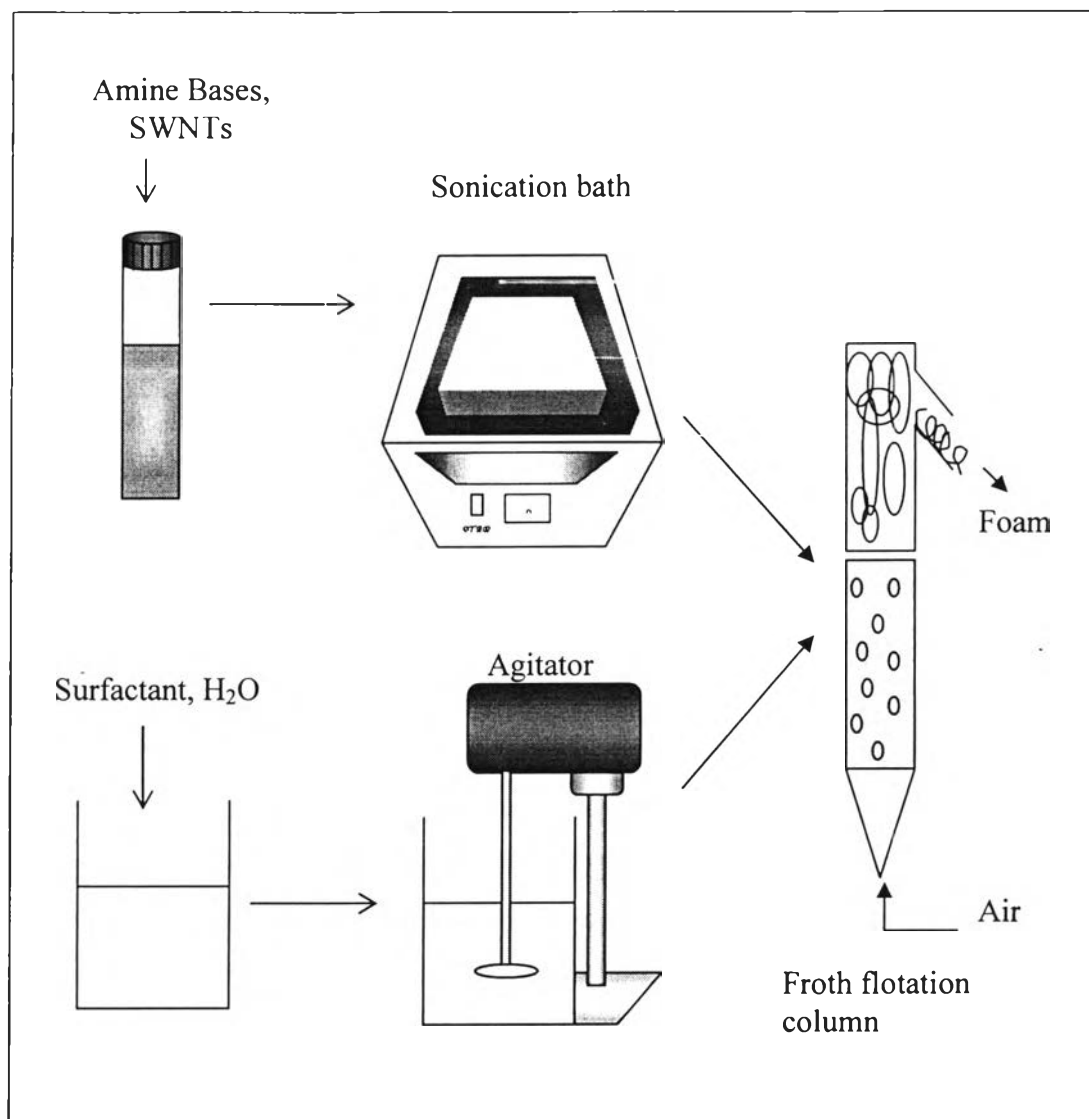


Figure 3.3 Schematic of experiment procedure.

3.3 Analytical Methods

3.3.1 Analysis of Silica

The solid samples obtained from all the experiment were analyzed for silica. First, the samples were washed with acetonitrile. After that, the solid was separated from the solution by filtration using filter papers (number 42, 2.5 μm). For the next step, the filtered solid was prewashed with deionized water and then burn in a furnace at 550°C for more than 12 hours. The rate of heating was 1°C/min from room temperature to 60°C, for 2 hours, 1°C/min from 60°C to 80°C and for 2 hours

and then finally 5°C/min from 80°C to 550°C for 12 hours. The heat treatment was used to oxidize any residual organic residues (Laine *et al.*, 1999). The residue was weighed to represent the amount of undissolved fraction of silica gel. Then, the amount of dissolved silica gel or dissolution of silica gel was calculated.

3.3.2 Carbon Product Characterization

The collapsed froth solution, which was filtered and washed by distilled water and finally dried at 110°C, was taken to analyze for carbon content and carbon structures. The characterization of carbon products were carried out by a number of techniques including Laser Raman spectroscopy and Temperature programmed oxidation (TPO) which were used to both quality and quantity the solid samples.

3.3.2.1 *Laser Raman Spectroscopy*

Raman spectroscopy is a non-destructive analysis technique and measurements can be made over a wide range of temperatures or pressures. It can provide unique information about vibrational and electronic properties of materials. Even though it is not a direct method, it can also be used to determine the structures of materials. Because the Raman intensity of a vibration or phonon in a crystal depends on the relative directions of the crystal axis and the electric wave polarization of the incident and scattered light, it may also be used to determine the orientation of nanotubes in polymer matrices or within nanotube bundles (Richard, 2000).

The sample before and after purification by froth flotation were studied by comparing laser Raman spectra. The Raman spectroscopy used in this study was Yvon-Horiba LabRam 800 equipped with a CCD (charge-couple device) with laser excitation sources having a wavelength of 632 nm (He-Ne laser). The laser powers used were in the range of 3.0 to 5.0 mW.

3.3.2.2 *Temperature Programmed Oxidation (TPO)*

This TPO technique can investigate for quantitative properties of carbon nanotubes. The TPO analysis was performed at a continuous flow of O₂/He (ratio 2:1) with a total flow rate of 40 sccm. A carbon sample about 10-12 mg was placed in the quartz tube and it was secured with packing quartz wool the sample

temperature was linearly increased with a constant rate of $13^{\circ}\text{C}/\text{min}$ to reach a maximum temperature of 850°C . The carbon fraction of the sample was reacted with oxygen (O_2) to produce oxidation products such as water (H_2O) and carbon dioxide (CO_2). After this reaction, CO_2 and H_2 in the effluent gas were passed to a methanator containing $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst to convert into carbon dioxide (CO_2) to methane (CH_4). Consequently, CH_4 was detected with a flame ionization detector (FID SRI model 110). The area under the curve obtained was used to calculate carbon content in the sample. Moreover, the shape of the curve can be used to determine the type of carbon formation. In other words, carbons with different morphology or different locations are burnt at different temperatures.