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APPLICATIONS OF REACTION CALORIMETRY IN LIGNIN CHEMISTRY

BY

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Abstract. The thermodynamic properties of lignin and its solutions are important in the design and operation of the machines used in the biomass biorafination schemes. In the literature, there are few thermodynamic data on the main chemical components of biomass (cellulose, hemicellulose and lignin). In this paper we present the heat dissolution (ΔH_{dis}) of the lignin alkaline solutions obtained by the reaction calorimetry. 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 involves the dissolution of lignin, it is very important to know the thermodynamic properties of these solutions as well as the characterization of chemical reactions in terms of heat of reaction.

Keywords: lignin; reaction heat; dissolving heat; specific heat; biomass.

1. Introduction

Lignin is one of the main chemical components of aromatic nature biomass: almost a quarter of the mass of dry wood consists of lignin which is deposited in cell walls and in intercellular spaces (Măluțan and Popa, 2007).

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Lignin resulting from the Latin term “lignum” meaning wood, is the second richest renewable natural resource next to cellulose (Naseema *et al*., 2016).

According to Freudenberg, natural wood lignin is insoluble in organic solvents, and solubility occurs only after treatment of lignin with an organic solvent (glacial acetic acid or alcohols) in the presence of a catalyst. In the opinion of this author, the lignin closest to natural lignin is cupro-ammoniacal, but it is likely that this lignin is more condensed than natural lignin. When treating with acidic calcium bisulfite solutions in the case of sulphite boiling, cupro-ammoniacal lignin, unlike natural lignin, dissolves hard in the boiling liquid; acid lignins and lignins isolated with organic solvents do not dissolve when boiling sulphite under normal conditions (Rogovin and Sorighina, 1958).

In higher plants, lignin content reaches about 25% in hardwood species and up to 27-29% in conifers (Măluțan and Popa, 2007).

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

The present paper aims to present some data obtained on the thermodynamic properties of alkaline lignin solutions by using the reaction calorimetry.

Three important thermodynamic data can be determine using the instrument: the heat of reaction of liquid+ a liquid or a liquid+ a solid, the heat capacity of a solvent or a mixture and a theoretical value of the increase of temperature in adiabatic mode. It is possible to determine the heat capacity before, during and after the chemical reaction. The calculation of the heat capacity C_p in isoperibolic mode is based on the heat balance - of the calorimeter - obtained during an electrical calibration, which is produced in the measuring reactor.

2. Experimental

2.1. Materials and Methods

For the study of the thermodynamic properties of lignin alkaline solutions, we used a commercial types of lignin made available by Granit S.A. from Switzerland, **L1** (wheat straw lignin).

All experiments were performed on a reaction calorimeter, built in the Analysis of Wood Chemical Analysis Laboratory of the Natural and Synthetic Polymers Department. The calorimeter consists of a 100 mL reaction vessel fitted with a glass heating jacket, a recirculation bath with a temperature control of ± 0.1°C, a magnetic stirrer, a Joule heating element with a 15 ohm resistance, a variable voltage source of 12 V thermocouple temperature sensors J and PT

100 thermal resistors, Labjack U3 HV acquisition board as well as current reading modules and signal amplifiers (LJTick-InAmp).

All working parameters (inlet jacket temperature, **TJ_in** and outflow, **TJ_Out**, temperature in the reaction medium, $\mathbf{T_r}$, reagent temperature, $\mathbf{T_{doz}}$, voltage and supply current of the Joule element, $\mathbf{U_{Joule}}$ and $\mathbf{C_{Joule}}$) were monitored With AzeoTech's DAQ Factory program.

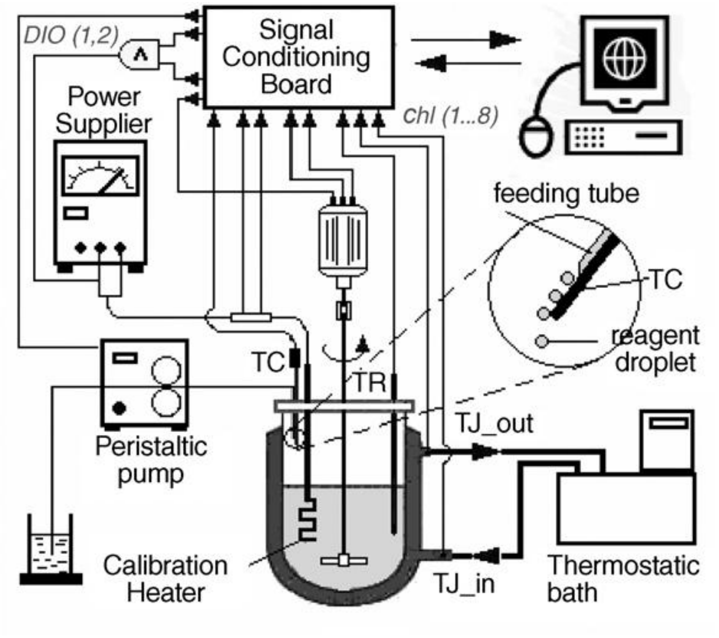

Fig. 1 – Scheme of the reaction calorimeter.

The experiments were performed at 4 temperatures (25°C, 30°C, 50°C, 70°C) on 5% NaOH solutions in which were dissolved lignin L1 and then we calculated the heat dissolution of NaOH.

3. Results and Discussion

3.1. 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 time t_{cal} time will produce a heat, QC (J) according to the equation:

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

where S* is the area of the calibration peak, [°C·s] and UA, the calibration constant of the calorimeter.

Knowing the UA calibration constant and performing two calibrations before and after lignin dissolution can determine the lignin dissolution heat: Q_{dis} = UAS, where S is the peak area of the dissolution (Grolier and Dan, 2006).

In Fig. 2 shows how to calibrate the calorimeter as well as determine the constant of the reaction calorimeter.

Table 1

The Calibration Parameters of the Calorimeter

Temperature, [°C]	UA, [W/°C]	S, [°C/W]
25	3.21(± 0.064)	0.312
30	3.62(± 0.156)	0.276
50	3.89(± 0.785)	0.257
70	3.47(± 0.028)	0.288

For the temperature range 25-70°C a mean value of the calorimeter constant of 3.55 W/°C and sensibility of 0.278°C/W were obtained.

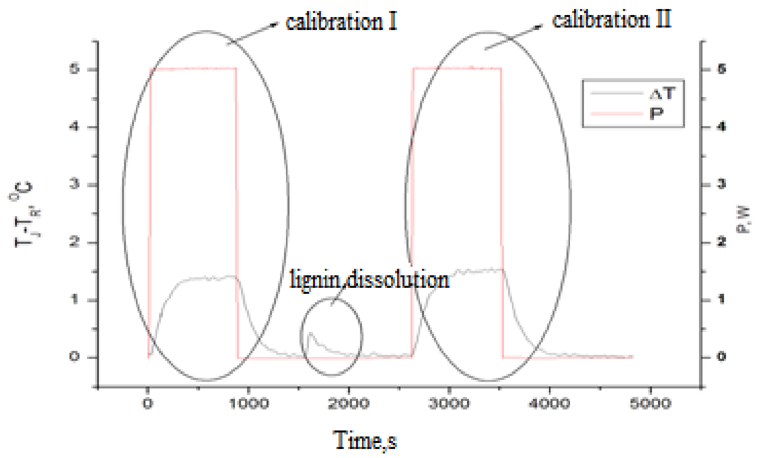

Fig. 2 – Processing of experimental curves to determine the calorimetry constant and heat dissolution of lignin.

3.2. Determination of Heat of Dissolution

The dissolution study of L1 lignins in alkaline 5% 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 for the heating jacket reactor has the following form:

$$C_P\frac{dT_r}{dt} = UA(T_j - T_r) + Q_{reaction} + Q_{losses} + Q_{agitation} \qquad (2)$$

In Eq. (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 (Grolier and Dan, 2006).

Using Eq. (2) and performing two calibrations before and after lignin dissolution and monitoring the T_J-T_R temperature difference, the experimental values of dissolution heat were determined. For each temperature, we take 2 parallel experiments.

Table 2
Dissolution Heat of NaOH Depending on Temperature

Temperature, [°C]	ΔH_{dis}, [kJ/mol]	S, [°C/W]
25	45.173	0.318
30	36.989	0.266
50	49.167	0.256
70	40.709	0.300

From literature data the dissolution heat of NaOH at 25°C is -44.51 kJ/mol.

Table 3
Dissolution Heat of L1 Lignin in 5% NaOH Solution Depending on Temperature

Temperature, [°C]	Q_{dis}, [J]	ΔH_{dis}, [J/g]
25	846.01	419.74
30	310.22	628.64
50	753.09	368.48
70	680.74	337.17

From the data obtained, the dissolution heat decreases from 419.74 J/g to 337.17 J/g.

4. Conclusion

A laboratory plant was developed based on the principles of reaction calorimetry to determine the thermodynamic properties of lignin alkaline solutions.

The lignin dissolution heat and the specific heat of the lignin alkali solutions were determined over a temperature range of 25-70°C.

Using reaction calorimetry we can make epoxidation, hydroxymethylation and oxidation reactions of lignins to obtain important data on reaction heat and adiabatic temperatures.

The obtained results are a novelty in the determination of the thermodynamic data of the lignin solutions.

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APLICAȚII ALE CALORIMETRIEI DE REACȚIE ÎN CHIMIA LIGNINEI

(Rezumat)

Proprietățile termodinamice ale ligninei și soluțiilor sale sunt importante în proiectarea și exploatarea utilajelor utilizate în schemele de biorafinare a biomasei.

În literatura de specialitate sunt puține date termodinamice privind componenții chimici principali ai biomasei (celuloza, hemiceluloze și lignina). În lucrarea de față se prezintă căldura de dizolvare (ΔH_{diz}) ale soluțiilor alcaline de lignină obținute prin calorimetria de reacție. Lignina se caracterizează prin insolubilitate în majoritatea solvenților simpli. Majoritatea aplicațiilor în care lignina este supusă reacțiilor chimice implică dizolvarea acesteia, astfel este foarte important să se cunoască proprietățile termodinamice ale acestor soluții, precum și caracterizarea reacțiilor chimice și a căldurii de reacție.