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## The Effect of the Duration of Alkali Treatment on the Solubility of Polyoses

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**Abstract:** Holocelluloses from the wood of pine and oak species growing naturally in Turkey were extracted with 5% KOH solution under specified conditions, and soluble polyoses and lignin were examined. The extractions of both pine and oak wood holocelluloses followed the mechanism of second order reaction. While the glucomannan of pine was poorly dissolvable during the extraction, xylan, the main polyose of hardwoods, was removed very efficiently upto almost 90 %. The solubility of xylane also obeyed the same kinetics. By the equation  $[A]^{1-n} - [A_0]^{1-n} = (n-1)kt$ , where  $n=2$ , for the second order mechanism, kinetic parameters  $[A_0]$  and  $k$  were calculated to be 29.55%, 0.04417 for pine and 44.675%, 0.03018 for oak. Using these kinetic parameters, the predicted yields were in very close agreement with their counterparts from the experiments. Moreover, the holocelluloses and certain residues obtained after alkali were analyzed with regard to their anhydromonosaccharides. Galactoglucomannan, the main polyose of pine wood, was resistant to alkali, and about half of the more easily soluble arabinoxylane was removable. In contrast to mannane, nearly 90% of the hard wood xylane was dissolved by alkali, and its extraction also followed the second order mechanism. Thereafter, the kinetic parameters related to this extraction were calculated.

### Alkali ile İşlem Süresinin Polyozların Çözünürlüğü Üzerine Etkisi

**Özet:** Ülkemizde doğal olarak yetişen çam ve meşe gibi iki önemli iğne yapraklı ve yapraklı ağaç odunlarından elde edilen holoselülozler %5'lik KOH çözeltisi ile belli koşullar altında ekstrakte edilmiştir. İşlem sırasında polyozların, özellikle çözünür polyozlar ile birlikte holoselülozda kalıntı olarak bulunan ligninin durumu incelenmiştir. Her iki odun türünde de ekstraksiyon ikinci mertebeden reaksiyon kinetiğine uymaktadır.  $[A]^{1-n} - [A_0]^{1-n} = (n-1)kt$  genel eşitliğinde ikinci derece reaksiyon mekanizması için  $n=2$  alınarak  $[A_0]$  ve  $k$  kinetik parametreleri hesaplanmış ve bu değerler çam için %29.55, 0.04417, meşe için %44.675, 0.03018 olarak bulunmuştur. Bu değerlerin yukarıdaki eşitlikte kullanılmasıyla hesaplanan ekstraksiyon verimleri, deneysel verilerle iyi bir uyum göstermektedir. Ayrıca holoselülozlar ve alkali ekstraksiyonu sonrası elde edilen kalıntılar asit hidrolizi ile monosakkaridlerine dönüştürülerek analiz edilmiştir. Buna göre, iğne yapraklı ağaç polyozu glukomannanın zayıf çözünürlüğüne karşın, yapraklı ağaç ksilanının %90'a yakın bir bölümünün çözüldüğü görülmüştür. Meşe ksilani çözünürlüğünün ayrıca ikinci derecede reaksiyon kinetiğine uyduğu anlaşılmış, bununla ilgili kinetik parametreler hesaplanmıştır.

### Introduction

The non-cellulosic polysaccharides among the cell wall components are called polyoses or hemicelluloses (1). Polyoses are characterized by their alkali solubility. Some polyoses from *Larix* species and hardwoods are dissolved in appreciable amounts even by hot water. In many cases, the distinction between water soluble polyoses and other extractives is questionable; thus, starch soluble in hot water and pectic substances largely soluble in cold water, e.g. arabinogalactans, are classed with the extractives (2). For the structural analyses and/or general wood analyses, the polyoses are almost always separated from wood or holocellulose by aqueous alkaline solutions, especially of potassium and sodium hydroxide. The direct isolation from wood avoids possible negative effects of delignification on polyoses (oxidative changes,

degradation and losses). But only some woods, or rather some polyoses, can be extracted directly in appreciable amounts, such as arabinogalactans and hardwood xylans. To obtain the polyoses in significantly higher yields, preceding delignification is a necessity, especially for the softwoods. It is well known that the extractability by alkali solutions differs widely depending on the polyoses and the dissolving power of the alkali, i.e., the kind and concentration of the base. Some polyoses, especially softwood glucomannans, can not be removed quantitatively with the most commonly used bases (KOH-NaOH-solutions). In order to increase their dissolution, either boric acid or borates have to be added during the alkali treatment, or mannose units can be complexed with barium hydroxide as insoluble forms (3).

In the present study, the effect of the duration of alkali treatment was investigated with respect to the solubility of polyoses. Two common and widely distributed wood species, oak (*Quercus petrea*) and pine (*Pinus sylvestris*), were chosen. The greatest number of polyoses went into solution at the very beginning of extraction. Therefore, the use of a dilute aqueous solution of alkali was adequate for more accurate observation of the preferential removal and the rate.

**Materials and Methods**

The wood samples (*Quercus petrea* and *Pinus sylvestris*) were chipped, ground and sieved. The fraction of 40-100 mesh for each wood was selected. The wood meal was extracted first with a mixture of benzene-ethanol, and then with ethanol acc. to TAPPI standards. The standard procedure of delignification with acidified sodium chlorite solution was used for preparing the holocelluloses from extracted wood meal (4). The Klason-lignin content was determined in extracted wood meal according to Runkel and Wilke (5). The holocelluloses were extracted with 5% aqueous potassium hydroxide under nitrogen atmosphere at 25.0±0.2°C with 100 mL of base solution for different times. Before each treatment, 5% alkali solution was brought to extraction temperature and immediately after the designated time had elapsed the suspension was quickly transferred to a fritted-glass crucible, the alkali surplus was sucked out by light vacuum, and washed once with 50mL of KOH solution. The duration of these operations was added to the entire time of extraction leading to the following extraction times: 2min, 10 min, 30 min 1h and 2h. The dissolved polyoses within alkali solution were discharged; the fibrous residue was washed thoroughly with distilled water and air-dried. To estimate the preference and the extraction rate of polyoses, the quantitative saccharifications were carried out in residues. The trifluoroacetic acid method (6) was used under appropriate conditions. By means of automated sugar analysis based on ion-exchange chromatography, the

monosaccharides derived from polyoses after hydrolysis were identified and quantified.

**Results and Discussions**

The yields of holocelluloses and the residues after alkali extractions for different times are shown in Table 1. The material balances obtained by addition of the holocellulose yields to the lignin contents in woods were in excess of 100% apparently due to residual lignin in the holocelluloses. The major part of the substance was removed right at the beginning of extraction, and thus about 80% of the whole material dissolved in 2 hours went into the solution within 2 minutes.

After 10 minutes, the soluble parts were in the neighbourhood of 94%, if estimated in the same way. It was then determined whether or not the yields of residues would fit one of the kinetic equations.

From Table 1, it is apparent that the solubility had almost reached its limit after 2 hours and that prolongation of extraction with 5% potassium hydroxide for several hours or more would not bring about any improvement. After inspection of the yields obtained after 60 and 120 minutes, it was concluded that the final practically achievable percentages of residues would be on the order of 55.4, perhaps 55.3, for oak and around 70.5 for pine. The trial and error solutions revealed that the data would fit the mechanism of second order reactions according to Equation 1:

$$[A]^{1-n} - [A_0]^{1-n} = (n - 1) kt \tag{Eq.1}$$

where  $n = 2$  for the second order mechanism.

For determination of the rate constants, the experimental data from the 2-minute extractions were rather inaccurate because the timing could not be kept exact. In the case of oak the rate constants for  $[A_0]$ -values, 44.60 (100-55.40), 44.65 (100-55.35), 44.675 (100-55.325), 44.70 (100-55.30) and 44.75 (100-55.25) were calculated for each particular extraction and the following formula was suitable for finding the average of the rate constants:

Species	Holocellulose (%) (Lignin in wood)*	Residues after Alkali Extractions (%)#					
		2 Min	10 Min	15 Min	30 Min	60 Min	120 Min
Oak	81.37 (24.19)	65.23	58.30	57.54	56.46	55.82	55.59
Pine	83.01 (26.79)	76.42	72.58	71.84	71.20	70.81	70.65

Table 1. The Yields of Holocelluloses and Residues After Alkali Extractions

\* Based on extract free wood,  
# Based on holocellulose

$$k_{avg} = \frac{\sum [A]k}{\sum [A]} \quad (\text{Eq. 2})$$

For the pine 29.50 (100-70.5), 29.55 (100-70.45), 29.60 (100-70,40) were tested as  $[A_0]$  to estimate the rate constants. With the averaged rate constants with their respective  $[A_0]$ -values the yields were calculated and compared with the experimental data (Table 2). Since the minus and plus differences cancel very well for each case, the  $[A_0]$ -percentage which delivers the minimum total absolute difference from the experimental yields was taken as the most suitable one.

Thus,  $[A_0]$  and  $k$  -pairs for oak and pine are 44.675, 0.03018 and 29.55, 0.04417, respectively. Using these kinetic parameters, the predicted yields were then in very close agreement with their counterparts from the

experiments. According to the second order rate law, the rate expression (Eq.1) above can only be derived when the differential equation of an irreversible bimolecular-type reaction,  $2A \rightarrow \text{Products}$ :

$$-\frac{d[A]}{dt} = k[A]^2 \quad (\text{Eq. 3})$$

is integrated. In the equations both  $[A]$  and  $[A_0]$  are concentrations in  $\text{mol L}^{-1}$ . In this study, the concentrations were replaced by percentages. Because the percent numbers were obtained based on the weights of residues, the successive replacement can be explained as follows: As the  $A_0$  %-value is the weight of total polyoses in 100 g holocellulose obtained, which is the achievable amount of polyoses from 5% KOH-extraction over a reasonably long period. For example, let the value be

Table 2. Experimental Yields vs. Predicted Ones for Various Kinetic Parameters

OAK (Residues after alkali extractions)										
TIME (min)	$[A_0] = 44.60$ $k = 0.03192$		$[A_0] = 44.65$ $k = 0.03074$		$[A_0] = 44.675$ $k = 0.03018$		$[A_0] = 44.70$ $k = 0.02964$		$[A_0] = 44.75$ $k = 0.028615$	
	Pre. Yield %	Diff. %	Pre. Yield %	Diff. %	Pre. Yield %	Diff. %	Pre. Yield %	Diff. %	Pre. Yield %	Diff. %
10	58.33	+0.03	58.38	+0.08	58.41	+0.11	58.44	+0.14	58.49	+0.19
15	57.40	-0.15	57.42	-0.12	57.43	-0.11	57.44	-0.10	57.46	-0.08
30	56.42	-0.04	56.41	-0.05	56.40	-0.06	56.40	-0.06	56.39	-0.07
60	55.92	+0.10	55.89	+0.07	55.87	+0.05	55.86	+0.04	55.82	+0.00
120	55.660	+0.07	55.619	+0.02	55.599	0.00	55.579	-0.01	55.539	-0.06
Absolute sum of differences	0.39		0.34		0.33		0.35		0.40	
PINE (Residues after alkali extractions)										
TIME (min)	$[A_0] = 29.50$ $k = 0.04662$		$[A_0] = 29.55$ $k = 0.04417$		$[A_0] = 29.60$ $k = 0.04192$		$[A_0] = 29.33$ $k = 0.040013$		$[A_0] = 29.355$ $k = 0.03909$	
	Pre. Yield %	Diff. %	Pre. Yield %	Diff. %	Pre. Yield %	Diff. %	Pre. Yield %	Diff. %	Pre. Yield %	Diff. %
10	72.50	-0.08	72.55	-0.03	72.61	+0.03	2.303	+0.00	2.353	+0.03
15	71.86	+0.02	71.89	+0.05	71.91	+0.07				
30	71.20	±0.00	71.19	-0.01	71.17	-0.03	0.810	±0.00	0.829	-0.01
60	70.85	+0.04	70.82	+0.01	70.79	-0.02				
120	70.678	+0.02	70.637	-0.02	70.597	-0.06	0.207	-0.00	0.212	-0.02
Absolute sum of differences	0.16		0.12		0.21		0.01		0.06	

44.65 %. Here 44.65 mean the mass of polyoses ( $m_{AO}$ ). In the same way, the percent value of polyoses remaining in the holocellulose after a certain period of extraction represents the mass of polyoses in 100 g holocellulose ( $m_A$ ):

$$m_{AO} = n_{AO} M_A, \quad m_A = n_A M_A \quad \text{and}$$

$$[A_0] = n_{AO} V^{-1}, \quad [A] = n_A V^{-1}$$

The above expressions clearly show that percentages can be substituted for concentrations, since  $M_A$  and  $V$  do not change. The application of the most suitable kinetic parameters ( $[A_0]$  and  $k$ ) to two-minute extractions resulted in predicted yields that were about 2% lower than experimental ones. Apparently, a greater amount of substance was dissolved, especially during the washing

steps of these residues, since the addition of distilled water for the first time could only dilute the surplus base in the crucible, which may continue to dissolve more polyoses. This effect can not be detected after an extraction time of 10 minutes because easily soluble polyoses were already in the solution. The data from experiments, then correlated very well with the predicted data.

The holocelluloses and certain residues were analyzed with regard to their anhydromonosaccharides to determine the preference and the extent of solubility of individual polyoses. The results based on holocelluloses are shown in Table 3. The data reveal that the xylane of hardwood dominated in the dissolved part whereas the removable polyoses played a subordinate role, in the case

SUGARS SUBSTANCE	RHA (%)	MAN (%)	ARA (%)	GAL (%)	XYL (%)	GLU (%)
OAK						
Holocellulose	0.38	4.69	0.54	0.66	33.33	47.66
2 min Residue	0.17	3.96	0.22	0.43	10.03	n.d.
10 min Residue	0.09	3.02	0.15	0.36	6.30	n.d.
30 min Residue	0.09	2.97	0.14	0.35	4.81	n.d.
120 min Residue	0.07	2.93	0.13	0.33	4.21	n.d.
PINE						
Holocellulose	0.07	14.94	1.66	3.22	7.63	52.43
2 min Residue	0.02	13.04	0.70	2.51	2.89	n.d.
10 min Residue	0.02	11.53	0.49	2.08	2.10	n.d.
30 min Residue	0.01	11.10	0.41	1.96	1.70	n.d.
120 min Residue	0.01	10.87	0.39	1.85	1.61	n.d.

Table 3. Anhydrosugars in Holocelluloses and Residues Obtained after Alkali Extractions

All data based on holocellulose, n.d. not determined

SPECIES	SOLIDS	HOLO CELL	2 min RESIDUE	10 min RESIDUE	30 min RESIDUE	120 min RESIDUE
OAK						
Yield %		100.00	65.23	58.30	50.46	55.594
Total Solubles % ①		-	34.77	41.70	43.54	44.406
ΣSugar in Solid %②		39.60	14.81	9.92	8.36	7.67
Dissolv. Sugar % ③		-	24.79	29.68	31.24	31.93
Losses % ④		-	9.98	12.02	12.30	12.476
PINE						
Yield %		100.00	76.42	72.58	71.20	70.655
Total Solubles % ①		-	23.58	27.42	28.80	29.345
ΣSugar in Solid %②		27.52	19.16	16.22	15.18	14.73
Dissolv. Sugar % ③		-	8.36	11.30	12.34	12.79
Losses % ④		-	15.22	16.12	16.46	16.555

Table 4. Material Balances of Dissolved Sugars and in Sugars Remaining in Residues Except Glucose

- ① 100-Residue yield in percent,
- ② Sum of Sugars determined in solids (for holo except. glu),
- ③ Total sugars in holocellulose except glucose-total determined sugars in residues,
- ④ Total solubles-dissolved sugars i.e. ①-③ All data based on holocellulose.

of softwood holocellulose even after 2-hour extraction.

In pine wood 5% alkali was only capable of removing approximately a third of the galactoglucomannan, whereas the arabinoxylane exhibited much greater solubility. Table 4, prepared with the above data, is a better illustration of the material balances between the extraction steps. In both cases the losses that occurred were due in particular to the residual lignins in holocelluloses. Pine exhibited more missing substance because its holocellulose apparently contained more residual lignin. As shown in Table 1, the lignin content of softwood and holocellulose yield for oak were 109.8% and 105.56% respectively.

Moreover, no delignification is known where all polysaccharides in wood safely survive. Thus, the holocelluloses should have even more residual lignin than indicated by the excess values, i.e. 9.8% for pine and 5.6% for oak. But total residual lignin, as dissolved by alkali, would not cover the entire absent substance, and undetermined glucose from glucomannan, acetyl groups easily cleaved off during alkali treatments, and some uronic acids would contribute to the rest. Taking this kind of material belonging to the polyoses into consideration, in the case of pine, the soluble sugars would be in the neighborhood of half the amount originally present in holocellulose. In oak, the holocellulose has acetylmethylglucuronoxylan as the prevalent polyose which was dissolved efficiently by alkali up to 88% of its original value. In contrast to xylan, the solubility of hardwood glucomannan hardly exceeds one third of the amount found in holocellulose.

For acetylmethylglucuronoxylan as main polyose the attempt was made to find a possible mechanism. Here once again, the data followed the kinetics of second order

reaction when considering the determined xylose quantities in 10, 30 and 120 min residues. As the percentage of  $[A_0]$  just a bit higher values than the difference between the xylose content of oak holocellulose and its 2h residue, i.e.  $\geq (33.3-4.2)$ , should be tried (Table 2). 29.33%, as  $[A_0]$ , and its  $k_{avg}$  0.040013 provide the same xylose yields observed in above residues. Since the xylose content of oak holocellulose was 33.33%, the deficit 4.00% represented the part of this polyose which would not be available with a reasonably long extraction time using 5% aqueous potassium hydroxide.

## Conclusions

5% aqueous potassium hydroxide dissolves the polyoses and residual lignin from softwood and hardwood holocelluloses as demonstrated for pine and oak but to different extents. The dissolution can be expressed by means of second order reaction kinetics. In case of pine, the main polyose galactoglucomannan was resistant to alkali and with the easily soluble arabinoxylane about half of the polyoses were removable. The rather high amount of residual lignin in holocellulose of pine should have also been dissolved to a wide extent. In contrast to mannane nearly 90% of the hardwood xylane was dissolved by alkali, and its extraction also followed the second order mechanism.

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