

CHAPTER IV

EXPERIMENTS



4.1 Reagents and Chemicals

4.1.1 Phenol The phenol which was used in this laboratory was purified by distillation at atmospheric pressure. The colorless fractions at 180-181°C, were collected in a bottle wrapped in aluminium foil to prevent the exposure to light.

4.1.2 Furfural Since furfural is very sensitive to light and decomposes at high temperatures, therefore, before being used every time, it was distilled twice under reduced pressure and collected in the same manner as phenol. The pressure of the distillation was reduced to 2-3 mm.Hg resulting in lowering of its boiling point to 32-33°C. According to this condition, pure furfural ranging from very pale yellow to colorless liquid was obtained.

4.1.3 Ethyl alcohol The Carlo Erba absolute ethyl alcohol whose purity was specified by manufacturer was used as solvent in this laboratory without further purification.

4.1.4 Hydrochloric acid In the experiments, AR grade hydrochloric acid from Mallinckrodt, Inc. was used as catalyst.

4.1.5 Other chemicals The chemicals used in the preliminary works are listed below. Some of their preparations are given in the appendix.

- 4.1.5.1 0.05M Iodine solution.
- 4.1.5.2 0.1 M Sodium thiosulfate.
- 4.1.5.3 3.3 M Sulfuric acid.
- 4.1.5.4 1.0 M and 6.0 M Sodium hydroxide.
- 4.1.5.5 0.025 M Potassium iodate standard solution.
- 4.1.5.6 15 % Potassium iodide.
- 4.1.5.7 Starch solution.
- 4.1.5.8 Ferric chloride solution.

4.2 Apparatus

4.2.1 UV-VIS Spectrophotometer In the kinetic study, ultra-violet and visible absorption spectra were recorded using a Varian Techtron Model 635 Spectrophotometer and a Perkin Elmer Double Beam Spectrophotometer Model 124.

4.2.1.1 Varian Techtron Model 635 Spectrophotometer : This instrument was used in the earlier part of this work to find out the optimum conditions used in following of the rate of reaction. Based on the Varian Techtron chart recorder, the following conditions were most suitable, other conditions if used are stated in the figures.

Light source	=	UV-VISIBLE	
Reference blank	=	Ethyl alcohol	
Wavelength range	=	800-180	nm
Slit width	=	1.0	nm
Path length (cell length)	=	10	mm
Scan speed	=	100	nm/min
Recorder range (absorbance range)	=	1	

4.2.1.2 Perkin Elmer Double Beam Spectrophotometer Model 124 :

In the kinetic study , this model was found to be more convenient with ± 0.5 absorbance accuracy. Based on the Perkin Elmer 56

Recorder, the following conditions were employed:

Light source	=	VISIBLE	
Reference blank	=	Ethyl alcohol	
Wavelength range	=	720-500	nm
Slit width	=	1.0	nm
Cell length	=	10	mm
Scan speed	=	20	mm/min
Range	=	0	mV
Absorbance scale	=	0-1, 0-2	

4.2.2 Balance To prepare the solutions of phenol and furfural, a Mettler type H-20 semimicrobalance with 160 g capacity and ± 0.1 mg accuracy was used for weighing the solutes.

4.2.3 Thermostat bath The reaction between phenol and furfural was carried out in the thermostat bath from Lab-line Instruments, Inc. The temperature could be controlled to within $\pm 0.5^{\circ}\text{C}$.

4.2.4 vacuum pump A Kaiser Type RS 5 Vacuum Pump with 2×10^2 Torr capacity was employed in the reduced pressure purification of furfural. According to a manometer, the pressure could often be reduced to 2-3 mm Hg.

4.2.5 Viscometer To measure the relative viscosity of the solution, the BS UA, JPL, No 9408 Ostwald Viscometer with 13 cm^3 capacity was used.

4.3 Procedure

4.3.1 Preliminary works In order to study the kinetics of the phenol-furfural reaction, the following various methods were explored :

4.3.1.1 Volumetric titration Rates of reaction were measured by following the change of quantities of furfural at various times. To determine the quantities of furfural, the method of Hugh R. Rogers' furfural determination⁽¹⁸⁾ was adapted.

4.3.1.1.1 Determination of percentage oxidation of furfural Various volumes of 2.002% furfural (see Table 5.1.1.1) were pipetted into 250-cm³ Erlenmeyer flasks. To each flask 10 cm³ of approximately 6 M sodium hydroxide were added. Immediately following this, 10 cm³ of 0.05 M iodine were added and the solution was swirled during the addition. The volume was then adjusted to 60 cm³ or approximately 1 M with respect to the sodium hydroxide and the solution was allowed to stand at room temperature for 10 to 12 minutes. It is important that the sodium hydroxide must be added before the iodine, since to obtain a quantitative oxidation the alkali concentration has to be rather high at the beginning of the reaction. Otherwise, the iodine is converted to the iodate and iodide by the strong alkali before the hypiodite initially formed has a chance to oxidize all the furfural quantitatively.

Approximately 10 cm³ or an excess of the 3.3 M sulfuric acid were added to the sample after it had stood 10 to 12 minutes and the excess iodine released was titrated with standard 0.1 M

sodium thiosulfate using starch indicator.

Calculation :

$$\% \text{ Furfural oxidized} = \frac{(\text{M. of } I_2 \times 10 - 2 \text{M. of } S_2O_3^{2-} \times x) 0.024 \times 100}{\text{g. of furfural}}$$

where

$x = \text{cm}^3$ of thiosulfate used.

$10 = \text{cm}^3$ of iodine added.

4.3.1.1.2 Relation of standing time with percentage oxidation of furfural 4 mg. of furfural in doubly distilled water was measured into 250 cm^3 Erlenmeyer flasks. The method of Rogers was used as in section 4.3.1.1.1 otherwise, the times allowing the solution to stand were varied from 10 to 35 minutes (see Table 5.1.1.2). Since volume of thiosulfate used in the titrations is linear function with % furfural oxidized, it was recorded in the table instead of % furfural oxidized.

4.3.1.2 Viscometry It is known that the viscosity of a solution varies with its concentration, so relative viscosities at various times were measured in this work in order to follow the kinetics of the reaction. Catalysts of the reaction were chosen from two chemicals, ferric chloride hexahydrate and concentrated hydrochloric acid.

4.3.1.2.1 Effect of ferric chloride hexahydrate on one reactant at 25°C A test tube containing 1 cm^3 of 0.2 M furfural was immersed in a thermostated bath whose temperature was controlled at 25°C . One cm^3 of 5% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to the tube which was

then stoppered and shaken. The initial and final results were observed.

In the case of phenol, 3 cm^3 of 0.7M phenol was used. The experiment was carried out in the same manner as described above.

4.3.1.2.2 Effect of hydrochloric acid on one reactant at 25°C

The experiment was set up as in the case of ferric chloride hexahydrate but the results were observed at various times (see Table 5.1.2.2.1).

4.3.1.2.3 Effect of hydrochloric acid on both reactants

at 25°C One cm^3 of 0.2M furfural and 3 cm^3 of 0.7M phenol were mixed together in a test tube which was immersed in a thermostated bath whose temperature was controlled at 25°C . Various quantities of conc. HCl were added to the mixture which was then shaken. The results were recorded in Table 5.1.2.2.2

4.3.1.2.4 Kinetic study of the reaction between furfural

and concentrated hydrochloric acid Into a round bottom flask, immersed in a thermostated bath with its temperature controlled at $30.4 \pm 0.1^\circ\text{C}$, containing 10 cm^3 of 0.2M furfural, 10 cm^3 of conc. HCl was added then the solution was shaken. Six 1 cm^3 aliquots were pipetted, and diluted to 25 cm^3 each. The diluted solution was cooled down in an ice bath with temperature ranging from 8 to 10°C and then its viscosity was measured. The times at which the aliquots were pipetted were recorded and given in Table 5.1.2.3.1. The efflux times of the doubly distilled water, which was used as solvent, were presented in Table 5.1.2.3.2.

4.3.1.2.5 Study of the phenol-furfural reaction at various temperatures 15 cm³. of 0.7M phenol and 5 cm³. of 0.2M furfural were mixed together in a 2-neck round bottom flask which was immersed in a thermostated bath with desired controlled temperatures. Into the flask, 1 cm³. of conc. HCl was added. Eleven 1 cm³. aliquots of the solution were pipetted at various times, and diluted to 25 cm³. each. The pipetting times of the aliquots were given in Tables 5.1.2.4.1, 5.1.2.4.2, and 5.1.2.4.3

4.3.1.3 Spectrophotometry To have sufficient products for spectrophotometry, the reaction at 50°C was repeated but the amounts of phenol, furfural and conc. HCl were increased ten times. The ultra-violet and visible spectra of the products were recorded in Figure 5.1.3.1

4.3.1.3.1 Spectrum of phenol The solution of phenol was prepared by dissolving 0.103 g. of distilled phenol in ethyl alcohol. The volume was adjusted to 25 cm³. The solution was diluted 625 times and then its spectrum was recorded using a Varian Techtron 635 spectrophotometer. The spectrum was shown in Figure 5.1.3.2

4.3.1.3.2 Spectrum of furfural 0.235 g. of freshly double distilled furfural was dissolved in ethyl alcohol and the volume adjusted to 50 cm³. and then the solution was diluted 1250 times. Spectrum of the diluted solution was presented in Figure 5.1.3.3

4.3.1.3.3 Spectra of reactants in the presence of conc. HCl Diluted solution of each reactant was put in a quart cell and 1 drop of conc. HCl was added. Ultra-violet spectra were recorded

with wavelength range of 370-200 nm and absorbance range of 0.5. The spectra were shown in Figure 5.1.3.4

4.3.1.3.4 Reproducibility check in the presence of phenol and furfural 10 cm^3 of diluted solutions of phenol and furfural were equally pipetted into a volumetric flask. The mixture was transferred to the cell and absorbances at wavelengths of 206, 217, 224, 270 and 275 nm were recorded every 15 minutes as shown in Table 5.1.3.1

4.3.1.3.5 Reproducibility check of furfural-conc.HCl system The furfural solution with concentration of 0.235 g./50 cm^3 was diluted 1250 times and 10 cm^3 of the diluted solution was pipetted into a 25- cm^3 volumetric flask. 0.3 cm^3 of concentrated hydrochloric acid was added, and the solution was shaken. It was then transferred to the cell and absorbances at wavelengths of 215, 224 and 270 nm were measured at various times. Table 5.1.3.2 shows the variation of absorbance with reaction time.

4.3.1.3.6 Effect of hydrochloric acid on the phenol-furfural mixture Conc. HCl was added dropwise to the mixture of phenol and furfural. Effect of the hydrochloric acid on the mixture was shown in Figure 5.1.3.5

4.3.1.3.7 UV absorption in the kinetic study Phenol-furfural reaction at $50.0 \pm 0.4^\circ\text{C}$ was studied kinetically by following ultra-violet absorbance of its diluted solution. Concentrated hydrochloric acid was used as catalyst. The reaction

was followed within 22 hours. Figure 5.1.3.6 and Table 5.1.3.3 shows the ultra-violet absorbance at various times. After 22 hours, the result was diluted to several concentrations and visible absorbance of them were recorded and shown in Figure 5.1.3.7

4.3.1.3.8 UV-VIS absorption in the kinetic study

According to 4.3.1.3.7, ... it was found, by following the reaction at $50.0 \pm 0.4^\circ\text{C}$ for 22 hours, that there was no absorption in the ultra-violet region. It was now decided to study the rate of reaction by following, in addition to ultra-violet, the visible absorbance of the diluted solution. Measurement was made under the same condition as in 4.3.1.3.7, i.e., 1cm^3 of concentrated hydrochloric acid used as catalyst; reaction temperature at $50.0 \pm 0.4^\circ\text{C}$; and following time of 22 hours. The experiment was repeated with 3cm^3 of catalyst.

4.3.1.3.9 Visible absorption in the kinetic study

Since change in the visible absorbance was found as shown in Figure 5.1.3.8 and 5.1.3.9, it was convenient to choose wavelengths of 720-500 nm to follow the change. Using the same condition as in 4.3.1.3.8 but with Perkin Elmer Double Beam Spectrophotometer Model 124, absorbance change was obtained and shown in Figure 5.1.3.10 and Table 5.1.3.6

4.3.2 Kinetic study According to the preliminary works, it was found that the kinetics of the phenol-furfural reaction could be conveniently studied by using a spectrophotometer. To follow the concentration disappearance of reactants, absorbances

at wavelengths of 635 nm of the one-half diluted solutions were recorded.

4.3.2.1 Temperature effect Three optimum reaction temperatures, 45, 50, and 53°C were used in this work. Other variables were kept unchanged. The following amounts of materials were fixed in this work:

0.7M Phenol	45	cm ³
0.2M Furfural	15	cm ³
conc. HCl	3	cm ³

4.3.2.2 Catalyst effect The following amounts of concentrated hydrochloric acid, the reaction catalyst, were used: 1, 3, and 6 cm³. The concentrations of reactants were the same as in 4.3.2.1 and the reaction was carried out at 50°C.

4.3.2.3 Concentration effect In order to evaluate the reaction order with respect to each reactant, the concentration of the other reactant was made ten times as concentrated and therefore could be regarded as virtually constant. By doing this, the order of the reaction with respect to the less concentrated reactant was determined. The reactions were carried out at 47, 50, and 55°C and 3 cm³ of catalyst was used.