

Inverse gas chromatography analysis of spruce fibers with different lignin content

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Abstract Unbleached TMP spruce fibers were stepwise delignified by $\text{KMnO}_4/\text{H}_2\text{SO}_4$ and five partly delignified samples were obtained. Fibers were characterized in terms of carboxylic groups, lignin and hemicelluloses content. IGC measurements were performed in the untreated fibers and in the five delignified fiber samples, as well as in microcrystalline cellulose (MCC). Different parameters, such as the dispersive component of the surface free energy (γ_s^d), the free energy and the enthalpy of adsorption with nonpolar probes (ΔG_a^d and ΔH_a^d , respectively), as well as the specific interactions with polar probes,

quantified by the free energy and the enthalpy of adsorption (ΔG_a^s and ΔH_a^s , respectively), were determined. The values of γ_s^d and ΔG_a^d are for all samples lower than for pure cellulose and vary slightly with the amount of lignin. For small contents of lignin, the values of ΔG_a^s of the acidic probes decrease with the delignification whereas those of the basic probes increase, pointing to a rather acidic character of the fibers due to the increase of the relative amount of the carbohydrates. The values for MCC corroborate these findings. Despite the substantial variation in the carboxylic group content during delignification, no clear tendencies were detected regarding the affinity with the basic probes.

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Introduction

Inverse gas chromatography (IGC) is an efficient and accurate method for the physicochemical surface characterization of some materials, used for instance in pharmacy, polymer and particle technology, coatings, pulps and papers. The use of various nonpolar and polar probes, interacting with a given surface, enables the assessment of several surface free energy related parameters, such as its dispersive component and the specific, acceptor–donor or acidic-basic properties.

Inverse gas chromatography has been used by several authors for studying different types of paper-making fibers like unbleached and bleached hardwood and softwood chemical pulp fibers (Abdmziem et al. 2006; Belgacem 2000; Carvalho et al. 2005a; Carvalho et al. 2005b; Felix and Gatenholm 1993; Jacob and Berg 1994; Shen et al. 1998; Shen and Parker 1999), chemi-thermomechanical pulp fibers (Jacob and Berg 1994; Börås et al. 1997; Kamdem and Riedl 1991) and thermomechanical pulp fibers (Dorris and Gray 1980). Various samples used as reference material for pure cellulose, like cotton fibers (Shen and Parker 1999; Dorris and Gray 1980; Buschle-Diller et al. 2005), microcrystalline cellulose (Abdmziem et al. 2006; Jacob and Berg 1994; Belgacem et al. 1996) and a powder of hardwood α -cellulose fibers (Belgacem et al. 1995) were also extensively examined. Lignin rich fiber samples with different lignin contents were compared by using IGC (Shen and Parker 1999; Belgacem et al. 1996).

The authors of the present study have been involved in evaluating the adsorption characteristics of fibers with distinct surface compositions (in terms of lignin, hemicelluloses and cellulose), by using cationic dyes with selected structural properties (Peterlin et al. 2009). For that purpose, pulp fibers with decreasing amounts of lignin, obtained by stepwise oxidative delignification with acidic permanganate, were prepared. This atypical delignification laboratory procedure was applied to selectively remove lignin and preserve the carbohydrates as much as possible undamaged and, simultaneously, more and more exposed (Li and Gellerstedt 1998a, b). Since it is known that adsorption depends on the presence and concentration of certain functional groups at the fiber surface which possess electron donor/acceptor abilities, it was decided to compare the results with those obtained by IGC, in order to get a deeper insight on the fibers surface chemistry and a better understanding of the complex interactions of the dye molecules with the fibers. Although IGC utilizes as probes compounds with small and simple molecules which are not directly comparable to the larger and usually ionic molecules of the dyes, it was decided to use the technique for the fibers surface characterization, in order to find out whether the results could add for interpreting the dye adsorption characteristics.

Materials and methods

An unbleached Norway spruce thermomechanical pulp with kappa number 134, sampled in a Swedish mill, was used as initial fiber sample. This sample was stepwise oxidized with an acidic potassium permanganate solution and five samples with various lignin contents, corresponding kappa numbers of 107, 75, 33, 17, 5, were prepared. The lignin content of pulp samples was determined according to the TAPPI T 236 om-99 standard method and reported in terms of kappa number. After oxidation the pulp samples were exhaustively washed with deionized water at 60 °C in order to remove all dissolved and colloidal substances and then washed with deionized (miliQ) water until the conductivity was lower than 2 $\mu\text{S cm}^{-1}$. After washing, samples were filtered and stored at 5 °C for further analyses. A powder of microcrystalline cellulose (Cellulose powder DS-0 Fluka) was used as a pure cellulose reference material.

The carboxylic acid group content was determined by conductometric titration according to the SCAN-CM 65:02 standard method.

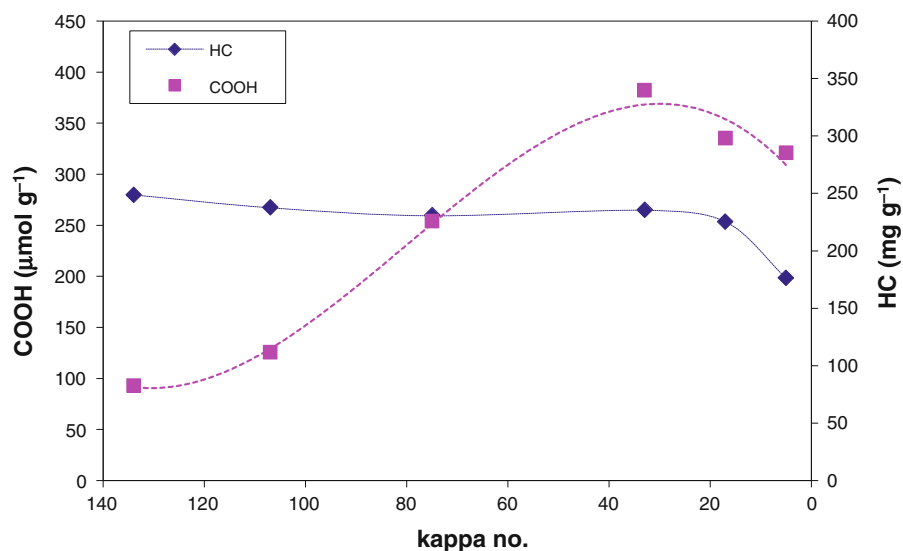
The carbohydrate content of hemicelluloses and pectins was quantified by acid methanolysis followed by derivatization and gas chromatography analysis (Sundberg et al. 1996).

The inverse gas chromatography measurements were carried out using the Agilent Technologies 6890 N (USA) gas chromatograph equipped with a flame ionization detector. The injector and detector were operated at 150 and 250 °C, respectively. The flow rate of the carrier gas (helium 5.0, Messer, Slovenia) was set at 5 mL min^{-1} .

The fluffed fiber materials were packed into glass chromatographic columns with 4 mm inner diameter and 0.3 m length. The columns were washed with distilled water and acetone before packing. The packed columns were conditioned overnight at 60 °C under a constant stream of helium with a flow rate of 5 mL min^{-1} to remove volatile molecules adsorbed at the stationary phase surface, which could affect the retention of the probe molecules. IGC measurements at infinite dilution were performed at five column temperatures (30, 35, 40, 45 and 50 °C), with two replicates for each temperature.

To determine the dead volume of the column methane was used as a non-interacting reference

Fig. 1 The content of hemicelluloses and carboxylic groups during delignification



probe. All probes were used at analytical grade without further purification. The nonpolar probes used were *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane. The polar probes were tetrahydrofuran (THF) as basic probe, ethyl acetate (EtOAc)¹ and acetone (MeCOMe) as amphoteric probes, and chloroform (CHCl₃) and dichloromethane (CH₂Cl₂) as acidic probes.

The physicochemical properties of all probes used in IGC calculations and the theory of IGC are given elsewhere (Belgacem 2000; Carvalho et al. 2005a; Jacob and Berg 1994; Shen and Parker 1999; Dorris and Gray 1980; Fowkes 1987; Kunaver et al. 2004; Matuana et al. 1999; Santos et al. 2002, Santos and Guthrie 2005, Schultz et al. 1987).

Results and discussion

Determination of hemicelluloses and carboxylic groups

During pulp delignification, the content of lignin decreased steadily, whereas the content of

hemicelluloses remained nearly constant until the last sample (Fig. 1). The plausible explanation for this is the reaction of hemicelluloses with the acidic permanganate when there is not enough lignin to react with and therefore they become exposed to the attack of permanganate (Li and Gellerstedt 1998a). As for the amount of carboxylic groups, there is an initial increase as a consequence of the oxidation of the lignin aromatic structures, followed by a decrease when the total amount of lignin becomes very low (Fig. 1).

Determination of the dispersive component of the surface free energy of the fibers

The dispersive component of the surface energy, γ_s^d , determined by IGC in the temperature range 30–50 °C decrease linearly with temperature, as expected (Fig. 2) (Carvalho et al. 2005a, Shen et al. 1998, Santos et al. 2001). The slopes of the lines are negative and their absolute values generally increase with the progress of lignin removal, as can be confirmed from the results obtained at 40 °C (Table 1) (The pulp with kappa number 75 is however, an outlier).

The value of γ_s^d for microcrystalline cellulose is considerably higher than those of the tested fiber samples and also higher than the literature values for cellulose and hemicelluloses rich fibers such as bleached pulps. Nevertheless, it coincides fairly well with the literature data (Table 2).

¹ Ethyl acetate is regarded by most authors as an amphoteric probe. However, in the measurements presented in this paper, its behavior resembles more closely basic THF than amphoteric acetone, Figs 6 and 7. See also Jacob and Berg (1994).

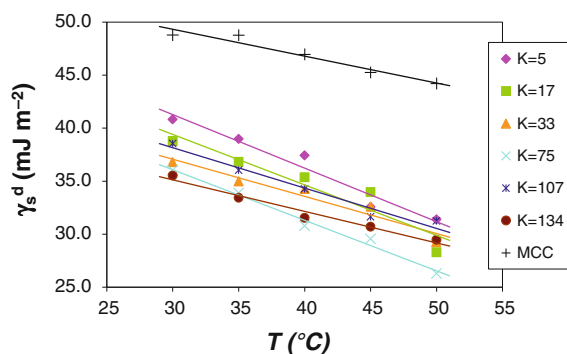


Fig. 2 Temperature dependence of the dispersive component of the surface energy of TMP fiber samples with distinct kappa numbers (K) and of microcrystalline cellulose

Table 1 γ_s^d values of fiber samples at 40 °C

Kappa number	γ_s^d (mJ m ⁻²)	$d\gamma_s^d/dT$ (mJ m ⁻² K ⁻¹)
134	32.2	-0.30
107	34.4	-0.38
75	31.3	-0.48
33	33.6	-0.35
17	34.7	-0.48
5	36.2	-0.51
MCC ^a	46.8	-0.25

^a Microcrystalline cellulose (Cellulose powder DS-0 Fluka)

For all tested temperatures, and with few exceptions, the values plotted in Fig. 2 are smaller than those reported in the literature (Table 2). One reasonable explanation is that the methodology used in the present study for the fiber delignification leads in its early stages merely to the thinning of the lignin layer and the carbohydrates remain more or less buried. Only when the content of lignin decreases to a very small value, the carbohydrates become increasingly exposed, thus contributing to the higher values close to those of the TMP and bleached kraft pulps listed in Table 2 for the same temperatures.

Even for the lignin rich fibers (higher kappa numbers), the γ_s^d values do not match those of the isolated lignins reported in the literature. The most logical explanation is that the isolated lignins are chemically modified and their properties are considerably altered (Forss and Fremer 2000; Kubo and Kadla 2005).

Table 2 γ_s^d values of different pulp samples, MCC and lignins

Sample	γ_s^d (mJ m ⁻²)	T (°C)
TMP	38.8	30 ^a
Norway spruce wood	42	20 ^b
CTMP	25.2	40 ^c
Unbleached pulps	38–42	37 ^d
Bleached kraft pulp	38.4	40 ^e
	45.0	40 ^f
	41.3	40 ^g
Bleached sulfite pulp	44.0	— ^h
Filter paper	56.6	37 ^d
Cotton cell. paper	49.9	40 ^a
α -Hardwood cell.	31.9	40 ⁱ
α -Hard. cell. extract.	47.4	40 ⁱ
MCC	40.3	50 ^j
	52.3	39 ^k
Isolated lignins		
Organosolv	44.7	50 ^j
Kraft	46.6	50 ^j
Steam explosion	49.0	50 ^j
Soda lignin	48.2	37 ^d
Polystyrene	43.3	45 ^l

^a Dorris and Gray 1980, ^b Wälinder and Gardner 2000, ^c Kamdem and Riedl 1991, ^d Shen and Parker 1999, ^e Shen et al. 1998, ^f Carvalho et al. 2005a, ^g Carvalho et al. 2005b, ^h Felix and Gatenholm 1993, ⁱ Belgacem et al. 1995, ^j Belgacem et al. 1996, ^k Papirer et al. 2000, ^l Tze et al. 2006

Determination of the free energy and enthalpy of adsorption of the nonpolar probes on the fiber surface

The free energy (ΔG_a^d) and enthalpy (ΔH_a^d) of adsorption with nonpolar probes were determined at five different temperatures by measuring the retention times, according to the IGC theory (Santos et al. 2001). The absolute values of ΔG_a^d (Fig. 3) and ΔH_a^d (Fig. 4) increase regularly with the number of C atoms in alkane chains of nonpolar probes, which confirms that the chromatographic experiments were adequately performed (Santos et al. 2001). The values of ΔG_a^d for MCC are considerably higher than those of the other fibers, in spite of its slight increase by the end of delignification (kappa no. 17 and 5).

Noticeable variations of ΔH_a^d as a function of the kappa number were observed for *n*-hexane and

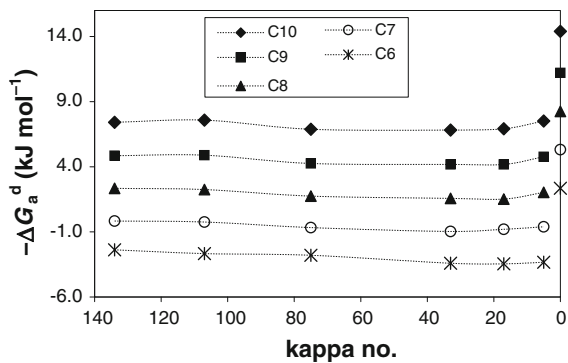


Fig. 3 Free energy of adsorption (ΔG_a^d) of the nonpolar probes versus the kappa number of the pulp samples at 40 °C (Data-points at kappa numbers = 0 are of microcrystalline cellulose)

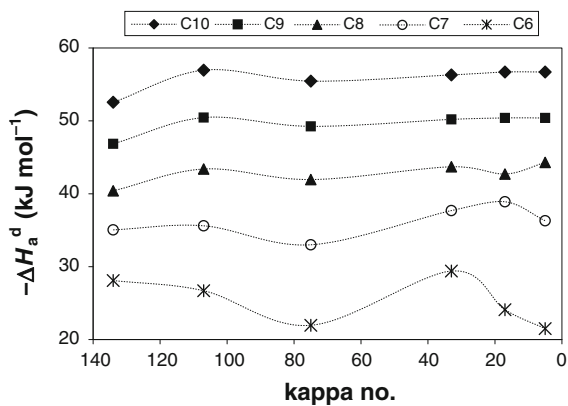


Fig. 4 The enthalpy of adsorption (ΔH_a^d) of nonpolar probes versus the kappa number of pulp samples

n-heptane (Fig. 4), while the values of ΔH_a^d for C₉ and C₁₀ were found to be predominantly constant.

Determination of specific interactions between polar probes and fiber surface

As an example of the specific interactions between the polar probes and the surface of the fibers, the results corresponding to the pulp with kappa number 17 are presented in Fig. 5. The specific free energy (ΔG_a^s) and the specific enthalpy (ΔH_a^s) of adsorption was also determined for all samples. The results are plotted in Figs. 6 and 7, respectively for ΔG_a^s and ΔH_a^s .

As can be seen in Fig. 5, the ΔG_a^s values for dichloromethane and chloroform derived from these measurements are quite distinct, despite the very similar total interaction (ΔG_a) and donor/acceptor

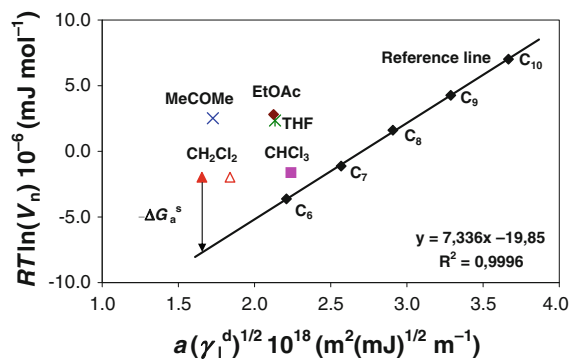


Fig. 5 Example of the specific interaction of polar probes with the fibers having a kappa number 17, at 40 °C

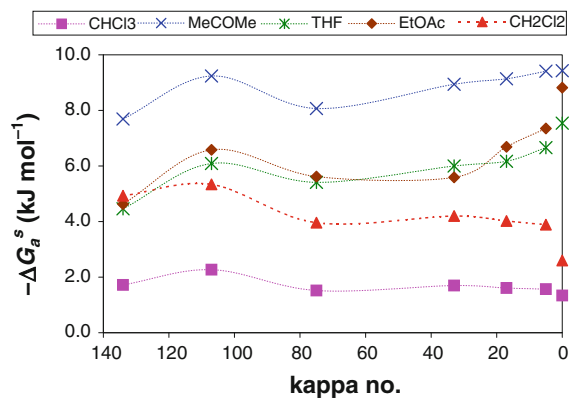


Fig. 6 Free energy of adsorption (ΔG_a^s) of the polar probes versus the kappa number of the pulp samples at 40 °C (Data-points at kappa numbers = 0 are of microcrystalline cellulose)

properties (Wälinder and Gardner 2000). Nonetheless it should be noted that experimental problems when using chloroform in IGC analyses are not uncommon, due to its closed and round-like shape. The specific interaction ΔG_a^s is calculated by the difference between the total interaction ΔG_a and the dispersive component ΔG_a^d :

$$\Delta G_a^s = \Delta G_a - \Delta G_a^d = RT \ln \left(\frac{V_{n,\text{ref}}}{V_n} \right) \quad (1)$$

The estimated cross-sectional area of the probe molecule, $a(\text{CH}_2\text{Cl}_2)$, plays a crucial role in the determination of specific interactions. Most authors in the field of pulp and papermaking fibers use the value 0.315 and 0.44 nm² for dichloromethane and chloroform, respectively (Carvalho et al. 2005a; Santos and Guthrie 2005; Santos et al. 2001;

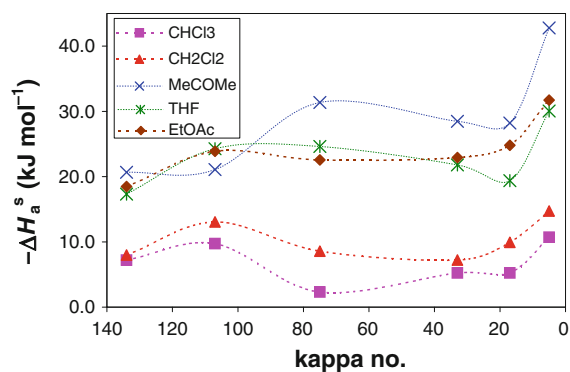


Fig. 7 The values of the enthalpy of adsorption for the polar probes, ΔH_a^s , on surface of pulp samples with different kappa numbers

Wälinder and Gardner 2000). Enormous differences in $a(\text{CH}_2\text{Cl}_2)$ values from 0.14 to 0.46 nm², determined by different methods, can be found in the literature. From these numbers, a mean value of 0.35 nm² can be obtained (if the extreme values are omitted), which is more close to the value of chloroform (Hamieh and Schultz 2002). One would expect intuitively that the values of a , for these two molecules, should not differ too much, since the molecules are similar with respect to the composition and molecular dimensions. If the value 0.35 nm² is taken instead of 0.315 nm² for the $a(\text{CH}_2\text{Cl}_2)$, substantially lower value of $\Delta G_a^s(\text{CH}_2\text{Cl}_2)$ is obtained, which lies more close to the values for chloroform (Figs. 5 and 6).

With few exceptions, the affinities of acidic probes remain essentially constant throughout the delignification. The values for MCC (kappa number 0) are more or less similar to the values of delignified fibers (kappa number 5) or even lower (CH_2Cl_2). At the same time, for the amphoteric and particularly for the basic probes, an increase in ΔG_a^s for fibers containing a small amount of lignin is detected. This increase is even more pronounced for the enthalpy of adsorption (Fig. 7).

The results obtained with pure cellulose (MCC) confirm this tendency. It is apparent that the fibers composed predominantly or exclusively of carbohydrates exhibit an increased affinity to basic probes. The possible reason for the increased “acidity” of these fibers can be the high content of hydroxyl groups at the fibers surface (Carvalho et al. 2005a). Similar or even higher affinity to basic probes would

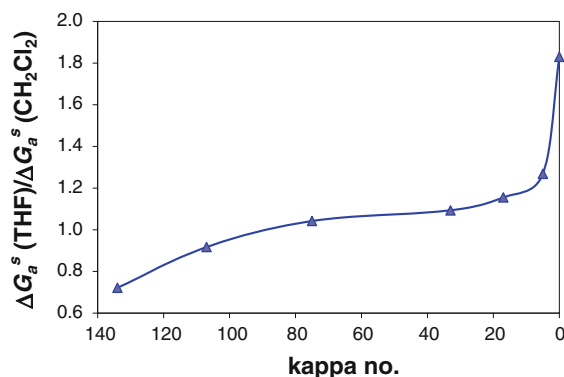


Fig. 8 The ratio $\Delta G_a^s(\text{THF})/\Delta G_a^s(\text{CH}_2\text{Cl}_2)$ versus the kappa number of the pulp samples at 40 °C (Data-points at kappa numbers = 0 are of microcrystalline cellulose)

be expected for the carboxylic groups, which are several orders of magnitude more acidic.² During the delignification process, the amount of carboxylic groups on our fibers varied substantially in the samples of the present study, being highest for the middle kappa numbers (from 75 to 5). Surprisingly, the affinities of basic probes to these fibers do not exhibit any correlation with the amount of carboxylic groups. Even the opposite, towards the end of delignification, where the amount of carboxylic groups begins to decline, “acidity” of the fibers increases (Figs. 7 and 8). The sample of microcrystalline cellulose with very low content of carboxylic groups shows the strongest interaction with THF and EtOAc.

The results presented in Figs. 6, 7 and 8 confirm that with the delignification process used in this study lignin is the prevailing substance at the fiber surface until the last stages of delignification, and therefore, for kappa numbers between 134 and 33, the fibers surface properties do not change considerably. At lower kappa numbers, lignin is removed and the carbohydrates become more exposed: the affinity of the basic probes begins to increase whereas that of the acidic probes tends to decrease. It is thus legitimate to conclude that the high affinity to basic probes is due to the carbohydrates, while lignin exhibits affinity to acidic probes.

² Carboxylic acids are ~ 10 orders of magnitude stronger than alcohols in aqueous medium. In gas phase, the difference in gas phase acidity of carboxylic acids and alcohols amounts to approx. 120 kJ mol⁻¹ (Isaacs 1987).

This considerable change of fiber surface properties only when the amount of lignin in fibers diminish to a very low content and the carbohydrate constituents become uncovered correlates well with the results reported in literature (Peterlin et al. 2009). In fact, the results of staining the same fibers with different types of dyes, show that the adsorption of some cationic dyes e.g. Methylene Blue and Crystal Violet correlates well with the amount of carboxylic groups. On the other hand, phthalocyanine cationic dye Astra Blue exhibits an entirely different behavior, which resembles largely the affinity of the basic probes (its adsorption begins to increase in the range of low lignin content).

Conclusions

During the delignification, γ_s^d remains essentially constant until the very low content of lignin (about 1/10 of the initial value), where a slight increase can be observed. The values are in accordance with the literature data for the similar samples of lignin rich materials. The values of γ_s^d for isolated lignins are considerably higher, indicating a drastic change in properties during the isolation of lignin. ΔG_a^d increases linearly with the number of C atoms in alkane probes and keeps rather constant throughout the delignification.

Specific interactions, expressed as ΔG_a^s , are also greatly unaffected by lignin content until the last stages of delignification. Acidic probes (CH_2Cl_2 and CHCl_3) exhibit a decrease in affinity, while basic ones (THF and EtOAc) show a substantial rise. The affinity of acetone, as an amphoteric probe, does not depend too much on the lignin content. With the depletion of the amount of lignin on fibers, the values of ΔG_a^s approach the values of microcrystalline cellulose. Despite the substantial variation in carboxylic group content during delignification, there was not observed a corresponding trend in the affinity of basic probes. Fibers, rich in carbohydrates and low in lignin exhibit an increased “acidity”, i.e. increased affinity to basic and decreased affinity to acidic probes.

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