STUDY OF THE PROCESS OF THE WATER DESORPTION FROM LIGNINS

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The water desorption process from two groups of lignins namely lignins from trees and agricultural crops has been studied by differential scanning calorimetry and FT-IR spectroscopy. The water content determined by the first two methods was compared with that determined by STAS method. Correlation between carboxyl or phenolic hydroxyl groups content and thermal characteristics have been established.

Key words: lignins, desorption, differential scanning calorimetry (DSC), FT-IR spectroscopy, kinetic parameters, phenylpropanoic, p-hydroxyphenyl, guaicyl, syringyl, functional groups.

1. INTRODUCTION

Characterization of the lignins is an extremely difficult task because of their diversity in respect with both sources and extraction method. The heterogeneity of lignin is due to the changes in polymer composition, size of the morphological units, crosslinking, nature of the functional groups, linkage types between various moieties such as phenylpropanoic, p-hydroxyphenyl, guaicyl, syringyl, etc. [1]. The amount of the absorbed water and the desorption process is influenced both on the mentioned factors and also by the number of functional groups able to interact via hydrogen bonds with water.

Lignins from trees and agricultural crops with different chemical composition and properties can be obtained by use of several extraction methods. Commercial chemical pulping processes (sulfite and kraft process) produce lignosulfonates and kraft lignins as residue. Recently commercialized alkaline pulping – precipitation process supply sulfur-free, free-flowing lignins.

To enhance the industrial use of lignins, there is need for a continuous supply of lignin products with constant quality as related to purity, chemical composition,
and functional properties. The purpose of this paper is to add new insights in lignin characterization and behaviour even for simple physical process of absorption/desorption of water and the interaction between it and functional groups of lignin.

2. EXPERIMENTAL

2.1 MATERIALS

Lignins from wheat straw, sisal, abaca, hemp, jute and flax were obtained from Granit SA (Lausanne, Switzerland). Alcell organosolv lignin from mixed hardwoods (maple, birch and poplar) was obtained from Repap Technologies Inc., (Valley Forge, PA, USA). Lignosulfonate from softwood (Borrespere 3A and WAFEX-P) and Kraft lignin from softwood (Curan 100) were obtained from Lignotech (Sweden). Sulfur free lignins from softwood were obtained from Kiram AB, (Sweden). General characterization of the lignins has been made by Boeriu et al. [2] by determination of the lignin content, phenolic and carboxyl groups and also sugars content.

2.2 METHODS

The methods of investigation were FT-IR spectroscopy and differential scanning calorimetry (DSC).

FT-IR spectra were recorded on solid samples in KBr pellets by means of a FT-IR Bomem MB-104 spectrometer (Canada) with a resolution of 4 cm\(^{-1}\). The concentration of the sample in the tablets was constant of 3mg / 500 mg KBr. The behaviour of the samples was followed both up to 105 °C with 1 °C/min. Processing of the spectra was done by means of Grams/32 program [Galactic Industry Corporation].

DSC curves were recorded on a Mettler instrument with a hitting rate of 10°C/min. in nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1 FT-IR RESULTS

The FT-IR spectra in the region of water absorption 3000–3700 cm\(^{-1}\), and also those were is possible the interaction with different functional groups 1550–1800 cm\(^{-1}\) and 900–1550 cm\(^{-1}\) are given in Figure 1.

The absorption band centred at about 3400 cm\(^{-1}\) (Figure 1a) is assigned to -OH groups of the water and also –OH in to aliphatic and aromatic groups [3]. This band has approximately the same shape for the lignin obtained from agricultural
plants and the peak position vary in the close limits between 3412 and 3417 cm\(^{-1}\), while for woody plants the band takes various shapes with two maxima as for pine Kraft or a shoulder as for softwood or its intensity is different for each samples the greatest being for lignosulfonate (1). For this later group of lignins the position of the peak is shifted at higher wavelengths denoted stronger interactions with of the water with lignin molecule or between functional groups. In the 1550–1880 cm\(^{-1}\) region (Figure 1b) appear many bands, that of 1700 cm\(^{-1}\) being assigned to the valence vibration of the carbonyl group in ketone or carboxyl groups. This band is better evidenced in lignins from agricultural plants and in majority of woody plants appears as a shoulder. In this later case a band at around 1600 cm\(^{-1}\) is much intense it being assigned to syringyl units.

![FT-IR spectra of the studied lignins](image)
The bands corresponding to phenolic OH groups are present at ~1370 cm\(^{-1}\) as has been expected in all spectra but its position is shifted at 1365 cm\(^{-1}\) for lignin from agricultural plants. These changes indicate interactions between functional groups and absorbed water which are different for each group of lignin woody plants and respectively annual plants.

Fig. 2 – The FT-IR spectra of the lignin from hardwood (a) and from straw (b) heated up to 105 °C. At each 3 minutes a spectra was taken, in figures the spectrum at each 15 minutes is shown.
Following the water desorption by recording spectra at various times of heating it can also observe the differences between two groups of lignins – Figure 2. The variation between spectra being bigger for the first group (Figure 2a) in comparison with the second (Figure 2b). That means that energetics of the process is different in these groups, depending on the content of functional groups and lignin structure.

The data of Figures 3 confirm this conclusion because the energy of the hydrogen bonds evaluated using the following formulae [4]:

$$E_H = \frac{1}{k} \left( \frac{\nu_o - \nu}{\nu_o} \right)$$

Fig. 3 – The variation of the energy of the hydrogen bonds with content of the functional groups: phenolic OH (a) and carboxyl (b).
where: \( \nu_o \) – standard frequency corresponding to vibration of free OH groups (3650 cm\(^{-1}\)) \( \nu \) - frequency corresponding to vibration of bonded OH; \( k \) – constant equals with 0.016Kcal\(^{-1}\).

The OH groups interact weakly with water being engaged in other types of interaction even in lignin molecule.

### 3.2. DSC RESULTS

The DSC curves presented in Figure 4 indicate also that the water desorption process is different in each group of studied lignins existing differences between the shape of the endothermic peaks and also between temperatures.

![DSC curves](image-url)

(a)

(b)

Fig. 4 – DSC curves of the lignins from woody plants (a) and lignins from annual plants (b).
This fact is much evident in Figure 5 where the variation of the peak temperature with content of the functional groups is plotted. The dehydration of the lignin from fibre crops occurring at lower temperature in respect with that of woody plants.

Both FT-IR and DSC methods evidenced the differences between lignins of various provenances. Other factors have also importance in determining differences between lignin as separation methods, plant type, etc.

REFERENCES