GRAVITATIONAL ANALYSES APPLIED TO PROTOBIND 1000 LIGNIN

ANALIZE GRAVITAȚIONALE APLICATE LA LIGNINA PROTOBIND 1000

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Abstract. *Lignin derivative (the commercial product - Protobind 1000) offered by the Granit Recherche Developement S.A. company, Lausanne-Schwitzerland was synthesized from annual plants. The lignin stands out by a very large range of applications in extremely various domains: agriculture, the pulp and paper industry, constructions or metallurgy. The adsorption-desorption capacity, ion exchange capacity and its catalytic properties are just a few specific characteristics which are emphasizing the importance of harnessing the lignins. Using the gravitational sedimentation, it can be determined in a shorter period of time the particle dimensions comparing with the sieving method, which is a much more complex one.*
Key words: sedomentometrical analyses, Protobind 1000 lignin, density, pycnometer, sedomentometrical curves.

Rezumat. *Lignina derivativă (produsul comercial Protobind 1000) oferită de firma Granit Recherche Developement S.A. Lausanne-Elveția a fost sintetizată din plante anuale. Lignina se remarcă printr-o gamă largă de aplicații în domenii extrem de diverse: agricultură, industria celulozei şi hârtiei, construcții, sau metalurgie. Capacitatea de absorbție-desorbție, capacitatea de schimb ionic, proprietățile catalitice sunt doar câteva repere specifice care recomandă şi evidențiază importanța valorificării ligninelor. Utilizând sedimentarea în câmp gravitațional, se pot evalua într-un timp mult mai scurt dimensiunile granulelor comparativ cu evaluarea prin sitare, operație ce este mult mai laborioasă.*
Cuvinte cheie: analize sedimentometrice, lignină Protobind 1000, densitate, picnometru, curbe sedimentometrice.

INTRODUCTION

In the last decades, research within the field of lignin has not sought only perfection of extraction processes, but also elucidation of structures of products separated from various vegetal sources, chemical characterization, reactivity, functional properties and developing new applications. (Ungureanu *et al,* 2009).

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At a global level, lignin resulted from cellulose fabrication or technologies of hydrolysis of vegetal mass can be considered as raw material with high capitalization potential, because of its provenience from regenerating sources and due to reduced price. Lignin is a macromolecular compound, much more active than cellulose or other natural polymers, due to functional groups contained in its macromolecule, constituting the main aromatic component of vegetal tissues, standing for 20%-30% of the mass at superior plants, where it is present within the cellular membrane and in intercellular spaces (Popa, 2015, 2016).

Due to its regeneration, capacity through photosynthesis, vegetal biomass and its components (including lignin) will become in the future sources of raw material with a high degree of capitalization.

Nowadays, it is important to replace synthetic wood preservatives by more environmentally friendly natural products. Furthermore, there is an enormous problem about the elimination of the vegetal waste from the agricultural, forest, pulp and food industries. Thus to obtain new natural wood preservatives from these residues is increasing (Mansouri et al, 2006).

At the same time the application of copper compounds in wood protection, due to their fungicidal activity is known for a long time. Although such protection is very commonly used, the mode of copper action and its way of binding to wood are still to be established accurately. Possible binding site for copper is lignin, due to several different functional groups present in its structure and its abundance in wood (Ungureanu, 2011).

MATERIAL AND METHOD

The following materials have been used:

- Protobind 1000 (Pb1000), commercial lignin offered by Granit Recherché Dévelopement Switzerland, with the following chemical characteristics presented in table 1;

Table 1

The characteristics Protobind 1000

Characteristics	(Pb1000)
Solide, %	97.5-98.6
Ash, %	1.4-1.8
pH (10 % dispersion)	~ 3.5
Densitatea, g/mL	~ 0.3
Aromatic OH, mmole/g	1.8-1.9
COOH, mmole/g	2.1-2.3
T softening, °C	~ 200
Solubility in furfuryl alcohol, %	40.1

- RS-71 Tensio-tixometer gravimetric sedimentation balance;
- Steel ball crusher;
- Toluene;
- Distilled water.

Methods

- picnometer method;
- gravitational sedimentometrical method.

Work procedure: 45 g of Protobind 1000 were weighed, crushed for 30 min. and dissolved in 1L of distilled water.

The electrostatic forces of attraction between the hydroxylic groups of the lignin and the dipoles of the dissociated water are so powerful that a colloidal-hydric aggregate is formed and its volume is smaller that the sum of volumes that interact (water-lignin). Experimental data were statistically processed with the aid of the *Unscrambler* application.

RESULTS AND DISCUSSIONS

Based on the standard curve (fig.1) 10 sedimentation curves were plotted according to the dependence q(g) = f(t, s), and the experimental data are also listed in tables.

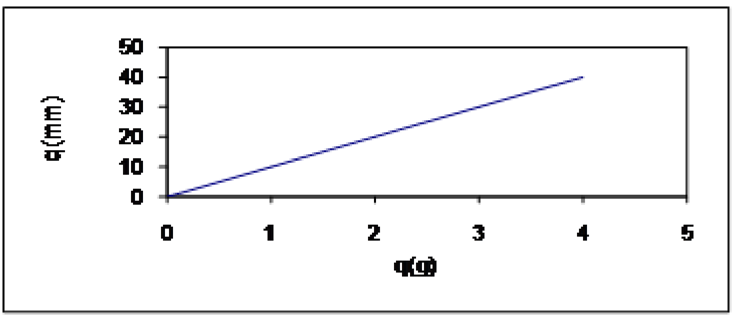

Fig. 1 The standard curve

10 sedimentation curves in q(mm) = f(t, s) coordinates were obtained using RS-71 Tensio-tixometer under constant conditions (mass lignin = 45 g/L water).

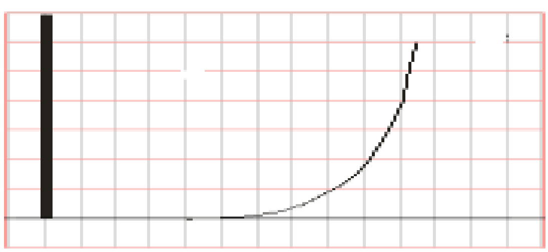

Fig. 2 Exemple of sedimentation curve

These sedimentation curves were also listed in table 2.

Table 2

Parameter values of the sedimentation curves

No det.	t (mm)	t (sec)	q (mm)	q (g)
1	3	7.85	3,5	0,25
2	6	15.7	5.2	0.42
3	9	23.49	7.0	0.58
4	12	31.40	8.1	0.61
5	15	39.25	9.0	0.73
6	18	47.10	10.7	0.83
7	21	54.95	11.1	0.85
8	24	62.80	11.3	0.84
9	27	70.65	12.1	0.91
10	30	78.50	12.6	0,98
11	33	86.35	12.7	0,98
12	36	94.20	13.0	1.02
13	39	102.05	13.6	1.025
14	42	109.90	13.6	1.04
15	45	117.75	14.1	1.10
16	48	125.60	14.1	1.10
17	51	133.45	14.5	1.16
18	54	141.30	14.5	1.16
19	57	149.15	15.0	1.17
20	60	157.00	15.0	1.17

Further on it was obtained the most expected sedimentation curve plotting the values of sediment quantity, q(g) and time t(s), for the reproductible measurements (2, 3, 4, 5, 9) (fig. 3).

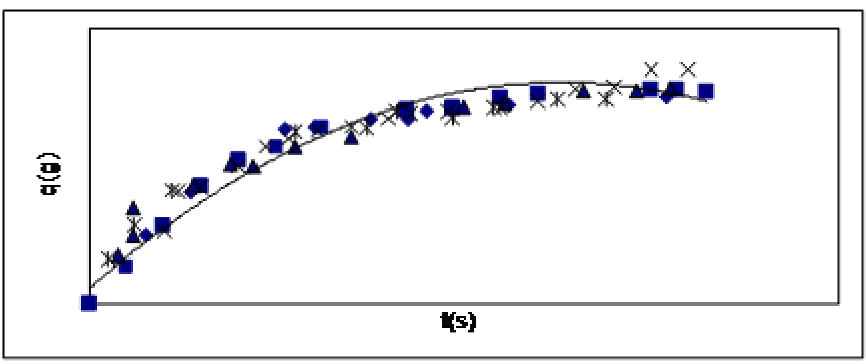

Fig. 3 General sedimentation curve

Measurements 1, 6, 7 and 10 are not reproductible due to a non-uniform distribution of the scattered particles obtained before the recordings (fig. 4a. and b.).

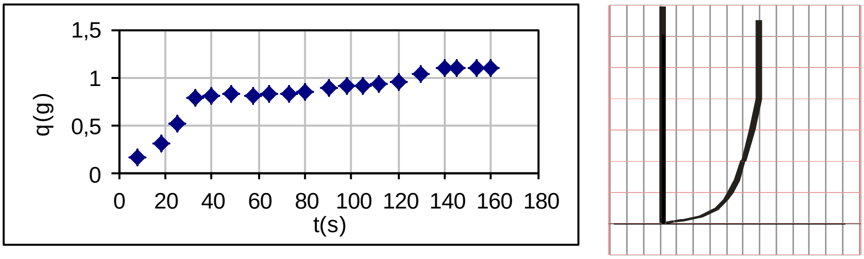

Fig. 4 Sedimentation curves using:
a. q(g) = f(t, s) dependence b. tensio-tixometer q(mm) = f(t, min.) dependence

Based on the general theory of sedimentation in gravimetric field of micro-heterogeneous systems, the radius boundaries of the scattered particles in ground lignin were evaluated. According to the determinations performed the amount of deposited lignin was Q = 1.18 g. In order to determine the density of lignin, the picnometer method was employed. In table 3 are presented the values obtained experimentally by weighing or theoretically determined.

Table 3

Density of lignin measured by picnometer method

m_1 (g)	m_2 (g)	m_3 (g)	m_4 (g)
13.6512	14.6512	23.0627	22.0627
13.6512	14.6514	23.0603	22.0600
13.6512	14.6502	23.0631	22.0632

m_1 – empty pycnometer mass; m_2 – pycnometer mass + solid; m_3 – pycnometer mass + solid + liquid; m_4 – pycnometer mass + liquid (toluene); ρ_s - solid density

By graphical derivation of the sedimentation curve (fig.2), the sedimentation rates were obtained at certain periods of time, t = 0, 14, 30, 70, 80, 90, 100, 105 s. These rates were used to determine various fractions radii of the disperse system (tab. 4).

Table 4

Sedimentation rates corresponding to the most expected sedimentation curve for the reproductible results

Time (s)	Sediment quantity (g)	Sedimentation rates (mm/s)
0	0	0.0360
14	0.22	0.0164
30	0.65	0.0141
70	0.91	0.0033
80	0.96	0.0029
90	1.02	0.0017
100	1.03	0.0012
105	1.04	0.0141

Based on the resulted sedimentation rates, the particle radii of lignin were obtained (tab. 5).

Table 5

Values of disperse particle radii of lignin obtained by sedimentation in gravitational field

Fractions number	Dimension of superior and inferior sieve mesh (mm)	Diameter a_i (mm)	Beam r_i (mm)	
			By rieving	By sedimentation gravitational feils
1	1.23 – 1.11	1.124	0.561	-
2	1.0 – 0.04	0.813	0.403	0.3200 (0)
3	0.64 – 0.22	0.440	0.211	0.1571 (14)
4	0.25 – 0.20	0.221	0.112	0.1400 (30)
5	0.21 – 0.126	0.162	0.0810	0.0742 (70)
6	0.17 – 0.11	0.131	0.0648	0.0629 (80)
7	0.10 – 0.08	0.098	0.0479	0.0522 (90)
8	0,08 – 0.07	0.084	0.0426	0.0441 (100)
9	0.07 – 0.06	0.072	0.0362	0.0381 (105

CONCLUSIONS

1. The sedimentometrical method applied in gravitational field confirms that the reproducibility of the experimental data depends on the uniform distribution degree of the analyzed disperse particle.

2. In order to determine the lignin density, the picnometer method was success fully employed.

3. The variation range of the disperse particle radius in ground lignin can be determined either by sieving or by sedimentation in gravitational field.

4. The analysis of the values obtained for particle dimensions of Protobind 1000 lignin using both methods leads to a general conclusion that the obtained data are reproductible.

REFERENCES

1. **Mansouri N.E., El Salvad´o J., 2006 -** *Structural characterization of technical lignins for the production ofadhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins,* Industrial Crops and Products, 24 (8-16), pp.213.

2. Popa V.I., 2015 - *Wood bark as valuable raw material for compounds with biological activity*, Celuloză şi hârtie, 64 (1), pp. 5-17.

3. **Popa V.I., 2016 -** *An example of biomass valorization as source of energy and chemical products*, Celuloză şi hârtie, 65 (1), pp. 14-21.

4.Ungureanu Elena, Ungureanu O.C., Căpraru Adina-Mirela Popa V.I., 2009 - *Chemical modification and characterization of straw lignin*, Cellul. Chem. Technol., 43 (7-8), pp.261-267.

5.Ungureanu Elena, 2011 - *Lignina, polimer natural aromatic cu ridicat potențial de valorificare*, Ed. PIM, Iaşi, pp. 112.