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ADVANCED TRADITIONAL METHODS OF ANALYSIS OF FIBRE SURFACE LAYERS

A Powerful Tool in Research of Lignocellulosics

The bulk parametres of lignocellulosics chemical composition and fibre wall structure do not provide sufficient knowledge about the properties and potential application of the materials.
Traditional methods improved during last years like peeling of fibre surface layers represent laborious processes but they provide reliable and detailed data especially when combined with the spectroscopy and other advanced instrumental methods.

Traditional analytical and preparative methods improved during last years are rather laborious. Nevertheless such procedures as peeling of lignocellulose and/or pulp fibre surface layers provide genuine fragments of the morphological layers - primary wall P and outer layer S_1 of secondary wall. An appropriate method is so called hydromechanical peeling. The process represents extended mixing (disintegration) of the fibres in water or specific solvent and subsequent separation of the disjoined fines ($P+S_1$) from the main part of fibres (S_2+S_3). Both in the fines and the main part of fibre wall it is admissible to determine the content of residual lignin and hemicelluloses as well as required functional groups. The “chemical peeling” process includes heterogeneous acetylation of fibre outer layers and dissolution of the esterified fibre wall fraction followed by the isolation of the material.

The evidence about the distribution of fibre wall constituents and functional groups contribute to the prediction of lignocellulose and pulp fibre properties, e.g., reactivity, also enzyme boosted bleaching.

The physical properties and chemical composition of the papermaking fibres or other lignocellulose containing materials are determined usually as bulk parameters for a certain lot of the selected samples. It is understandable that the wood cells consist of different anatomic elements and so the pulp fibre walls structure is quite heterogeneous The average bulk parameters, however, therefore do not provide possibilities to elucidate the mechanisms of the formation of important papermaking fibres properties and chemical composition. Nowadays the development of analytical methods provides new tools in order to investigate the parameters of individual fibres and of separate fibre wall layers. The results are reliable as well as applicable in practical life.

The results of recent research has demonstrated that certain data on composition and structure of pulp fibre walls are confirmed by scientists in different research centres. For example, higher residual lignin concentration in pulp fibre surface layers is supposed to be a "true" fact thanks to the studies by means of UV-microscopy and different fibre wall peeling techniques.

The interest in getting new information and data on the fibre wall fine structure has increased during last five years. As an example may serve the number of this topic related papers in the European Workshops on Lignocellulosics and Pulp. There were about 15 papers on this subject in 8th European Workshop on Lignocellulosics and Pulp (EWLP) in Riga, Latvia, in 2004, as compared to 4-5 reports in 7th EWLP in Turku, Finland, 2002.

Recently developed instrumental methods such as X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS) are estimeed tools for investigation of lignocellulose fibres surface composition. Still some problems persist: due to the different analysis depth and mechanism the obtained results frequently are contraversial. For example, lignin detected in bulk of bleached eucalyptus pulp fibres was found also on fibre surface by XPS method but not by applying ToF-SIMS [1].

Genuine fragments of fibre surface material can be obtained by improved traditional peeling methods which are presented in this paper. It is supposed that conjunction of traditional peeling procedures and routine or recently developed spectroscopy and chromatography methods is the most favourable way to elucidate the lignocellulose fibres composition.

To analyse the fibre wall outer morphological layers, the hydromechanical peeling method was initially proposed by Kallmes and Krause, then further developed by Purina, Treimanis and coworkers in Riga [2].

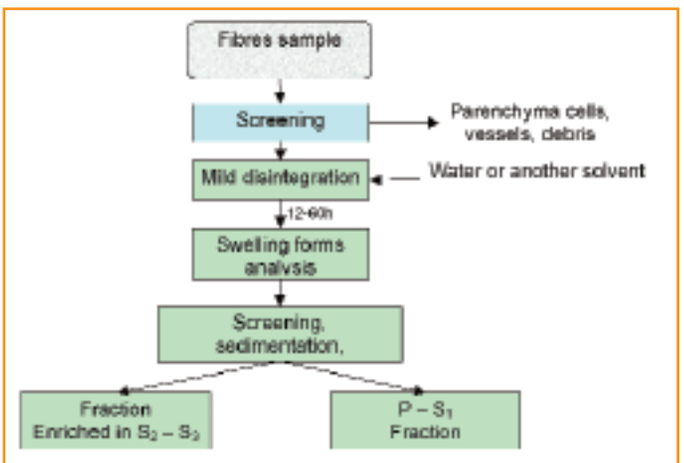

Fig. 1 - The sequence of the actions in order to perform the hydromechanical peeling of pulp fibres outer morphological layers

The fibres sample is first separated from the parenchyma cells, vessels and fibre debris (Fig. 1), then placed as a 3% fibre suspension in water or water/ethanol mixture (1:1, v/v) in a disintegrator. The pulp fibres suspension is treated in a disintegrator at 3,000 rpm and samples are withdrawn in every 3 or 5 hours (it depends on fibres properties). This kind of light beating (hydromechanical treatment) removes material from fibre surface. As a rule the separation of the layers occurs between S_1 and S_2 layers of secondary wall under the conditions employed. Using an optical microscope the fibres are classified according to the specific swelling forms in copper ammonium solutions. The degree of exposure (DE) of S_2 layer is calculated on the basis of the ratios of the fibre swelling forms:

$$DE\% = 1.0n_1 + 0.8n_2 + 0.5n_3 + 0.2n_4$$

where
n_1: percentage of fibres with "vermicular" swelling form in Cuoxam
n_2: % fibres with elongated-spherical forms,
n_3: % fibres with spherical swelling forms,
n_4: % fibres with occasional spheres in Cuoxam.

When DE reaches 75-85% and the fibres destruction has been intensified the peeling procedure is interrupted. The outer layers P-

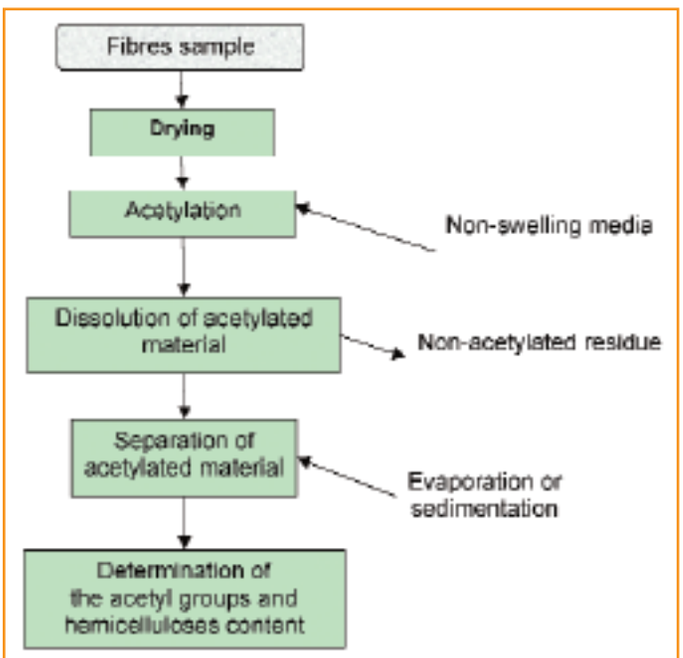

Fig. 2 - The sequence of the operations in the process of the chemical peeling of pulp fibres outer morphological layers

The composition of the fibre surface (P-S_1) and central (S_2-S_3) layers

Fractions	Lignin, %	Xylose, %	Mannose, %	Glucose, %
Whole sample	0.9	24.6	3.3	65.4
Peeling 20 h				
P-S_1 layers	3.3	26.8	5.1	64.5
Fraction enriched in S_2-S_3 layers	0.7	21.3	3.2	66.9

S_1 fraction is collected by a screening process using sedimentation, centrifugation and freeze drying. The S_2-S_3 fraction is collected from the sieves with 0.05 mm holes.
The peeling process and its monitoring can be accelerated significantly by using computerized equipment. It seems necessary to apply two types of instrumentation. The fibre dimensions are to be measured by optical equipment like "STFI Fibermaster" or "Kajaani FS-200". The decrease of the weight averaged fibre length indicates that the fibre destruction commences and the peeling process must be finalised. The fibre swelling forms may be identified and quantified by appropriate image analysis equipment.
Chemical peeling process (Fig. 2) involves heterogeneous acetylation of oven dry fibres in non swelling media (benzene) with acetic anhydride $(CH_3CO)_2O$ in presence of a catalyst. Then the esterified fraction is dissolved in an appropriate solvent and separated by evaporation or sedimentation. After the determination of the content of acetyl groups it is possible to calculate the weight of the peeled substance. Electron microscopy studies revealed that only 1-2 esterification cycles are practical as the next acetylation stages destroy fibre walls significantly. It must be remarked that this method is more appropriated for investigation of polysaccharides distribution. Residual lignin is partly destroyed during the process. Also so called enzymatic peeling method is being developed at the STFI-Packforsk research institute in Stockholm. It is not described here as it is not yielding physically intact fractions of the fibre wall morphological layers. But it is an useful tool in order to study the polysaccharide composition in fibre wall surface layers.

Some examples

The results obtained by hydromechanical and chemical peeling procedures are partly reported in published papers [2-4]. If the earlier data were related mainly to the concentration of the residual lignin and hemicelluloses in surface and central pulp fibre layers

(Table - birch wood ASAM pulp), afterwards the researchers paid attention also to the content of important functional groups (anionic groups, chromophores) in the morphological layers.
The composition of the fibre wall surface layers exerts quite meaningful influence on the properties of the material. Also fibres beatability and important interfibre bond strength parameters are influenced by fibre surface characteristics.
In recent years the attention was paid to the role of fibre wall composition in the enzyme assisted processes, including the use of cellulose binding domains. For example, it is well known that the use of hemicellulases (xylanases, mannanases, laccases) in the manufacture of kraft pulp enhance pulp bleaching.
At the laboratory of the Institute of Wood Chemistry kraft, sulphite and organosolv pulp fibres enzymes boosted bleaching processes were studied [5]. The residual amounts of lignin and hemicelluloses in the outer and central pulp fibre wall layers as well as lignin-hemicelluloses ratio were determined. It was concluded that the surface layers P and S_1 are noticeably more resistant to chemical or biological treatments. Under similar conditions of organosolv ("organocell " type) birch wood pulp fibre wall fractions treatment with xylanases and peroxide the authors have got the following brightness values:

P-S_1 layers → 34.5% ISO brightness
S_2-S_3 layers → 73.0% ISO brightness

The Size Exclusion Chromatography (SEC) after the fibre wall substance fractionation confirmed an essential difference between the morphological layers. The P-S_1 layers revealed a ten times higher amount of lignin soluble in organic solvents. No essential difference was discovered in the molecular mass (MM) parameters of the hemicelluloses between the layers but there was a remarkable distinction in the corresponding lignin MM parameters. It was concluded that in the fibre wall outer layers the chemical structure of the Lignin-Carbohydrate Complex (LCC) has been destructed insignificantly whereas in the S_2-S_3 layers almost lignin free hemicelluloses were found.
Making use of the application of fibre wall peeling methods we conclude that pulp fibres bleachability is influenced not only by residual lignin content, chromophores composition, hexenuronic acid content but also by fibre morphology features.

Conclusions

Important advantage of the peeling methods which are quite laborious is the capability to produce the "true" fractions containing the P-S_1 and S_2-S_3 layers. Hence the possibility of applying different chemical and spectroscopy analytical methods to separate fibre wall fractions is ensured.
Not much effort is put in the field of combining advanced instrumental methods and traditional peeling procedures. From this point of view very positive seems the initiative of the members of COST (European Co-operation in the field of Scientific and Technical research) Technical Committee in Forestry and Forest Products to set up a new project aimed to the further development of the fibre surface sensitive methods.

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Metodi tradizionali avanzati per l'analisi di strati superficiali di fibre. Un valido strumento nella ricerca su prodotti lignocellulosici

ABSTRACT

I parametri di composizione chimica e struttura della parete delle fibre non danno informazioni sufficienti circa le proprietà e le potenziali applicazioni dei materiali. C'è un interesse crescente nell'ottenimento di parametri più specifici specialmente riguardo la composizione della superficie delle fibre. I metodi tradizionali migliorati durante gli ultimi anni, sono processi laboriosi ma forniscono dati affidabili e dettagliati, specialmente quando utilizzati in combinazione con la spettroscopia e con metodi strumentali avanzati. Il metodo idromeccanico richiede un forte mescolamento delle fibre in acqua o in miscele acqua/etanolo e successiva separazione. Il metodo chimico di peeling include acetilazione degli strati esterni di fibre essiccate in forno e dissoluzione del materiale esterificato in solvente appropriato.