CHAPTER III

EXPERIMENT

3.1 Equipment and Apparatus

3.1.1 Nebulizer

The MICRO MIST, a small volume (Hudson RCI) jet nebulizer, was used in this study. Picture of the micro mist is shown in Figure 3.1. This nebulizer was designed for using in respiratory therapy. It is used to nebulize a liquid drug, i.e. a thin liquid with water like viscosity. This nebulizer has a narrow spray nozzle, approximately 0.015 inches in diameter. The nebulizer can be orientated at the angle up to 90°. It has a 6 mL capacity anti-spilled jar to prevent leakage. The droplet generated by this nebulizer has a mean particles diameter (MD) of 1-5 micrometer [50].

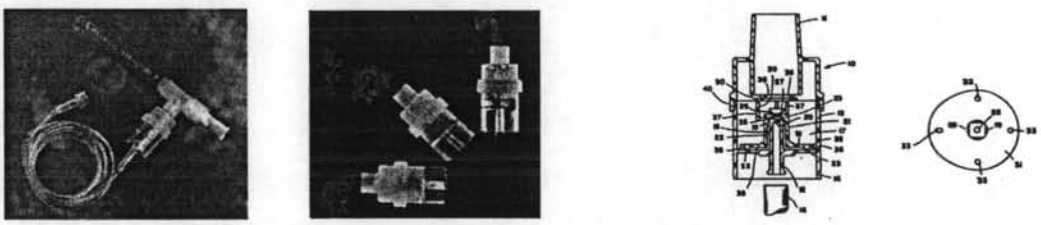

Figure 3.1 MICRO MIST small volume (Hudson RCI) jet nebulizer

3.1.2 Heater

This study uses a tubular band heater (Sang Chai Meter co., Ltd.) to attach the cylinder. This heater has a 25 mm diameter, with maximum potential at 220 V, and maximum power of 200 watt. The reactor has a maximum temperature at 300 °C.

3.1.3 Temperature controller

Model	Microcomputer Based Temperature Indicating Controller FCR-13A
Input	Thermocouple, RTD, DC current, DC voltage
Accuracy	within ± 0.2% FS ± 1digit
Sampling period	0.125 seconds
Control action	Fuzzy self tuning PID, Auto-tuning PID
Control output	Relay contact, Non-contact voltage, DC current
Supply voltage	100-240 V AC 50/60Hz
Thermocouple	SK-JB-10 (TYPE K)

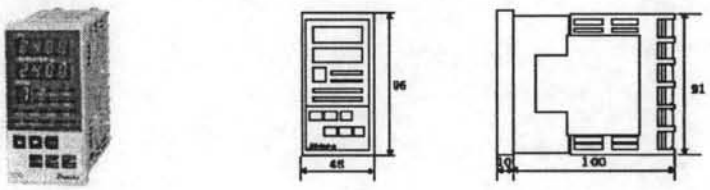

Figure 3.2 Microcomputer Based Temperature Indicating Controller FCR-13A

PID controller

A PID controller involves three parameters: Proportional band, Integral times and Derivative times. The PID controller was used to correct the error between a measured temperature and a desired temperature set point by calculating and then outputting a corrective action that can adjust the temperature accurately. Choosing the proper values for P, I and D can provide the minimum error which is called "PID Tuning" as shown in Figure 3.3. In this study, P, I and D values were set to 1, 50 min. and 5 min. respectively.

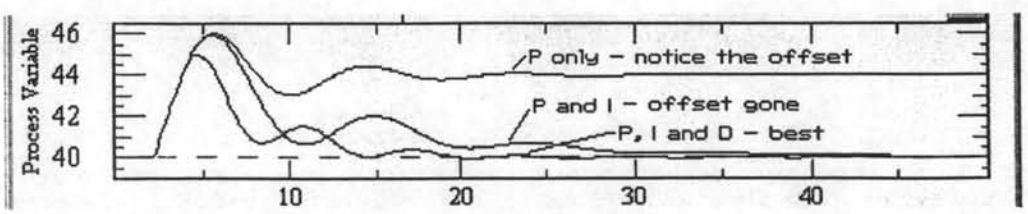

Figure 3.3 PID tuning

3.1.4 Air compressor

Air compressor used in this study was a rotary screw compressor model PUMA XM-2525, as shown in Figure 3.4. This compressor has a smooth pulse-free air output, high output volume (capacity 25 L), maximum flow-rate of 120 L/min and has a maximum pressure of 7 bars. It is used to feed air in to the nebulizer in order to generate droplet of precursor.

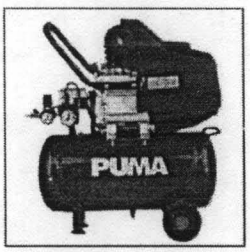

Figure 3.4 PUMA XM-2525

3.2 Chemicals and material

3.2.1 Silver nitrate
3.2.2 (+)-D-glucose
3.2.3 Ammonia solution
3.2.4 Sodium citrate
3.2.5 Ethylene glycol
3.2.6 Glycerol
3.2.7 Deionized water (DI)
3.2.8 Acetone
3.2.9 Nitric Acid

3.3 Synthesis of silver nanoparticles by chemical reduction method.

Silver nitrate solution was prepared by dissolving 0.170 g of silver nitrate in 100 mL distilled water and diluted to desired concentration prior to use. A reducing agent such as sodium citrate, glucose, glycerol, and ethylene glycol was added in to the silver nitrate solution (the mole ratio of the reducing agent to silver nitrate was about 10 times). Then, these solutions were heated until the reaction occurred and the reaction temperature was measured. The reaction was maintained for 15 min. The UV-Visible spectrum was collected during the reaction. The result indicated the most suitable reducing agent for thermal reduction of sprayed silver salt method.

3.4 Synthesis of silver nanoparticles by thermal reduction of sprayed silver salt method

A schematic diagram of thermal reduction of sprayed silver salt method is shown in Figure 3.5 and the apparatus was shown in Figure 3.6. To begin the reaction, the tubular reactor was heated to the reaction temperature (about 120 °C) and maintained for 10 min. Then, the nebulizer reservoir was filled with the precursor solution containing silver nitrate 0.5 mmol/L 10 mL mixing with glucose 0.5 g (0.27 mol/L). Subsequently, precursor solution was nebulized into the tubular reactor and the synthesizing silver nanoparticles were trapped in cold water. The UV-Visible spectrum of the trap water containing silver nanoparticles was collected. The synthesized silver nanoparticles solution was kept in refrigerator for further analyst.

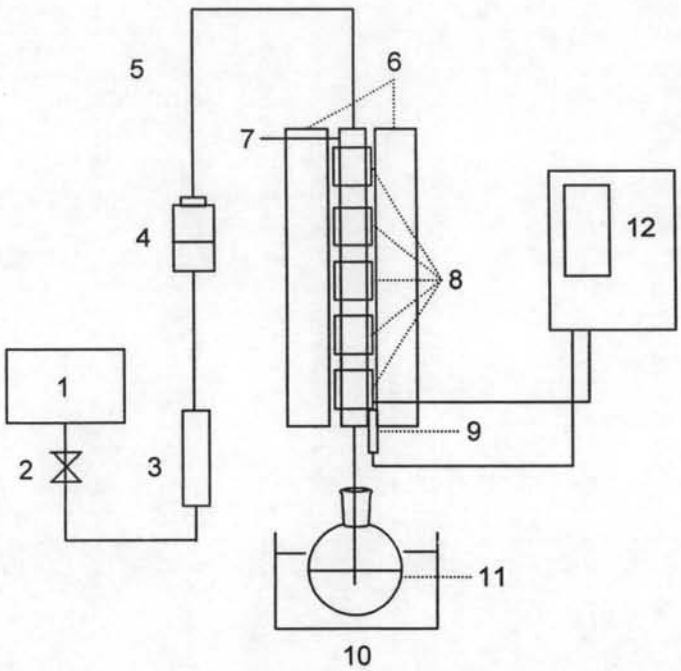

Figure 3.5 Schematic diagram of thermal reduction of sprayed silver salt

1 = Air compressor	2 = needle valve	3 = flow meter
4 = nebulizer	5 = glass tube	6 = ceramic insulator
7 = stales tube (reactor)	8 = band heater	9 = thermocouple
10 = ice bath	11 = trapped water	12 = temperature controller

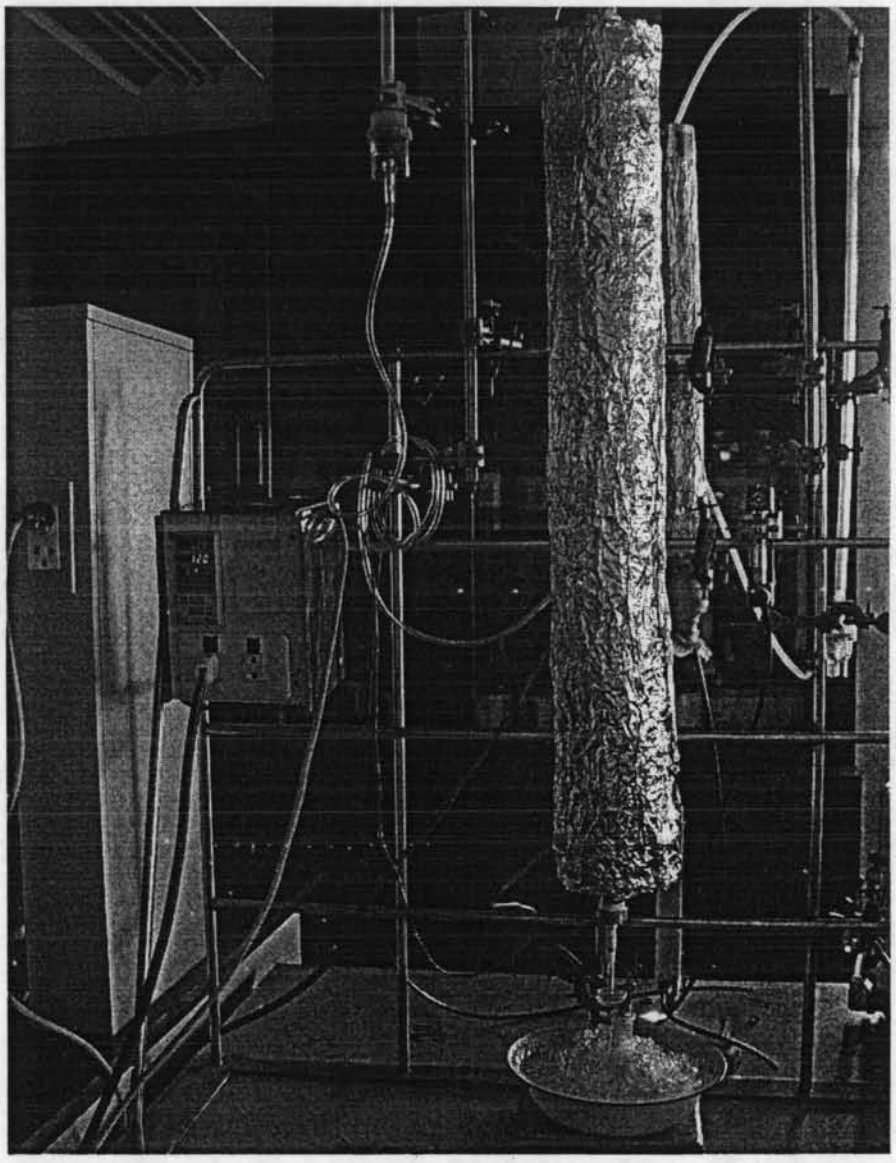

Figure 3.6 Apparatus for thermal reduction of sprayed silver salt method.

3.5 Preliminary study on the possibility of characterization technique (UV-Visible spectroscopy).

All precursor solution was prepared and collected the UV-Visible spectrum before and after nebulizing. This section used the same condition that use in synthesis of silver nanoparticles. This study preformed to make sure that there was no spectrum of the precursor interfering with the spectrum of silver nanoparticles.

3.6 Investigation of the various factors affecting the synthesis of silver nanoparticles by thermal reduction of sprayed silver salt.

In this method, size, size distribution, and morphology of silver nanoparticles depend on the various reaction conditions such as temperature, concentration of precursors, the flow rate that applied to the nebulizer, type of carrier gas.

3.6.1 The concentration of silver nitrate

The concentration of silver nitrate was varied from 0.3, 0.5, 0.7 and 1.0 mmol/L. Other synthesis conditions were similar to that reported in Section 3.4, except the concentration of glucose is varied by mole ratio of silver nitrate.

3.6.2 The concentration of glucose (reducing agent)

The concentration of glucose was varied form 0.001, 0.01, 0.25, 0.5 and 0.75 mol/L. The concentration of silver nitrate was maintained at 0.5 mmol/L. The other synthesis condition was the same as that of Section 3.4.

3.6.3 The concentration of ammonia solution

The concentration of ammonia solution was varied from 0.100, 0.010 and 0.001 mol/L. The other synthesis condition was the same as that of Section 3.4.

3.6.4 Temperature in tubular reactor

To study the effect of temperature on the synthesized silver nanoparticles, temperature in the tubular reactor was varied from 80 °C to 200 °C (the temperature must not higher than 200 °C in order to prevent thermocouple burning out). Other synthesis condition were similar to that reporting in Section 3.4.

3.6.5 Flow-rate in nebulizer

The applied flow-rate to nebulizer was ranging form 2.5 - 5.0 L/min. If flow-rate was higher or lower than 2.5 and 5.0 L/min, the nebulizer does not work properly. The flow-rate was varied in this study are 2.5, 3.5 and 4.5 L/min. The concentration of precursor and temperature was using the same condition as that of section 3.4.

3.6.6 Type of carrier gas

To study the effect of carrier gas in this reaction, air and nitrogen was used. Prior to starting the reaction, nitrogen was flowed in the nebulizer through out tubular reactor. The nebulizer reservoir was filled with the precursor solution. (which are purges with nitrogen gas for 3 min). The reaction condition was as the same as in section 3.4. The UV-Visible spectrum of synthesized silver nanoparticles was collected and compared with the method using air as a carrier gas.

3.7 Comparison of thermal reduction of sprayed silver salt, precursor injection, and precursor heating method.

UV-Visible extinction spectrum of synthesized silver nanoparticles by precursor heating method, precursor injection method, and thermal reduction of sprayed silver salt method were measured. The results were compared to investigate the size and size distribution of silver nanoparticles.

3.8 Long term stability of synthesized silver nanoparticles.

The synthesized silver nanoparticles by thermal reduction of sprayed silver salt method were kept for two weeks, a month and three months in refrigerator. UV-Visible spectra of the synthesized silver nanoparticles were measured as a function of time.

3.9 Characterization of synthesized silver nanoparticles.

3.9.1 UV-visible spectroscopy

The cuvette was rinsed by conc. nitric acid in order to wash all the residual of silver nanoparticles and subsequently washed with DI water. Before collecting the spectrum a reference of pure DI water is collected as the blank sample. If the absorbance of the sample was too high for collecting the spectrum, the sample was diluted. The USB4000 spectrophotometer was used and attached with the fiber optic and the light source. The instrument setup is shown in Figure 3.7.

The optical spectra were obtained with a standard duterium lamp (Thorlabs, 150 W) and a fiber coupled spectrometer (Ocean Optics, 350-1100 nm). A 5 mm cuvette was routinely used. For in-situ spectroscopy, a custom-made fiber sensor was introduced in the liquid close to the vessel wall while the vessel was extenally illuminated.

Instrument Setup

Model	Ocean Optics Portable UV-Visible spectrometer
Source	Deuterium-Halogen light source DH 2000
Wavelength range	UV-Vis-NIR
Detector	USB 2.0 Fiber Optic Spectrometer USB4000-UV-VIS
Grating	600 Line Blazed at 300 nm
Bandwidth	200-850 nm

Spectra Acquisition Parameter

Software	Ocean Optics Inc. Spectra Suit
Integration time	10 milliseconds
Scans to Average	128 scans
Box car width	10 nm
Spectra format	Absorbance
Spectra range	200-850 nm

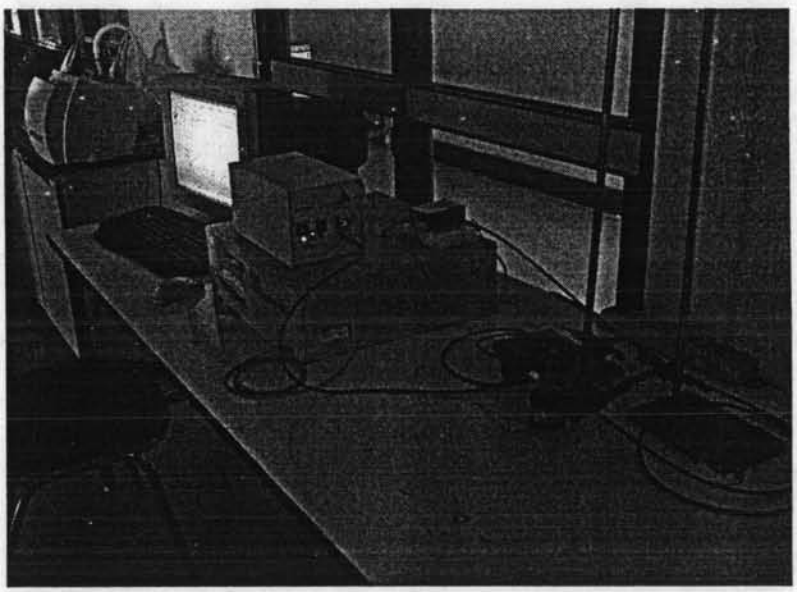

Figure 3.7 Ocean Optics Portable UV-Visible spectrometer

3.9.2 Transmission electron microscope (TEM)

A Transmission electron microscopy (TEM) image of Silver nanoparticles was recorded with a JEOL JEM-2010 analytical transmission electron microscope as shown in Figure 3.8. It has a LaB_6 electron gun and can be operated between 80 and 200 kV with a point resolution of 0.23 nm. Samples were prepared by placing a drop of silver nanoparticles solution onto a carbon-coated copper grid. After the solutions were left dried out, TEM images of these silver nanoparticles were collected.

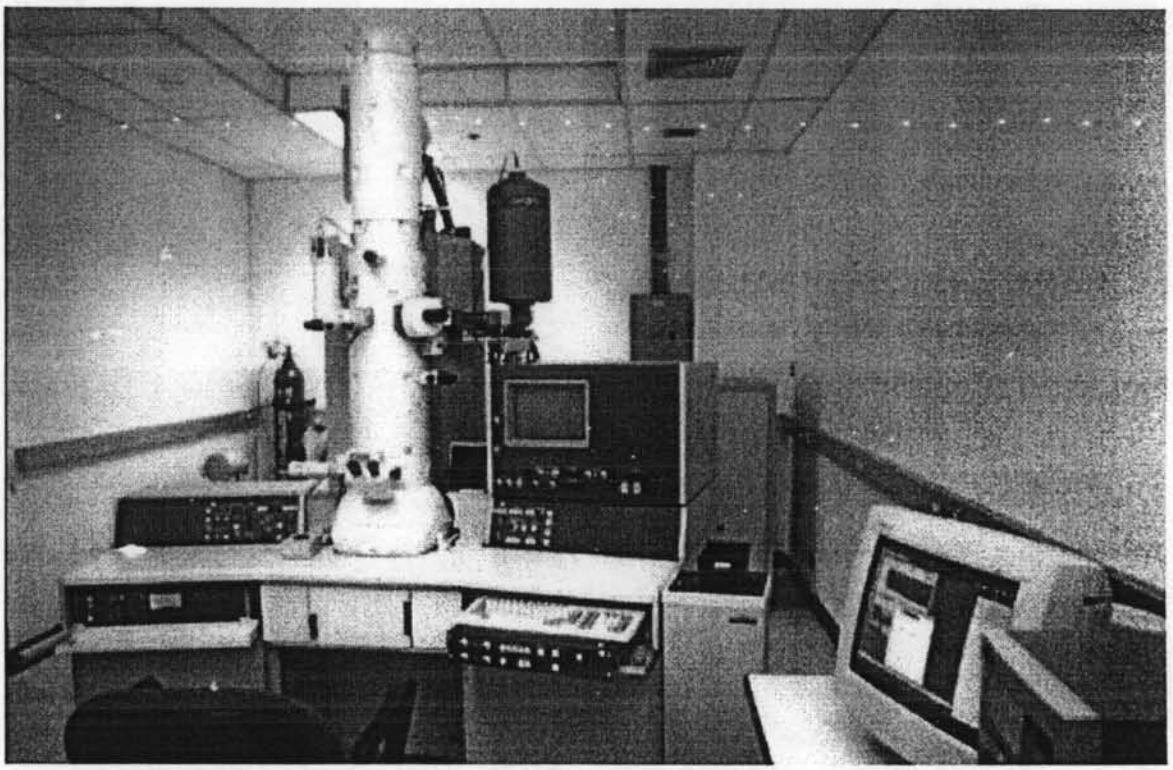

Figure 3.8 JEOL JEM-2010 analytical transmission electron microscope.