

## CONTROL OF LIGNIN EPOXYDATION BY REACTION CALORIMETRY

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Lignin is characterized by insolubility in most simple solvents. The solubility of lignin preparations also depends on the method used to isolate them. Since most of the applications in which lignin is subjected to chemical reactions involve the dissolution of lignin, it is very important to know the thermodynamic properties of these solutions, as well as the characterization of chemical reactions.

Chemical modification of lignin through the epoxydation reaction and knowledge of the thermodynamic properties using reaction calorimetry are ways to develop a new application field for lignin.

The paper presents the thermodynamic data obtained by reaction calorimetry for the epoxydation reaction of two commercial lignins (wheat straw-L1 and PROTOBIND 1000) in the temperature range between 30 °C and 70 °C.

**Keywords:** lignin, epoxydation, reaction calorimetry, heat dissolution, specific heat

**INTRODUCTION**

Lignin is a naturally occurring and widely abundant biopolymer found almost exclusively in terrestrial vascular plants and is used to obtain bioplastics, composites, epoxydation lignin and additives.<sup>1,2</sup> The amount of lignin formed annually in nature has been estimated to be in the range of to  $36 \times 10^8$  tons.<sup>3</sup>

The aromatic structure of lignins and the presence of a significant amount of OH groups (phenolic, aliphatic and carboxylic) make technical lignins an attractive raw material for bisphenol A (BPA) substitution, the latter being a commercial epoxy resin produced from petroleum-derived chemicals, capable of modification *via* the reaction of OH groups with epichlorohydrin.<sup>4</sup>

Lignin is a natural polyphenol, which is formed from monolignols through enzymatic dehydrogenative polymerization in plants. The monolignols forming the repeat units of lignin are para-coumaryl alcohol (H-type), coniferyl alcohol (G-type) and sinapyl alcohol (S-type), which may be connected with each other through various covalent bonds.<sup>5</sup>

The solubility of lignin is one of the main obstacles in its practical application. Most of industrial lignins, *e.g.* alkali lignin, enzyme hydrolysis lignin or organosolv lignin, can only

be dissolved in volatile organic solvents, corrosive basic solutions and hazardous ionic liquids. Organic solvents, such as dimethylsulfoxide (DMSO) and tetrahydrofuran (THF), are volatile and inflammable. NaOH aqueous solutions cannot dissolve lignin completely until their pH value exceeds 12, which makes them corrosive.<sup>6</sup>

Lignin, a much more chemically active macromolecular compound than either cellulose or any other natural polymer, due to the functional groups contained in its macromolecule, evidences high stability in the presence of acids, but reduced resistance when it is subjected to the action of oxidants.<sup>7</sup>

Since most applications in which lignin is subjected to chemical reactions involve the dissolution of lignin, it is very important to know the thermodynamic properties of the solutions, as well as to characterize the chemical reactions in terms of heat of reaction.

In this paper, we present some data obtained on the thermodynamic properties ( $\Delta H_{\text{dissolution}}$ ,  $\Delta H_{\text{reaction}}$ ,  $C_{\text{Psolution}}$ ) of alkaline lignin solutions and on the epoxydation of lignin samples with epichlorohydrin using reaction calorimetry. It is possible to determine the heat capacity before, during and after the chemical reaction.

The calculation of  $\Delta H_{\text{dissolution}}$ ,  $\Delta H_{\text{reaction}}$  and  $C_{\text{Psolution}}$  in the isoperibolic mode is based on the heat balance of the calorimeter obtained during electrical calibration, which is produced in the measuring reactor.<sup>8</sup>

## EXPERIMENTAL

### Materials and methods

Two commercial types of lignin (L): wheat straw lignin denoted L1 and Protobind 1000 (mixture of three of lignins: grass lignin, wheat straw lignin and hardwood lignin) were obtained from Granit S.A., Switzerland. The lignins were used to study the thermodynamic properties of lignin alkaline solutions and the reaction of lignin with epichlorohydrin (EPC). The characteristics of the investigated lignins were as follows: L1: acid-insoluble lignin, 90%; acid-soluble lignin, 1%; COOH groups, 3.8 mmol/g; aromatic OH groups, 1.7-1.8 mmol/g; OH/C9 groups ratio (chemical method), 1.02; pH (10% aqueous suspension), 2.7; molecular mass (HPSEC), Mw, 3510; softening temperature, 170 °C, alkali solubility, pH = 12, 98.5%; ash, 2.5%; Protobind 1000: solid, 97.5-98%; COOH groups, 2.1-2.3 mmol/g; aromatic OH groups, 1.8-1.9 mmol/g; pH (10% aqueous suspension) ~3.5; softening temperature, ~200 °C, furfuryl alcohol solubility, 40.1%, alkali solubility, pH = 12, 94%; ash, 1.4-1.8%.

All the experiments were performed using a reaction calorimeter built at the Department of Natural and Synthetic Polymers. The calorimeter consists of a 100 mL reaction vessel fitted with a glass heating jacket, a recirculation bath with a temperature control of  $\pm 0.1$  °C, a magnetic stirrer, a Joule heating element with a 15 ohm resistance, a variable voltage source of 12 V cc, EI1034 temperature sensors, Labjack U3 HV acquisition board, as well as current reading modules and signal amplifiers (LJTick-InAmp). All working parameters ( $T_{\text{Jin}}$  – inlet jacket temperature,  $T_{\text{Jout}}$  – out jacket temperature,  $T_{\text{r}}$  – reaction medium temperature,  $T_{\text{dos}}$  – temperature of added reagent,  $U_{\text{joule}}$  – voltage, and  $A_{\text{joule}}$  – current) were monitored with AzeoTech DAQ Factory program, with Labjack U3 HV acquisition board, as well as current reading modules and signal amplifiers (LJTick-InAmp).

The experiments were performed at 5 temperatures (30 °C, 40 °C, 50 °C, 60 °C, 70 °C) and the reaction time was monitored by the reaction calorimetry at the ratios of L:NaOH = 1:3 (w/w) and L:EPC = 1:10 (w/w).

Two fractions of lignin epoxy were obtained: a totally water-soluble one and a water-insoluble solid. The solid lignin-epoxy was separated from the liquid lignin-epoxy by centrifugation (15 min at 2500 rpm), washed twice with 100 mL of distilled water and dried at 50 °C. The reaction mixture was neutralized with  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  up to pH = 7.5-8.0.<sup>7,9</sup>

## RESULTS AND DISCUSSION

### Calibration calorimeter

In the isoperibolic regime, it is necessary to determine the calorimeter constant by comparing the heat released to the heating with a Joule element, knowing the electrical power (up to 10 W).

Thus, with the thermal effect generated in the calorimeter, the dissipated power  $P$  (W) during the calibration over a known  $t_{\text{cal}}$  time will produce the heat,  $QC$  (J), according to the equation:

$$Q_c = P \cdot t = UA \int_0^{t_{\text{cal}}} \Delta T_R dt = UAS^* \rightarrow UA = \frac{Q_c}{S^*} \quad (1)$$

where  $S^*$  is the area of the calibration peak (°C.s) and  $UA$  (W/K) is the calibration constant of the calorimeter.

By Equation 1, the  $UA$  calibration constant is determined, while performing two calibrations before and after lignin dissolution can help determine the lignin dissolution heat:  $Q_{\text{dis}} = UA \cdot S$ , where  $S$  is the peak area of the dissolution. For the temperature range of 30-70 °C, a mean value of the calorimeter constant of 3.55 W/°C and sensitivity of 0.278 °C/W were obtained.

### Lignin solubilization

#### Determination of heat of dissolution

The dissolution study of L1 (wheat straw lignin) and Protobind 1000 in alkaline 6% NaOH solutions was performed using an isoperibolic calorimeter with a volume of 100 mL. In the isoperibolic regime, the reaction mass is maintained at constant temperature by means of a heating jacket through which a thermal agent is circulated. The thermal effect of the reaction will cause a change in the temperature of the reaction medium. The baseline heat exchange equation (2) for the heating jacket reactor is the following:

$$C_p \frac{dT_r}{dt} = UA(T_j - T_r) + Q_{\text{reaction}} + Q_{\text{losses}} + Q_{\text{agitation}}$$

In equation 2,  $UA$  is the global heat transfer coefficient multiplied by the thermal transfer area, W/K. By accepting the heat loss produced by the known (negligible) stirring power, the heat of reaction can be determined. Using equation 2 and performing two calibrations before and after lignin dissolution, as well as monitoring the  $T_{\text{Jout}} - T_{\text{r}}$  temperature difference, the heat dissolutions were determined. The experimental values of the dissolution heat were determined, as shown in Table 1. For each temperature, two parallel experiments were performed.

### Determination of specific heat

To determine the specific heat of lignin alkaline solutions, it is necessary to know the specific heat of the alkaline solution, of the Joule element, of the temperature sensor from the reaction medium and that of the agitator. With the help of the first calibration, the specific heat of the elements in the reaction medium (agitator, Joule element, temperature sensor) can be determined using the following relations:

$$q_c = UA \cdot \Delta T + (m_r \cdot C_{pr} + C_{pi}) \cdot d\Delta T/dt \quad (3)$$

$$\Delta T(t) = \left(1 - e^{-\frac{t}{\tau_s}}\right) \cdot q_c / UA \quad (4)$$

$$\tau_s = (m_r \cdot C_{pr} + C_{pi}) / UA \quad (5)$$

Knowing the specific heat of the elements inserted in the reaction medium, the specific heat of the reaction products  $C_p$  can be determined.

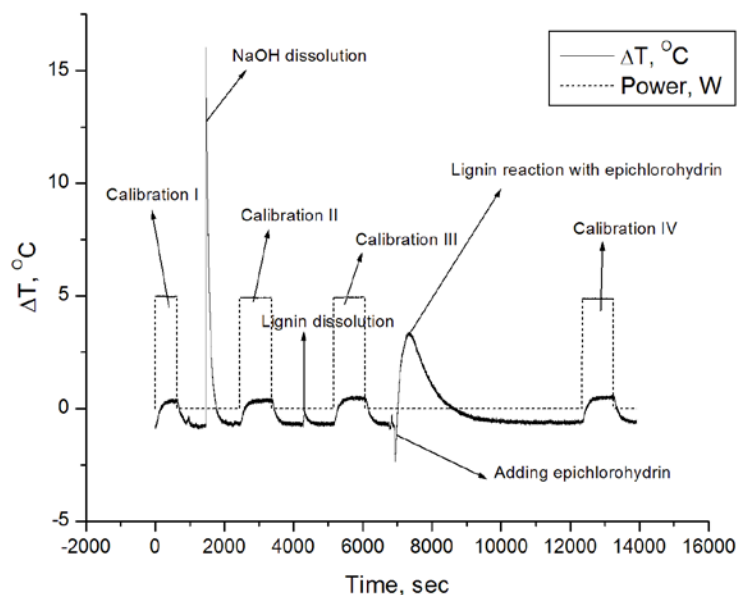


Figure 1: Experimental curve of epoxydation reaction (solid line) versus calibration curve (dashed line)

In the experiments performed, the first water calibration was used as the reaction medium, in which a quantity of NaOH, corresponding to the concentration of 6%, was dissolved, and then an amount of about 2 g of lignin was added.

Proper processing of the curves obtained for the dissolution of lignin in the two solutions of NaOH enabled obtaining the values of the specific heat of the lignin solutions (Table 1).

From the data obtained, it can be observed that, in dilute solutions of 6% NaOH, upon the increase in the dissolution temperature from 30 to 70 °C, the dissolution heat rises from -206.27 J/g to -167.49 J/g for L1 and for Protobind 1000 – from -382.3 J/g to -203.86 J/g. The dissolution time decreases from 35 min to 22 min for L1, and from 33.5 min to 23.5 min for Protobind 1000, as the temperature increases from 30 to 70 °C. The experimental data obtained by reaction calorimetry demonstrate that 40 minutes are sufficient to dissolve lignin in 6% NaOH solution.

### Lignin epoxydation

We studied the epoxydation reaction with epichlorohydrin, using reaction calorimetry, and we determined the heat of the epoxydation reaction (Table 2 and Fig. 2). From the data obtained, it can be observed that, at the ratios L:NaOH = 1:3 (w/w) and L:EPC = 1:10 (w/w), with the increase in reaction temperature from 30 to 70 °C, the reaction heat of lignin epoxydation decreases from  $\Delta H_r = -7189.5$  J/g to  $\Delta H_r = -8443.5$  J/g for L1, and for Protobind 1000 – from  $\Delta H_r = -6480.2$  J/g to  $\Delta H_r = -9356.5$  J/g. The duration of the epoxydation reaction decreases from 172 min to 39 min for L1, and from 138 min to 62 min for Protobind 1000, as temperature rises from 30 to 70 °C. In order to achieve lignin epoxydation, the experimental data indicate that, at a temperature of 30-40 °C, the epoxydation reaction takes about three hours to complete, while at 70 °C, an hour is sufficient to achieve it. This duration of the process is much lower, compared to the data

presented in the literature.<sup>9</sup> Therefore, the reaction calorimetry is a useful tool in estimating the length of a process and in determining the

thermodynamic properties of some chemical systems.

Table 1  
Values of dissolution heat of lignins (L1 and Protobind 1000) in 6% NaOH determined by reaction calorimetry

Lignin L1				
Temperature, °C	Time, min	$\tau$ , 1/s	Cp sol, J/g K	$-\Delta H_{diss}$ , J/g
30	34.8	219.90	3.46	206.27
40	28.2	231.90	4.49	190.63
50	28.1	197.80	3.41	177.97
60	25.2	201.30	4.16	171.71
70	22.0	147.70	3.12	167.49
Protobind 1000				
Temperature, °C	Time, min	$\tau$ , 1/s	Cp sol, J/g K	$-\Delta H_{diss}$ , J/g
30	33.5	175.20	5.54	382.30
40	34.4	234.50	3.73	228.93
50	23.4	166.30	3.45	170.79
70	23.4	154.00	3.32	203.86

Table 2  
Heat of lignin epoxydation

Lignin L1				
Temperature °C	Time min	$\tau$ 1/s	Cp sol J/g K	$-\Delta H_{diss}$ J/g
30	171.9	236.7	3.29	7189.5
50	95.8	224.3	3.37	9188.7
60	54.3	193.9	3.09	9054.9
70	39.8	189.6	3.06	8443.5
Protobind 1000				
Temperature °C	Time min	$\tau$ 1/s	Cp sol J/g K	$-\Delta H_{diss}$ J/g
30	138.3	175.2	3.27	6480.2
50	76.6	201.7	3.34	8866.3
60	52.3	227.1	4.40	9083.3
70	61.9	173.2	3.63	9356.5

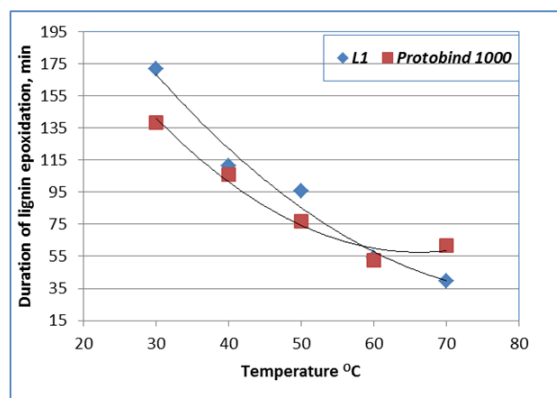


Figure 2: Variation of lignin epoxydation time with reaction temperature

## CONCLUSION

The study presents novelty by using reaction calorimetry to determine the thermodynamic data of lignin solutions. A laboratory setup, based on the principles of reaction calorimetry, was created to determine the thermodynamic properties of alkaline solutions and chemical reaction of lignin.

The lignin dissolution heat and the specific heat of the lignin alkali solutions were determined over a temperature range of 30-70 °C. Similarly, the lignin epoxydation heat and the specific heat of the epoxy-lignin solutions were determined over the same temperature range. From the data obtained, it was observed that, in dilute 6% NaOH solutions, at the ratios L:NaOH = 1:3 (w/w) and L:EPC = 1:10 (w/w), the heat of the lignin epoxydation reaction decreases from -7189.5 J/g to -8443.6 J/g for L1, and from -6480.2 J/g to -9356.5 J/g for Protobind 1000, when the reaction temperature enhances from 30 to 70 °C. In addition, the reaction time for epoxydation decreases from 172 min to 39 min for L1 and from 138 min to 62 min for Protobind 1000, as the temperature rises from 30 to 70 °C.

The experimental data indicate that, at a temperature of 30-40 °C, it takes about three hours to achieve lignin epoxydation, while at 70 °C, one hour is sufficient.

Thus, using reaction calorimetry, thermodynamic data of lignin solutions have been obtained with regard to the dissolution and epoxydation of lignin.

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