

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

Octadecyltrichlorosilane (ODS) was received from Gelest Company. Precipitated silica (Hi-Sil[®] 233) from PPG-Siam Silica had a reported BET surface area of 136 m²/g. Toluene 99.5%, Methanol (HPLC grade) and trichloroethylene 99.5% were received from Lab-Scan Company. Potassium dihydrogenphosphate (KH₂PO₄), Potassium Chloride (KCl), and Sodium-hydroxide (NaOH) as a buffer solution were received from Merck Company. Ozone was produced by using the ozone generator OG20 of Verfahrenstechnik Universal GmbH Company. All solutions were prepared with distilled water .

3.2 Catalyst preparation

The basic procedure to construct the chemical bonded monolayer of hydrocarbon on precipitated silica (Thakulsukanant et al., 1997) is given as below:

An octadecyl immobilized silica was prepared by treating silica Hi-Sil[®] 233 with octadecyltrichlorosilane (ODS). Typically, silica (6g), octadecyltrichlorosilane (5 ml) and toluene (180 ml) were put in a dry 500 ml round bottom flask equipped with a condenser and drying tube. The mixture

was refluxed for 12 h. then methanol (24.85 ml) was added and refluxed for additional 3 h. The mixture was then filtered through a membrane filter and the solid was washed by distilled water (400 ml), followed by toluene (400ml). Further, the solid was washed with toluene by means of Soxhlet extractor for a day, and then dried overnight at 80°C.

3.3 Catalyst characterization

3.3.1 Fourier transform infrared spectrometry (FTIR)

The spectra of the silica treated with octadecyltrichlorosilane was measured on a Bio-Rad FTS-45A infrared spectrometer by the Transmission technique as a KBr disc.

3.3.2 Elemental analysis

The Perkin Elmer Elemental Analyzer was applied to measure the carbon weight percentage which contain in 1 mg of silica treated ODS. The amount of the ODS bonded to the silica could be calculated from the carbon weight percentage.

3.4 Apparatus

The experimental system is shown in Figure 3.1. The system consists of 2 major parts : Ozone generator, Semibatch reactor.

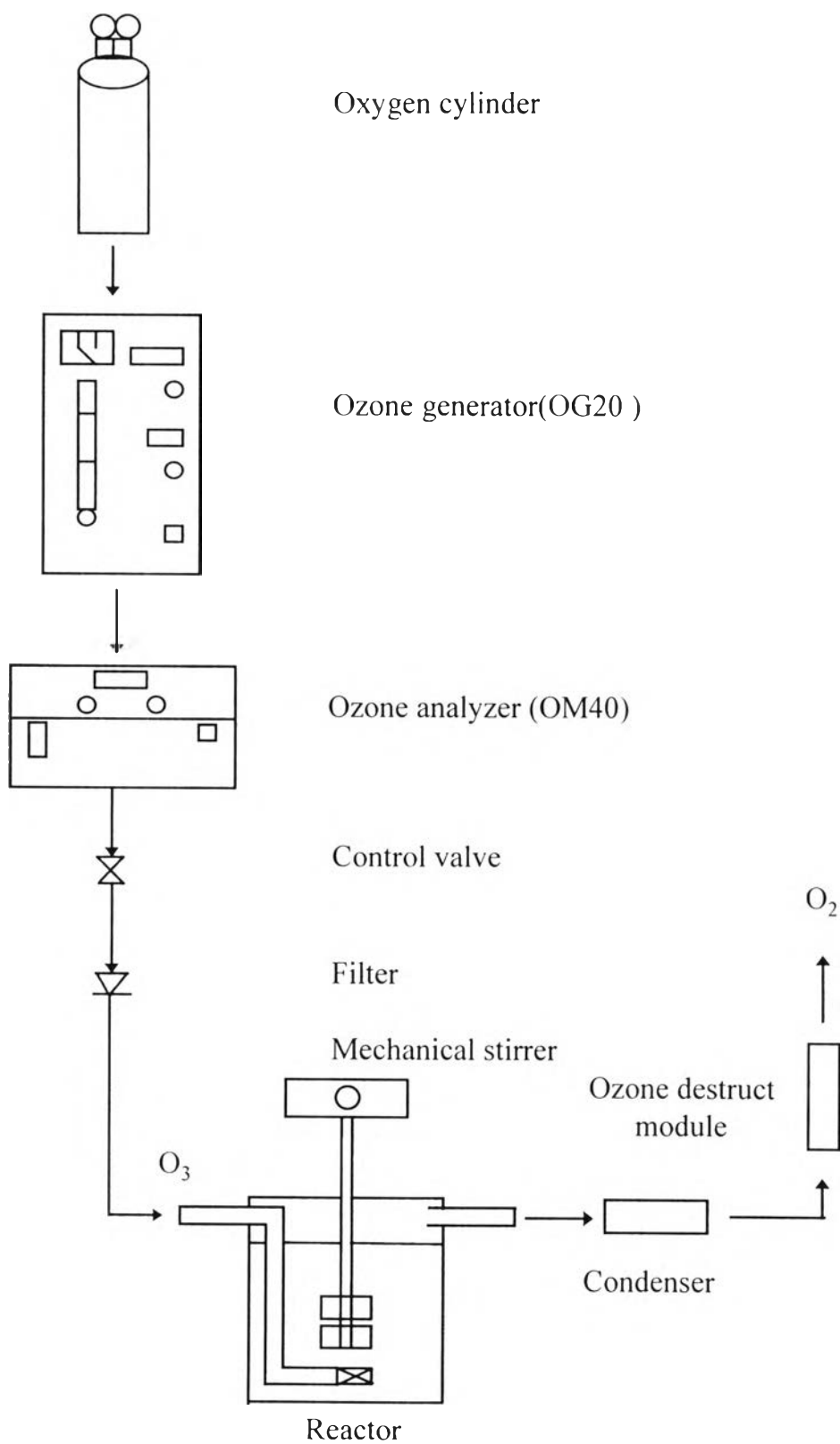


Figure 3.1 Schematic flow diagram.

3.4.1 Ozone generator system

Ozone generator system consists of 3 major parts: ozone generator, ozone analyzer and ozone destructor.

3.4.1.1 Ozone generator. Oxygen gas was passed through the ozone generator OG 20 Verfahrenstechnik Universal GmbH Ozone Generator feeding the electrical energy to produce the mixture gas of ozone and oxygen gas. The concentration of the effluent gas can be controlled by adjusting the oxygen inlet gas flow-rate and the voltage adjuster.

3.4.1.2 Ozone analyzer. The concentration of the ozone gas could be monitored by using the Ozone Measuring Device OM40. This device used the UV photometric basis principle to determine the amount of ozone concentration by measuring the spectrum at the absorption 254 nm in the ultraviolet radiation spectrum.

3.4.1.3 Ozone destructor. The residual output ozone gas from the reactor could be destroyed by passed through the ozone destructor converted to the oxygen gas.

3.4.2 Semibatch reactor system

Before passing through the reactor, the ozone gas had to pass through a 7 micron filter in order to remove any small particles. The flow rate of the ozone gas was controlled by a Swagelok needle valve and a fine metering valve to achieve the desired flow rate. A check valve was installed to prevent the back flow of gas.

The reactor made of glass was a one litre size with a Teflon lid and silicone gasket to prevent the ozone leakage. Ozone inlet gas was passed through the reactor via a coarse sintered glass sparger at the bottom of the reactor. Residual ozone gas passed through the condenser before leaving the reactor to condense out the stripping volatile contaminant.

The vessel contents were stirred by a ALC quiet -sL mechanical stirrer equipped with a two-pitch blade turbine Minicking a Disk Style Turbine.

3.4.3 Head space gas chromatograph

Gas chromatograph (GC) was used to measure trichloroethylene (TCE) at the specific time. Perkin Elmer gas chromatograph equipped with flame ionization detector (FID) was used. The analysis was conducted using a Carbowax 10 micropacked column at the constant temperature of 105, 250 and 150 °C for column, detector and injector, respectively.

The Headspace was also operated at the constant temperatures of 80, 100 and 100 °C for sample vials, needle and transfer line temperatures, respectively with thermostat time 10 minutes.

Trichloroethylene was analyzed from the chromatogram. The retention time and peak areas of the analyte were compared with those of the standard solution of known compositions. From the retention time, TCE was identified while the relative concentration of trichloroethylene was obtained from the integration of peak areas.

A needle syringe was automatically injected the 1 μ l vapor equilibrated with the aqueous solution 2 ml in a 14 ml vial into Gas chromatographer for analysis. From the decrease of the trichloroethylene concentration at the specific time, the rate of reaction was determined.

3.5 Adsolubilization measurement

The adsolubilization measurements were carried out in a 1 litre reactor at 20 °C both with and without catalyst. The amount of catalyst used was 25 g with TCE concentration of 400 ppm. After equilibrium time (which was about 2 hrs), the aqueous solution was sampling 2 ml by using the syringe. TCE in aqueous solution was determined by using the Headspace Gas chromatograph. TCE in admicelles was calculated by subtracting the value found in the aqueous phase from the total concentration.

A series of the adsolubilization measurement at 20 °C were carried out in the same manner described above except that TCE concentration was changed to 300, 200 and 100 ppm.

3.6 Reaction rate studies

3.6.1 Mass transfer limitation

After adsolubilization of TCE was completed, the ozone gas was passed into the reactor to react with the solution. The reaction could be performed in the region of no external limitation. Generally, there are two types of mass transfer limitations: internal mass transfer and external mass transfer limitation. Since the catalyst mixture contained very small particles, it was assumed that the effect of internal concentration and temperature gradients could be neglected. External transfer resistances depend strongly on the stirring speed. Test of external limitations were conducted to find the stirring speed in the region of no external limitation. A series of experiments were conducted at ozone concentration of 50 g/m³, TCE concentration of 400 ppm and temperature at 20 °C. The stirring speeds of 550, 750, 900 and 1,000 rpm were

used for the above condition. Rate of reaction was plotted against stirring speeds. The stirring speed in the region of no external limitation was determined from the region where the rate remained the same when the stirring speed increased.

TCE could easily lose due to its volatility. Its loss then came from stripping effect and ozonation effect. The ozonation effect was calculated by subtracting of the stripping rate from the total rate. The stripping rate could be determined by passing only the oxygen gas through the solution. The total concentration of TCE could be calculated by using the adsolubilization curve.

3.6.2 Reaction order

The reaction order of TCE could be evaluated by plotting the equation (7) in chapter 2 which the slope is equaled to the apparent pseudo first order rate constant.