

## CHAPTER IV

### RESULTS AND DISCUSSION

This study aimed to convert styrene waste, obtained from polystyrene manufacturing plant, to useful products by ozonolysis. The achievement of this research was to synthesize benzaldehyde, benzoic acid, and benzyl alcohol. The reaction involves cleavage of the double bond of styrene to these products by ozone. The results of this research were described below.

#### 1. Styrene waste analysis

Styrene waste was analyzed by infrared spectrophotometry. The infrared spectrum of standard styrene (Figure A3-A7) and calibration curve (Figure A10) was obtained by varying concentration of styrene in chloroform. The percentage of styrene in waste sample was presented in Table 4.1.

**Table 4.1** Percentage of styrene in styrene waste

Items	Sample 1	Sample 2
Styrene waste (ml)	3.0	2.0
%Styrene in solution	21.02	13.99
%Styrene in waste	70.06	69.95

From this results, we concluded that the sample of styrene waste contained approximately 70% of styrene.

The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectrum of styrene waste were shown in Figure A11 and A12 respectively. The spectrum indicated that styrene was a main component of styrene waste. The prominent peaks were arisen from double bond at 5.45 (q) and 6.65 (q) ppm for  $^1\text{H}$ -NMR and 113.5 and 138.0 ppm for  $^{13}\text{C}$ -NMR. Figure A12 was compared with  $^{13}\text{C}$ -NMR of standard ethyl benzene. Signals at 16.0 and 29.5 ppm were methyl and methylene group of ethyl benzene.

## 2. Preparation of benzaldehyde from styrene waste

Benzaldehyde was obtained by ozonolysis of styrene waste in dichloromethane at  $0^\circ\text{C}$ , followed by reduction of the ozonolysis product. Zinc powder and acetic acid were used for the reduction. The optimum condition was obtained by varying the mole ratio of styrene and zinc, acetic acid concentration, and reaction time. The product from this reaction was benzaldehyde which was quantitated by conversion to 2,4-dinitrophenyl-drazone derivative.

### 2.1 The effect of acetic acid concentration

The first parameter to be varied was the acetic acid concentration. The reaction was carried out under the conditions in Table 3.1. Acetic acid concentration was varied from 25, 40, 50, 60, and 80 percent. The percentage yields (based on styrene in styrene waste) were presented in Table 4.2. From Table 4.2, it was found that the %yield was increased when % of acetic acid was increased. When acetic acid concentration was more than 50%, the % yield was fairly unchanged. This result demonstrated that the optimum concentration of acetic acid was 50%.

**Table 4.2** The percentage yields of benzaldehyde at various acetic acid concentrations

Acetic acid concentration, %	Yield, %
25	68
40	80
50	96
60	93
80	96

## 2.2 The effect of mole ratio of zinc and styrene

In these experiments the mole ratio of zinc and styrene was varied from 1:1, 1:2, 1:3, 1:4 and 1:5. The reaction was performed under the conditions in Table 3.1. The percentage yields of benzaldehyde (based on styrene in styrene waste) were presented in Table 4.3.

**Table 4.3** The percentage yields of benzaldehyde at various mole ratios of zinc : styrene

zinc : styrene mole ratio	Yield, %
1:1	51
1:2	86
1:3	95
1:4	80
1:5	45

The result indicated that the percentage yield of benzaldehyde was increased when zinc : styrene mole ratio was increased. Because benzaldehyde is known to be readily oxidized to benzoic acid in the presence of air, therefore, the yield of benzaldehyde in each reaction could be varied depending on reaction condition. This process could be accelerated by light and by addition of peroxide or heavy-metal salts [2]. When the mole ratio was more than 1:3, the %yield was decreased. It could be concluded that the optimum mole ratio of zinc to styrene was 1:3.

### 2.3 The effect of reaction time

The optimum reaction time was determined by operating the reaction at 1, 2, and 3 hours under fixed condition (Table 3.1). The percentage yields of benzaldehyde (based on styrene in styrene waste) were presented in Table 4.4.

**Table 4.4** The percentage yields of benzaldehyde at various reaction times

Reaction time, hours	Yield, %
1	57
2	96
3	93

From Table 4.4, the %yield was increased with increasing reaction time. The result suggested that the optimum reaction time was approximately 2 hours.

### 3. Preparation of benzoic acid from styrene waste

Benzoic acid was obtained by ozonolysis of styrene waste in methanol at 0°C, followed by oxidation of the ozonolysis product with acetic acid and hydrogen peroxide mixture. The optimum condition was obtained by varying the mole ratio of styrene and hydrogen peroxide, mole ratio of hydrogen peroxide and acetic acid, and reaction time.

#### 3.1 The effect of mole ratio of styrene and hydrogen peroxide

In this study, the mole ratios of styrene and hydrogen peroxide were varied from 1:1, 1:2, 1:3, 1:4, and 1:5. The percentage yields (based on styrene in styrene waste) of benzoic acid were shown in Table 4.5.

**Table 4.5** The percentage yields of benzoic acid at various mole ratios of styrene and hydrogen peroxide

styrene : H <sub>2</sub> O <sub>2</sub> ratio	Yield, %
1:1	52
1:2	53
1:3	53
1:4	50
1:5	52

From Table 4.5, it indicated that the yield was fairly unchanged when the mole ratio was varied. This results pointed out that only one mole of hydrogen peroxide per mole of styrene was needed.

### 3.2 The effect of mole ratio of hydrogen peroxide and acetic acid

The reaction was operated at fixed condition in Table 3.2. The percentage yields (based on styrene in styrene waste) of benzoic acid were shown in Table 4.6.

The result from these experiments indicated that the percentage yield of benzoic acid was unaffected by the varying of mole ratio of acetic acid to hydrogen peroxide.

**Table 4.6** The percentage yields of benzoic acid at various mole ratios of hydrogen peroxide and acetic acid

$\text{H}_2\text{O}_2 : \text{CH}_3\text{COOH}$	Yield, %
1:1	59
1:2	58
1:3	58
1:4	58
1:5	57

### 3.3 The effect of reaction time

The optimum reaction time was determined by operating the reaction at 0.5, 1, and 2 hours. The percentage yields (based on styrene in styrene waste) of benzoic acid were shown in Table 4.7.

**Table 4.7** The percentage yields of benzoic acid at various reaction times

Reaction time, hours	Yield, %
0.5	57
1.0	60
2.0	48

From the data above, the percentage yield was optimized at the reaction time of 1 hour. Longer reaction time slightly decreased the yield, possibly due to the decarboxylation reaction of benzoic acid or sublimation of benzoic acid under prolong heating [2].

#### 4. Preparation of benzyl alcohol from styrene waste

Benzyl alcohol was obtained from ozonolysis of styrene waste in methanol at 0°C followed by two-steps catalytic hydrogenation. The first step of hydrogenation was occurred at low temperature and low hydrogen pressure to avoid the radical decomposition of hydroperoxide to the corresponding ester [21]. The second step of hydrogenation was carried out at higher temperature and pressure than those of the first step to complete the transformation.

##### 4.1 The effect of catalyst concentration

The first variable parameter to be varied was 10%Pt on activated charcoal catalyst concentration. The hydrogenation reaction was performed under fixed condition (Table 3.3) with varying catalyst concentrations of 5, 10, and 15% weight by weight of styrene waste. Percentage yields (based on styrene in styrene waste) of benzyl alcohol were presented in Table 4.8.

**Table 4.8** The percentage yields of benzyl alcohol at various catalyst concentrations

Catalyst concentration, %	Yield, %
5	17
10	42
15	39

The results from this experiment indicated that when the catalyst concentration was increased, the %yield of benzyl alcohol was increased. However, the catalyst concentration above 10% wt of styrene waste, did not significantly change the yield. The result suggests that the optimum catalyst concentration is about 10% wt of styrene waste.

#### 4.2 The effect of reaction temperature on hydrogenation

The hydrogenation reaction was carried out under fixed parameter as shown in Table 3.3. The temperature of the first step was varied from 5, 15, and 30°C and the second step was varied from 35, 75, and 100°C. The percentage yields (based on styrene in styrene waste) of benzyl alcohol were shown in Table 4.9.

From Table 4.9, the percentage yield was decreased when the temperature was increased. However, the percentage yield was not differ enormously from those of 5 and 15°C. Thus, the appropriate temperature of the first step was 15°C



**Table 4.9** The percentage yields of benzyl alcohol at various temperatures

Temperature, °C		Yield, %
Step 1	Step 2	
5	75	44
15	75	43
30	75	38
15	35	22
15	50	40
15	100	43

For the second step, the percentage yield was increased while increasing temperature. However, the percentage yield was not differ enormously from those of 75 and 100°C. It could be concluded that the appropriate temperature was 75°C.

#### 4.3 The effect of hydrogen pressure on hydrogenation

The effect of hydrogen pressure on hydrogenation was studied by operating at pressure from 50, 75, and 100 psig at the first step and 100, 150, and 200 psig at the final step. The percentage yields (based on styrene in styrene waste) of benzyl alcohol were presented in Table 4.10.

The results indicated that the percentage yield of benzyl alcohol was decreased when the first step reaction was operated under higher pressure. The optimum hydrogen pressure was 50 psig.

**Table 4.10** The percentage yields of benzyl alcohol at various hydrogen pressures

Pressure, psig		Yield, %
Step 1	Step 2	
50	100	43
75	100	33
100	100	29
50	150	44
50	200	53

From the second step, the percentage yield was increased when the second step hydrogenation pressure was increased. The optimum hydrogen pressure of the second step was 200 psig.

#### 4.4 The effect of reaction time on hydrogenation

The last variable parameter to be considered for the hydrogenation reaction was the reaction time. The hydrogenation was performed under optimum parameters (Table 3.3) with varying reaction time. The percentage yields (based on styrene in styrene waste) of benzyl alcohol were shown in Table 4.11.

The results indicated that the optimum reaction time for the first step hydrogenation was 1 hour. The percentage yield of benzyl alcohol did not depend on reaction time.

**Table 4.11** The percentage yields of benzyl alcohol at various reaction times

Reaction time, hours		Yield, %
Step 1	Step 2	
1	1	53
2	1	54
3	1	54
1	2	54
1	3	60

For the second step, the percentage yield of benzyl alcohol was increased when the reaction was performed for a longer period of time. Therefore, these observation suggested that the optimum time of the second step hydrogenation was 3 hours.