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NMR SPECTROSCOPIC STRUCTURAL STUDIES OF WOOD AND PULP COMPONENTS

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ABSTRACT

Various NMR spectroscopic techniques were applied to investigate the polymeric components of wood and pulp. The main aim of the work was to obtain new information on the structural- changes occurring in the morphology of cellulose and inthe lignin structure during various chemical pulping related processes in order to help optimise the conditions for efficient delignification and bleaching reactions without affecting pulp yield or strength properties. One of the main objectives of this research was to investigate, the residual lignin structure and the crystallinity of cellulose in ray cells and on the fibre surface compared to the corresponding structuresinside the fibre by isolating fines fractions before and after refining of kraft pulp .Mainly softwood components were considered throughout this research.

Keywords: NMR, Delignification, Kraft Pulp,

I. INTRODUCTION

Increasing environmental concern has forced the modern pulp and paper industry to seek more selective and environment friendly pulping and bleaching procedures. This has led for example to the preferential utilisation of elemental chlorine free (ECF) and total chlorine free (TCF) bleaching sequences instead of traditional chlorine bleaching. In those bleaching sequences oxygen delignification is a very important stage because of its many environmental and economical benefits. However, due to its limited selectivity the reaction conditions of oxygen delignification still need optimisation.1 The better understanding of the structure and morphological distribution of not only residual lignin, but all woodcomponents, may aid in optimising conditions for efficient delignification and bleaching reactions without compromising pulp yield or strength properties. Therefore, much effort has been focused on the thorough structural investigation of residual lignin, as well as the other woodcomponents, of unbleached and bleached pulps.

II. WHAT IS PULPING?

Pulping is a process of making pulp or fibrous materials or separation of wood fiber from wood.

1.1 Chemical Pulping

The layered ultrastructure of wood cell is complex.In chemical pulping the components that keep wood cells together, mainly lignin, are dissolved in order to obtain fibers for papermaking. The aqueous solutions of cooking chemicals are transferred through the cell walls towards the middle lamella and the lignin rich middle lamella, which actually binds wood cells together, is dissolved last.1,3The most important chemical pulping processes are the kraft and sulphiteprocesses, but due to the better yield and strength properties, the more effective kraft process dominates the sulphite process.

In the sulphite process the water, sulphur dioxide gasand a base cation (Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+}) is the cooking liquor and the reaction product.1-3 By regulating the composition of cooking liquorsulphite pulping can be carried out in acidic, neutral or alkaline conditions. During sulphite pulping the ether bonds of lignin are hydrolysed and hydrophilic sulphonic acid groups are introduced into lignin. In addition to lignin degradation by hydrolysis, the build up of the phenolic and sulphonic acid groups increases the hydrophilicity of lignin thus improving its solubility.

In kraft, or sulphate, process an aqueous solution ofsodium hydroxide and sodium sulphide, i.e. in white liquor, at elevated temperatures is used[1-3].During kraft pulping lignin fragmentation is also performed by the cleavage of aryl etherbonds and formation of new phenolic groups, which increase the hydrophilicity andsolubility of lignin. The reactions of lignin in a kraft cook are complex and still notcompletely understood, but the main reactions leading to the lignin degradation in alkalineconditions have been well reviewed[1,2,4-5]. The most important delignifying reaction inalkaline conditions is the cleavage of β-aryl ether linkages, which are the most prominentlignin structures. The cleavage of phenolic β-aryl ether bonds is initiated by the formation ofquinonemethide and elimination of an α-substituent from the phenolate (Fig. 1-1). In kraftpulping conditions the reaction of hydrosulphide ions with quinonemethides leads to thecleavage of β-O-4-linkages, whereas in the absence of hydrosulphide ions, such as in thesoda cook, the dominating reaction is the elimination of γ-hydroxymethyl or β-proton, whichleads to the formation of formaldehyde and enol ether structures .The cleavage of non-phenolic β-aryl ether bonds is the dominating and rate determining reaction in alkaline lignin degradation.. The etherified β-aryl ether linkages are cleaved byhydroxide ions via an oxirane intermediate. This reaction is not affected by sodiumsulphide or anthraquinone,[4] but for example α-carbonyls have been shown to accelerate thecleavage of β-aryl ether linkages in non-phenolic lignin units [8,9] Because the reaction isintramolecular, the stereostructure also affects the reactivity and the e*rythro*form of the β-O-4 structure has been found to be more reactive than the corresponding *threo*form [10-13].

A recently discovered dibenzodioxocin structure, which involves both α- and β-aryl etherbonds within a 8-membered ring, has been reported to be in alkaline pulping conditions lessreactive than non-cyclic α-aryl ethers, but more reactive than the ordinary β-O-4structures.[14,15] During kraft pulping the dibenzodioxocine structures are degraded releasingmainly 5,5'-biphenyl structures, whereas in the absence of HS- ions enol ethers,5,5'-biphenyls and vanillin are formed [14].

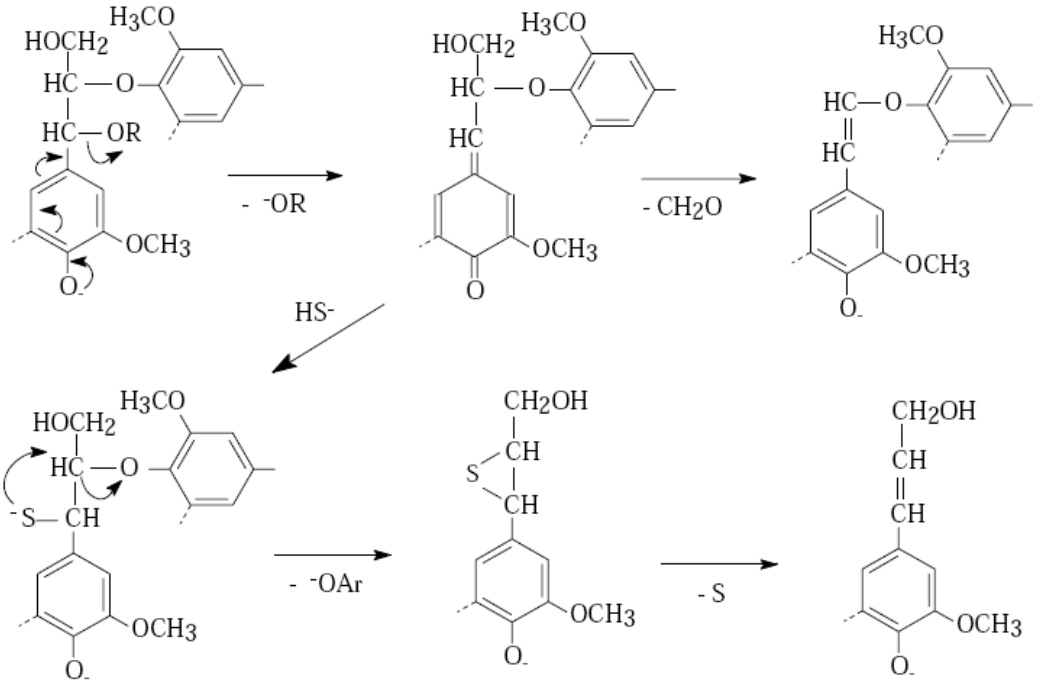

Figure 1-1.Main reactions of the phenolic □-aryl ether structures in soda and kraft pulping conditions.

2.2 Delignification by Oxygen and Bleaching

In order to avoid severe carbohydrate degradation, further delignification is generally continued by more selective alkaline oxygen delignification .However, only 50% of the residual lignin can usually be removed by oxygen delignification without deterioration of the pulp properties. The reactions involved in alkaline oxygen delignification are complex, including multitude radical chain reactions and the formation of some other oxygen containing species which may contribute to the delignification, e.g. hydroperoxides. According to the proposed reaction mechanism, the phenolic lignin units are converted to phenoxy radicals by the attack of oxygen.19-21 By further reaction with oxygen the phenoxy radicals are converted into peroxide anions whose intramolecularnucleophilic reaction leads to oxidation of the lignin molecule and formation of muconic acid type carboxylic acid structures as well as oxirane structures, thus increasing the solubility of lignin. Conjugated structures, such as stilbenes and enol ethers formed during pulping are also easily oxidised, leading to fragmentation of lignin by the cleavage of the Cα-Cβ bond and the formation of carbonyl structures. Demethoxylation and formation of muconic acids via cathecol intermediates have also been suggested to occur.22 Condensed 5-5'-biphenyl structures have been shown to be fairly resistant in alkaline oxygen delignification.23 However, small amounts of thedegradation products of 5-5'-biphenyl structures, i.e. 3-carboxy-4-hydroxy-5-methoxysubstituted phenolic units, have been found in residual lignin after oxygendelignification24.After oxygen delignification, the brightness of the chemical pulp is further improved by lignin-removing bleaching.

2.3 Objectives of the Study

In this research, modern NMR spectroscopic techniques were applied to investigate the structural changes occurring in the polymeric wood components during various chemical pulping related processes, NMR spectroscopy is a very valuable method in studies of lignocellulosics. By solid-state NMR methods the components of wood and pulp can be analysed*in situ* and investigations of the morphology of cellulose as well as the suggested interactions between lignin and carbohydrates are possible. Multidimensional NMR methods in solution can be utilised for more detailed structural analysis of lignin side-chain structures. Since cellulose morphology may have an effect on the strength properties of pulp, but also give information on the accessibility and degradation mechanisms of cellulose during pulping and bleaching, the high-resolution solid-state NMR spectroscopic techniques were used in this thesis to investigate the morphology of cellulose after various pulping processes as well as after oxygen delignification and TCF-bleaching. The degree of cellulose crystallinity and the relative proportions of cellulose polymorphs were determined. Technique One of the main objectives of this research was to investigate if some parts of the fiber are unequally affected by kraft pulping. Therefore the structure of residual lignin and the crystallinity of cellulose in ray cells and on the fiber surface were compared with the corresponding structures inside the fiber by isolating fines fractions before and after refining ofkraft pulp. In addition to the cellulose crystallinity, the lateral dimensions of cellulose fibrils and fibril aggregates were determined.

II.USES OF NMR SPECTROSCOPY

3.1 Solid-State NMR Spectroscopy in Celluloseand Lignin Studies

Due to its capability of measuring samples in their native state, 13C Cross-Polarization Magic.Angle Spinning (CPMAS) NMR spectroscopy can be applied to investigate both thechemical and physical structure of lignocellulosics. Therefore in addition to the chemicalstructure of lignin, 13C CPMAS was used in this research also to investigate the morphology ofcellulose and the interactions of lignin and carbohydrates within the cell wall.

3.1.1 13C CPMAS NMR spectroscopy in morphological studies ofcellulose

In NMR spectra chemically equivalent carbons can be distinguished ifthey are magnetically non-equivalent. So even though the corresponding carbons of differentanhydroglucose units of cellulose are chemically equivalent, they can be distinguished in a13C CPMAS spectrum if they are in different magnetic environments, for example due to thedifferent packing of the cellulose chains or distinct conformations. Separate signals foramorphous and crystalline carbons as well as splitting of crystalline signals due to cellulosepolymorphs can thus be detected.

The 13C CPMAS spectrum of spruce kraft pulp is shown in Figure 2-1. The most informativeregion in the cellulose spectrum is the C4 region between 79 and 92 ppm. The sharper signalat 86-92 ppm corresponds to the highly ordered cellulose of the crystallite interiors, whereasthe broader upfield signal (79-86 ppm) has been assigned to the disordered cellulose as wellas to the less ordered cellulose chains of the crystallite surfaces.63-68. Cellulose of thecrystallite surfaces has been shown to give the doublet at 83.5 and 84.5 ppm.69-71. Recently,based on solvent-exchange, spin-relaxation and spin-diffusion experiments, this doublet hasbeen reported to indicate the accessible fibril surface, whereas the broader signal assignedearlier to the amorphous cellulose, has been reported to indicate inaccessible fibril

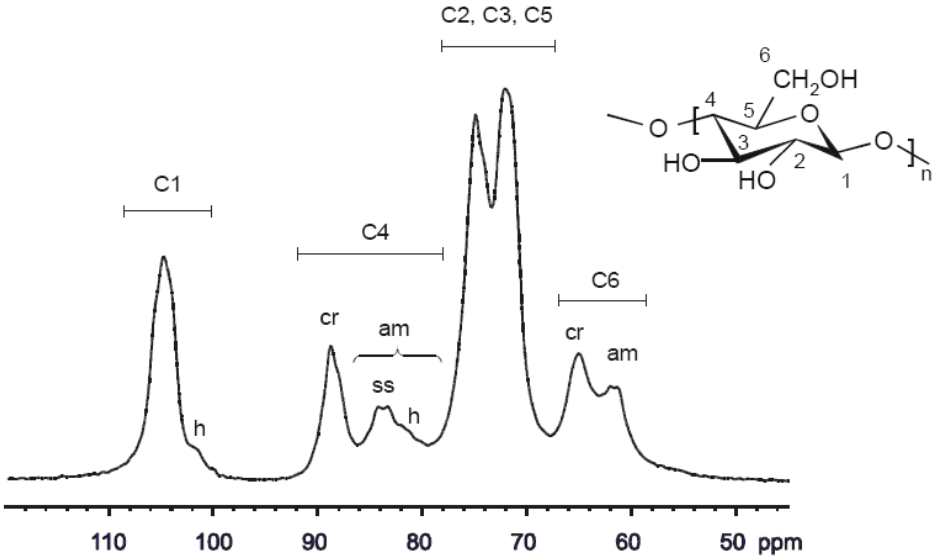

Figure 2-1. ^{13}C *CPMAS spectrum of spruce kraft pulp. Cr=crystalline, am=amorphous, s=crystallite surfaces and h=hemicelluloses.*

surfaces.Cellulose spectra have been shown to be quantitative within a few percent accuracy for both dry and wet samples,but in order to obtain quantitative spectra of pulp cellulose, the samples must be free of lignin and hemicelluloses.

3.1.1.1 Cellulose Crystal Linity Determination

Only the highly ordered cellulose in the interiors of the crystallites is considered here as 'crystalline' cellulose. The term 'amorphous' is correspondingly used to describe the remaining less ordered cellulose, thus also including the fibril surfaces. The degree of crystallinity in various pulp samples was determined as a crystallinity index (CrI) from the areas of the crystalline and amorphous C4 signals by deconvolution using a Lorenzian lineshape.

CrI = A86-92ppm / (A79-86ppm + A86-92ppm) . 100% (2.1)

Results obtained by this method for pure cellulose samples have been shown to well correlate with the corresponding results obtained by X-ray diffraction.However, in pulp and wood samples, hemicelluloses and lignin side-chains also contribute to the area of the 'amorphous region'. Therefore, the interfering hemicellulose and lignin signals must be removed either chemicallyor spectroscopically before the determination of CrI. The utilisation of chemometric methods has also been reported.

3.1.1.2 Spectral edition based on proton spin-relaxation

The proton spin-relaxation based spectral (PSRE) method has been frequently used to investigate the cellulose crystallinity in woodand pulp.In the PSRE-method the differences in the proton spin-relaxation times (T1⟩H) of different spatial domains are utilized to separate the components into subspectra of their own. In this way, the interference of lignin and hemicellulose signals resonating in the amorphous region can be removed spectroscopically and all the possible structural changes affected by chemical treatments are avoided.

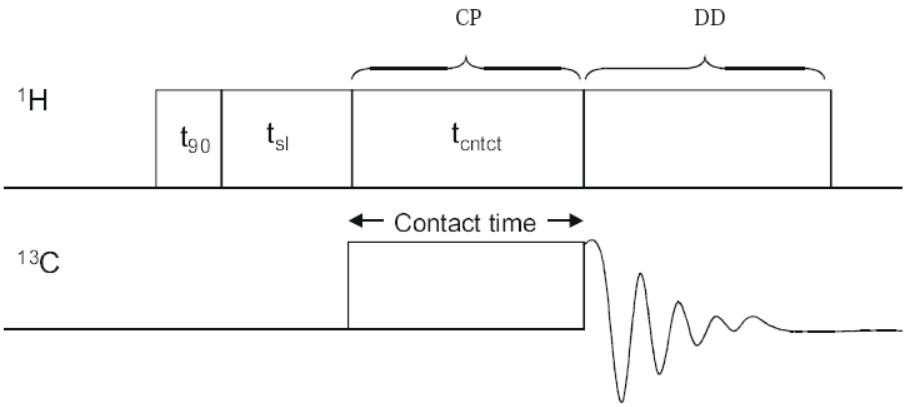

Figure 2-2. Delayed contact pulse sequence.[78]

The 'delayed contact' pulse sequence (Fig. 2-2) used in the PSRE-method was also appliedin this thesis to separate the subspectra of cellulosic and non-cellulosic componentsIII. Inaddition to the ordinary cross-polarization, this pulse sequence has a spin-lock delay (tsl)between proton preparation pulse (t90) and contact time (tcntct). During the spin-lock tsl, someloss of the magnetization occurs through relaxation, which is faster for the amorphous ligninand hemicellulose matrix than for the more ordered cellulose component. Based on differentrelaxation times due to the different mobilities, the subspectra of crystalline cellulose and theamorphous matrix can be separated. Since the relaxation times of the domains arequite similar in magnitude, a linear combination of two spectra measured with different spinlocktimes is required to obtain subspectra of the components. Relaxation times of lignin andhemicelluloses have been observed to be indistinguishable and therefore those componentsare inseparable.

3.1.1.3 Determination of Cellulose Polymorphs

Crystalline cellulose exhibits various polymorphs, of which the natively synthesized cellulose I is most common. Based on results from 13C CPMAS NMR spectroscopy,VanderHart and Atalla discovered that the crystalline region of native cellulose I is a mixturetwo crystalline forms, cellulose Iα and Iβ, and their relative proportions vary depending onthe species.Cellulose Iα is the dominant form in bacterial and algal celluloses, whereascellulose Iβ is the dominant form in higher plants, such as cotton and tunicate celluloses.In softwoods the proportion of cellulose Iα has also been reported to be higher than inhardwoods.It has been shown that cellulose Iα has a one-chain triclinic unit cell whereascellulose Iβ has a two-chain monoclinic unit cell. A difference in their hydrogen-bondingpattern has also been suggested. By annealing, the metastable cellulose Iα can be convertedto the more stable Iβ form, and by mercerisation or by regeneration from a solution, cellulose I can be transformed to cellulose II. Small amounts of cellulose II have also been detected in pulps93 and in samples commonly thought to contain only cellulose I, such ascotton93 or bacterial cellulose.The other cellulose polymorphs, III and IV, are notconsidered in this thesis.The occurrence of various crystalline forms of cellulose can be observed in the 13C CPMASspectrum as a splitting of the crystalline signals. The splitting is most prominent in thecrystalline C4 signal, which was used also in this thesis to determine the relative proportionsof cellulose polymorphs by using the signal areas determined by deconvolution.I-III .Theassignment of the

cellulose polymorphs was made using highly crystalline samples, rich ineither cellulose Iα (*acetobacterxylinum*), cellulose Iβ (cotton linter) or cellulose II(mercerised cellulose),I shown in Figure 2-4.

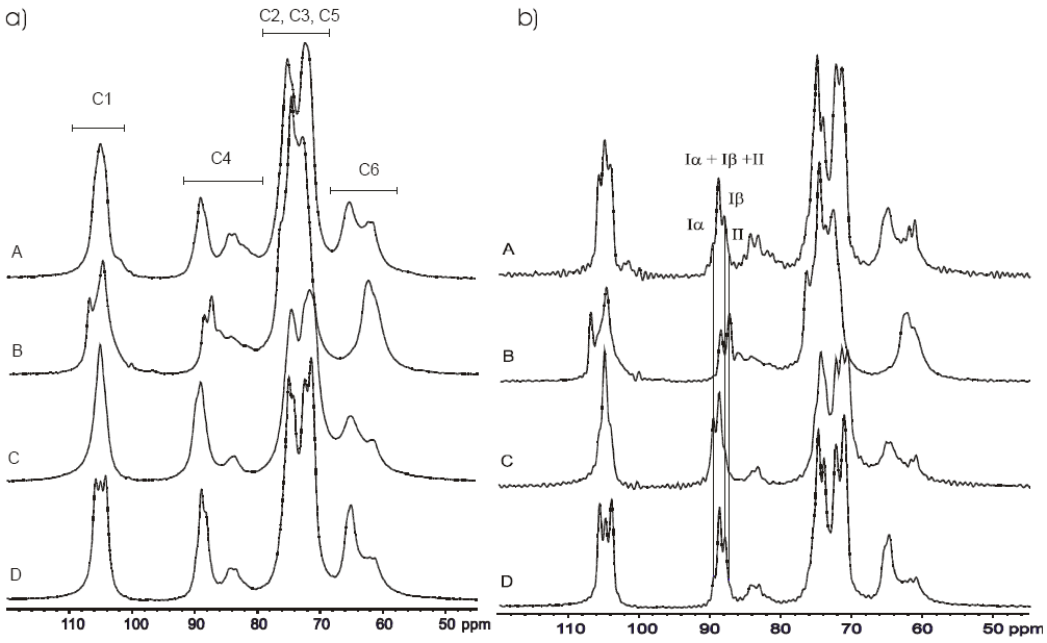

Figure 2-4. *a) Ordinary ^{13}C CPMAS spectra of kraft pulp (A), mercerised kraft pulp (B), Acetobacter xylinum (C) and cotton linter (D). b) The same spectra after resolution enhancement.*

3.1.2 Solid-state NMR Spectroscopy in Structuralstudies of Lignin

Solid-state 13C CPMAS spectroscopy provides a very valuable tool also for lignin studies. Itcan be very well utilised for example in studies of enzymatically isolated residual lignincarbohydratecomplexes (RLCC), which have restricted solubility. In this way the wholelignin sample can be analysed reliably and not just some soluble fraction of it. No chemicalmodifications for the sample preparation, such as acetylation that is often used in solutionNMR to improve the solubility, are needed. In addition, both free phenolic and etherifiedlignin units can be equally investigated. The major drawback of CPMAS spectroscopy is,however, its low resolution compared to the solution state NMR spectroscopy, and thereforeonly some structural features of lignin can be investigated instead of detailed structure. The low resolution can, however, be compensated by manyspecial techniques, which allow for example the determination of the degree of condensationin lignin or the investigation of interactions between lignin and other wood components.

IV.CONCLUSIONS

1). Various NMR methods both in solid and liquid state were applied to investigate the effects of chemical pulping related processes on the polymeric components of wood and pulp. It was shown that the NMR methods used in this research are very well applicable to versatile studies of lignocellulosics. Especially the PSRE method based on delayed contact pulse sequence proved to be better in the removal of interfering hemicellulose signals from softwood pulp spectra before determination of CrI than the chemical removal of hemicelluloses by

acid hydrolysis. However, all hemicellulose signals could not be removed from birch pulps by the PSRE method, and therefore birch pulps were suggested to contain larger amounts of well-ordered xylan. The dipolar dephasing method also proved to be a valuable method for determining the amount of condensed lignin structures. With this nondestructive method the relative amount of condensed lignin structures can be monitored both in phenolic and non-phenolic lignin units, and this determination is not dependent on the solubility of the sample. Most of the present results obtained by NMR methods support the previous suggestions for the various obstacles to delignification.

2).Solid-state NMR spectroscopic analyses showed that cellulose crystallinity increases during pulping. Due to the preferential removal of less ordered cellulose, a slight increase in cellulosecrystallinity was also observed during oxygen delignification. During the QPZPbleaching sequence the degree of cellulose crystallinity was found to decrease slightly as a result of more extensive cellulose degradation in the accessible parts of crystallites. Various pulping methods or hemicellulose contents were not observed to affect cellulose crystallinity, but after kraft pulping, the cellulose crystallinity was found to be lower in ray cells and on the fibre surface compared to the long fibre fractions. Refining was observed slightly to facilitate the cellulose fibril aggregation as well as crystallization, probably during drying due to the better swellability of the fibres and therefore improved mobility of cellulose chains.

Ordinary 13C CPMAS measurements could be used to monitor some important features of the lignin structure. Modern 2D HSQC and 3D HSQC-TOCSY measurements in solution could be applied for more detailed structural studies of bonding patterns of lignin. Those studies reveal that most of the original structures identified in MWL are still present in technicallignins, although their relative proportions vary after kraft pulping and oxygen delignification. The cleavage of aryl ether linkages during kraft pulping and the preserving effect of oxygen delignification on aryl ether linkages were observed in both solid-state and in solution NMR studies

3).According to the dipolar dephasing results, the condensed aromatic lignin structures are enriched into fibres during pulping and oxygen delignification, whereas the less condensed lignin structures are removed already in the early stage of pulping. However, the formation of new condensed structures cannot be excluded either, although the condensed diphenyl methane structures could not be found in residual lignins using multidimensional NMR measurements.

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