CHAPTER III

EXPERIMENT

Materials

1. Styrene waste was obtained from Thai Petrochemical Industry (TPI) Co., Ltd.

2. Methyl alcohol, CH_3OH (reagent grade) was obtained from J.T. Baker.

3. Dichloromethane, CH_2Cl_2 (reagent grade) was obtained from J.T. Baker.

4. Glacial acetic acid, CH_3COOH (analytical grade) was obtained from BDH.

5. Hydrogen peroxide, H_2O_2 (40% m/v; reagent grade) was obtained from Carlo Erba.

6. Zinc powder was obtained from Merck.

7. Diethyl ether, $(CH_3CH_2)_2O$ (reagent grade) was obtained from J.T. Baker.

8. Oxygen gas (high purity) was obtained from TIG Trading Ltd.

9. Hydrogen gas (high purity) was obtained from TIG Trading Ltd.

10. Platinum on activated charcoal, 10% Pt/C was obtained from Merck.

11. Potassium iodide, KI (reagent grade) was obtained from J.T. Baker.

12. Sulphuric Acid, H_2SO_4 (concentrated) was obtained from J.T. Baker.

Apparatus and Instruments

1. Ozone Generator

Ozone was generated by electric discharge in an oxygen stream, using a Fischer OZ 500 M Ozone generator. The ozone output of the generator was determined by allowing ozone to react with a potassium iodide solution within a timed period. The amount of liberated iodine was titrated with sodium thiosulphate solution. The technical data of the generator is shown in Table A1.

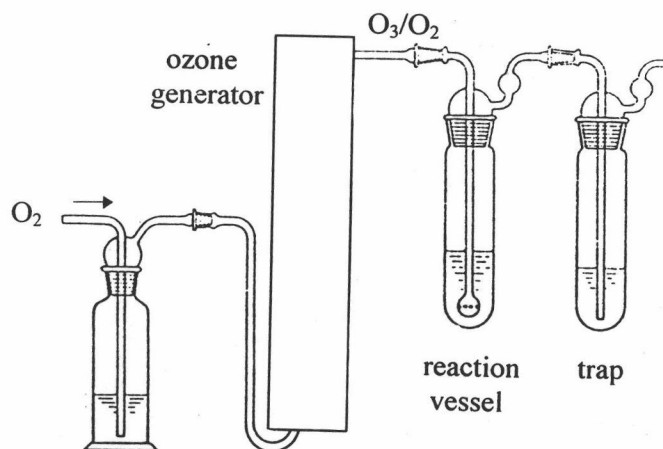### 2. Apparatus for ozonolysis of styrene waste (Figure 3.1)

Figure 3.1 Apparatus for ozonolysis of styrene waste

3. High Pressure Reactor

The hydrogenation was carried out in a high pressure reactor with automatic temperature controller model 4842 from the Parr Instrument company.

5. Nuclear Magnetic Resonance Spectrometer

The NMR model AC-F 200 from Bruker was used. ^{1}H-NMR and ^{13}C-NMR analyses were done on solution of compound in $CDCl_3$.

6. Fourier Transform Infrared Spectrometer

The FT-IR model impact 410 from Nicolet was used.

Procedures

1. Styrene waste analysis

The percentage of styrene in styrene waste was determined by quantitative infrared spectroscopy. From infrared spectrum of styrene which was shown in Figure A1, the band of =C-H (out of plane bending) at 910 cm^{-1} could be seen clearly. This band was used for quantitative analysis by calibration curve method. Standard and sample solutions were prepared in chloroform. The calibration curve was established by plotting concentration (%) versus absorbance. The % transmittance was converted to absorbance by the following equation.

$$A \ = \ abc \ = \ \log[1/T] \ = \ \log[100/\%T]$$

where

$\quad$ A = Absorbance

$\quad$ a = Absorptivity

$\quad$ b = Thickness of IR cell

$\quad$ c = Concentration of solution

$\quad$ T = Transmittance

Styrene waste was analyzed by ^{1}H-NMR and ^{13}C-NMR spectroscopy to determine its composition.

2. Preparation of benzaldehyde from styrene waste

A solution of 5.7 ml of styrene waste in 100 ml of dichloromethane was cooled to 0°C. Ozone was introduced into the vigorously stirred solution. The ozone was completely absorbed until 1 mole per mole of styrene had reacted. At this stage ozone passed through and released iodine in the adjoining potassium iodide trap. The solvent was removed by rotary evaporator.

The residue was dripped into a suspension of zinc powder in acetic acid, contained in a round bottom flask with dropping funnel, stirrer and reflux condenser. The mixture was refluxed, stirred until cold, then extracted with ether. Preparation of carbonyl derivative was affected by addition of 2,4-dinitrophenylhydrazine solution to the crude extract followed by titration of the product. The yield was calculated from the weight of 2,4-dinitrophenyl-hydrazone derivative. In order to optimize the yield of benzaldehyde, the reaction condition were varied as follow:

- the acetic acid concentration
- the mole ratio of zinc and styrene
- the reaction time

The effect of parameters above were shown in Table 3.1.

3. Preparation of benzoic acid from styrene waste

The solution of 5.7 ml of styrene waste in 100 ml of methanol was ozonized as shown in the first preparation. The residue was dissolved in glacial acetic acid and hydrogen peroxide was added. The reaction mixture was refluxed. When the oxidation was complete, the solution was allowed to come

to room temperature. Benzoic acid was filtered off and was recrystallized from distilled water. In order to optimize the yield, the following synthesized parameters were varied:

- the mole ratio of styrene and hydrogen peroxide

- the mole ratio of hydrogen peroxide and glacial acetic acid

- the reaction time

The effect of these parameters were shown in Table 3.2.

4. Preparation of benzyl alcohol from styrene waste

The solution of 5.0 grams of styrene waste in 100 ml of methanol was ozonized as described in the first preparation. After completion of ozonolysis, the ozonized solution was transferred to a high pressure reactor and platinum on activated charcoal catalyst was added. The gas in the reactor was replaced by hydrogen gas by successive dilution and then hydrogen gas pressure in the reactor was adjusted. The two-steps catalytic hydrogenations were operated at various conditions. When the hydrogenation was completed, filtered off the catalyst, then removed the solvent by the rotary evaporator. In order to approach the optimum condition, the synthesized parameters were varied as follow:

- the catalyst concentration

- the reaction temperature on hydrogenation

- the hydrogen pressure on hydrogenation

- the reaction time on hydrogenation

The effect of catalyst concentration, temperature, pressure, and reaction time were studied under condition which were shown in Table 3.3. The yield of benzyl alcohol was obtained from ^{1}H-NMR quantitative analysis.

^{1}H-NMR quantitative analysis [27]

The amount of benzyl alcohol was determined by quantitative ^{1}H-NMR. The following general equation was used for the calculation

$$W_u = W_s \frac{N_s M_u H_u}{N_u M_s H_s}$$

W_u and W_s	=	Weights of unknown and standard
N_u and N_s	=	Numbers of active nuclei of unknown and standard
M_u and M_s	=	Molecular weights of unknown and standard
H_u and H_s	=	The heights of their integrated resonances

Table 3.1 The various operating conditions for benzaldehyde preparation.

Parameters studied	Acetic acid concentration, %	zinc : styrene mole ratio	Reaction time, hrs
Acetic acid concentration	25	1:3	2
	40	1:3	2
	50	1:3	2
	60	1:3	2
	80	1:3	2
zinc : styrene mole ratio	50	1:1	2
	50	1:2	2
	50	1:3	2
	50	1:4	2
	50	1:5	2
Reaction time, hrs	50	1:3	1
	50	1:3	2
	50	1:3	3

Table 3.2 The various operating conditions for the benzoic acid preparation

Parameters studied	styrene : H_2O_2 mole ratio	H_2O_2 : CH_3COOH mole ratio	Reaction time, hrs
styrene : H_2O_2 mole ratio	1:1	1:3	1
	1:2	1:3	1
	1:3	1:3	1
	1:4	1:3	1
	1:5	1:3	1
H_2O_2 :CH_3COOH mole ratio	1:2	1:1	1
	1:2	1:2	1
	1:2	1:3	1
	1:2	1:4	1
	1:2	1:5	1
Reaction time, hrs	1:2	1:1	0.5
	1:2	1:1	1.0
	1:2	1:1	2.0

Table 3.3 The various operating conditions for benzyl alcohol preparation.

Parameters studied	Pt/C, %wt	Temperature, °C		Pressure, psig		Time, hrs	
		Step 1	Step 2	Step 1	Step 2	Step 1	Step 2
10%Pt/C, %wt	5	5	50	50	100	1	1
	10	5	50	50	100	1	1
	15	5	50	50	100	1	1
Temperature °C	10	5	75	50	100	1	1
	10	15	75	50	100	1	1
	10	30	75	50	100	1	1
	10	15	35	50	100	1	1
	10	15	50	50	100	1	1
	10	15	100	50	100	1	1
Pressure, psig	10	15	75	50	100	1	1
	10	15	75	75	100	1	1
	10	15	75	100	100	1	1
	10	15	75	50	150	1	1
	10	15	75	50	200	1	1
Time, hrs	10	15	75	50	200	1	1
	10	15	75	50	200	2	1
	10	15	75	50	200	3	1
	10	15	75	50	200	1	2
	10	15	75	50	200	1	3