

# BEHAVIOUR OF CARBOHYDRATE-BASED MATERIAL IN BLACK LIQUOR DURING HEATING

by

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*One industrial softwood kraft black liquor was heat-treated (at 175 °C and 190 °C for 15–60 min.) together with laboratory-made soda-AQ (wheat straw and reed canary grass) and kraft (reed canary grass) black liquors (at 190 °C for 30 min.). The feedstock black liquors were characterised with respect to their polysaccharide (mainly xylan) and aliphatic carboxylic acid contents before and after the heat treatments. It was noted that, due to the higher amount of polysaccharides in the nonwood black liquors (8.2-16.6% of d.s.) compared to that in the softwood black liquor (1.4% of d.s.), the heat treatment in the former case resulted in a 5-30% increase in the amount of aliphatic acids formed by various alkali-catalysed degradation reactions of the liquor polysaccharides. In addition, in each case detailed gas chromatographic studies revealed that as a general trend the content of higher-molecular-mass acids decreased on heating with the subsequent increase in the content of lower-molecular-mass acids.*

Key words: *wood, nonwood, polysaccharides, carbohydrates, aliphatic carboxylic acids, black liquor, heat treatment*

## Introduction

The purpose of chemical pulping is to liberate feedstock fibers through delignification with as small a loss of fiber wall carbohydrates as possible [1]. The kraft process is the dominant method for pulping wood raw materials, whereas the soda process is most used in case of nonwoods. When applied especially to wood delignification soda pulping with anthraquinone (AQ) should be used.

The chemical reactions that take place during kraft and soda pulping are complicated and still not completely understood. However, it is known that hydrogen sulphide ions (HS<sup>-</sup>) primarily react with lignin, whereas carbohydrate reactions are only affected by alkalinity (*i. e.*, HO<sup>-</sup> ions) [2]. The most important alkali-catalysed reaction of polysaccharides is the peeling reaction (primary peeling), which results in the formation of different aliphatic carboxylic acids (mainly hydroxy monoacids) as a consequence of the successive elimination of monosaccharide units at the reducing end (*i. e.*, a hemiacetal functional group) of each polysaccharide chain [1, 3]. Peeling takes place during the heating-up stage after the temperature has reached about 100 °C [4, 5]. The greater peel-

ing of hemicelluloses, compared to that of cellulose, is due to their amorphous structure and lower degree of polymerisation (DP). In all, 50-65 monosaccharide units are expected to be cleaved on an average by the peeling reaction until a competing reaction (stopping reaction) occurs terminating the degradation reaction [1, 6]. Without this competitive stopping reaction, it would be possible for a whole polysaccharide molecule to be destroyed by peeling.

In addition to the peeling reaction, the alkaline hydrolysis (depolymerisation) of polysaccharide chains becomes important at higher temperatures (160-170 °C) [1, 3]. In this relatively slow reaction, glycosidic linkages between monosaccharide moieties are randomly cleaved, resulting in the formation of new reducing end groups that can be subjected to further degradation reactions (secondary peeling). It should be pointed out that small amounts of dissolved polysaccharides are not completely degraded and can be found with varying molecular masses in the final black liquors.

In contrast to the acid formation by the peeling reaction, acetic acid is formed by the deacetylation of hemicelluloses, which occurs mainly already during the initial stage of the cook [7]. Furthermore, it is known that deacetylated xylan dissolved in the cooking liquor during delignification is partially redeposited on the fibers, especially at the end of the conventional kraft cook [8].

Heat treatment, developed to eliminate the high viscosity of strong black liquors, is performed at somewhat higher temperature than that applied to cooking [9]. In this process the degradation of carbohydrates and lignin has generally been assumed to be the primary reason for the decrease in viscosity [10, 11]. In this study, the detailed behaviour of carbohydrate-derived materials, *i. e.*, polysaccharides and aliphatic carboxylic acids, of both wood and nonwood black liquors on heating was investigated.

## Experimental

### *Samples*

The black liquors studied consisted of one industrial softwood kraft black liquor and several laboratory-made wheat straw and reed canary grass (*Phalaris arundinacea L*) black liquors. Soda-AQ pulping was performed for both nonwood feedstock materials [12] and, in addition, reed canary grass was delignified by kraft pulping (tab. 1). The softwood black liquor was heat-treated at 175 °C for 30, 40, 50, and 60 min., and at 190 °C for 15, 30, and 45 min., while each nonwood black liquors were heat-treated at 190 °C for 30 min. [10].

### *Analytical determinations*

The content of polysaccharides in the black liquors was analysed by the following procedure. Samples were first fractionated (*i. e.*, separation of polysaccharides) by dialysis (cut-off value of 6,000-8,000 Da) for 6 days and the polysaccharide concentration

**Table 1. Average distribution (%) of the monosaccharide moieties in polysaccharides of the untreated and heat-treated black liquors from soda-AQ pulping\* of wheat straw and reed canary grass, and kraft pulping\*\* of reed canary grass including the ranges of variation (in parentheses)**

Max temp.	Wheat straw, soda-AQ				Reed canary gras, soda-AQ				Reed canary grass, kraft			
	Untreated		Heat-treated		Untreated		Heat-treated		Untreated		Heat-treated	
Xylose	71	(69-72)	72	(70-74)	71	(69-72)	73	(72-74)	71	(70-72)	71	(69-72)
Arabinose	17	(16-19)	15	(13-16)	16	(14-17)	15	(14-17)	17	(17-18)	17	(16-17)
Galactose	5	(5-6)	5	(5-6)	7	(7-8)	7	(5-7)	7	(6-7)	7	(6-8)
Glucose	6	(6-8)	7	(6-8)	5	(4-6)	4	(3-5)	4	(4-5)	4	(4-5)
Mannose	1	(1)	1	(1)	1	(1)	1	(1)	1	(1-2)	1	(1-2)

\* Effective alkali (as NaOH) 18 % on o. d. feedstock, AQ charge 0.05% on o. d. feedstock, liquor-to-feedstock ratio 6:1 l/kg (wheat straw), 5:1 l/kg (reed canary grass), maximum temperature 145, 155, and 165 °C, time at maximum temperature 0 min. and 30 min., and time from 25 °C to maximum temperature 90 min.

\*\* Effective alkali (as NaOH) 180% on o. d. feedstock, sulphidity 15 and 38%, liquor-to-feedstock ratio 5:1 l/kg, maximum temperature 165 °C, time at maximum temperature 0 min. and 30 min., and time from 25 °C to maximum temperature 90 min.

was obtained by first hydrolysing the separated polysaccharides with sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and then, after per(trimethylsilyl)ation, by analysing the monosaccharides formed by GC/FID [10]. The conversion factors used to calculate the amounts of polysaccharides from the monosaccharide data were 0.90 for hexoses and 0.88 for pentoses.

The hydroxy monocarboxylic and dicarboxylic acids of the black liquors were determined as their per(trimethylsilyl)ated derivatives by GC/FID [13]. The identification of the individual acids was performed by GC/MSD. The volatile acids (formic and acetic acids) of the black liquors were determined as their benzyl esters by GC [14].

## Results and discussion

### Polysaccharides

The polysaccharide content of the softwood kraft black liquor (1.4% of d. s., fig. 1), was clearly lower than that of the nonwood black liquors; 9.9-16.6% of d. s. for the wheat straw black liquors (fig. 2) and 8.2-12.5% of d. s. for the reed canary grass black liquors (fig. 3). It was noticed that the content of polysaccharides in the reed canary grass black liquors was at the same level in kraft and soda-AQ black liquors.

It was shown that in case of the softwood kraft black liquor the polysaccharide content decreased along with reaction time during the heat treatment (fig. 1). In addition, the results indicated that a higher temperature (*i. e.*, 190 °C vs. 175 °C) accelerated to some extent the degradation of polysaccharides. Due to an incomplete degradation of soluble

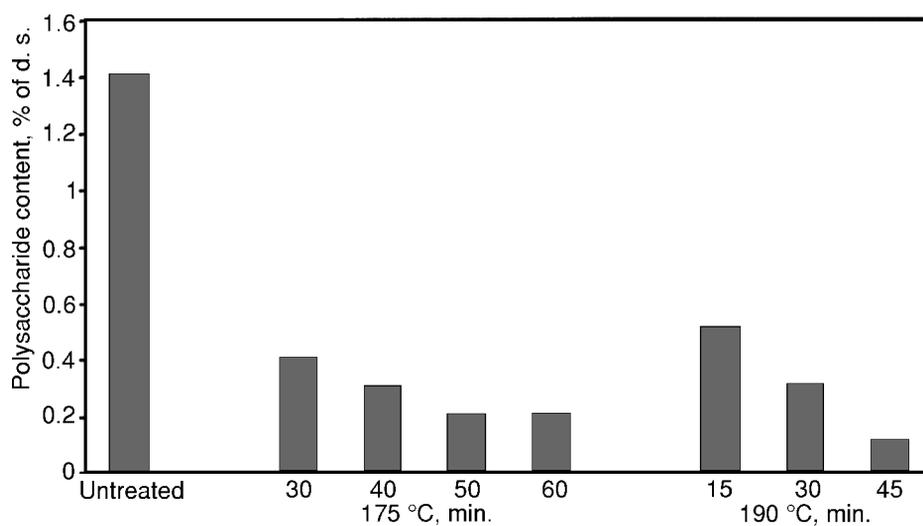


Figure 1. Polysaccharide content of the softwood kraft black liquor before (untreated) and after heat treatment at 175 °C and 190 °C

polysaccharides during cooking, the decrease in the polysaccharide content of the wheat straw soda-AQ liquors was greater in the liquors with the shorter cooking time (0 min., fig.

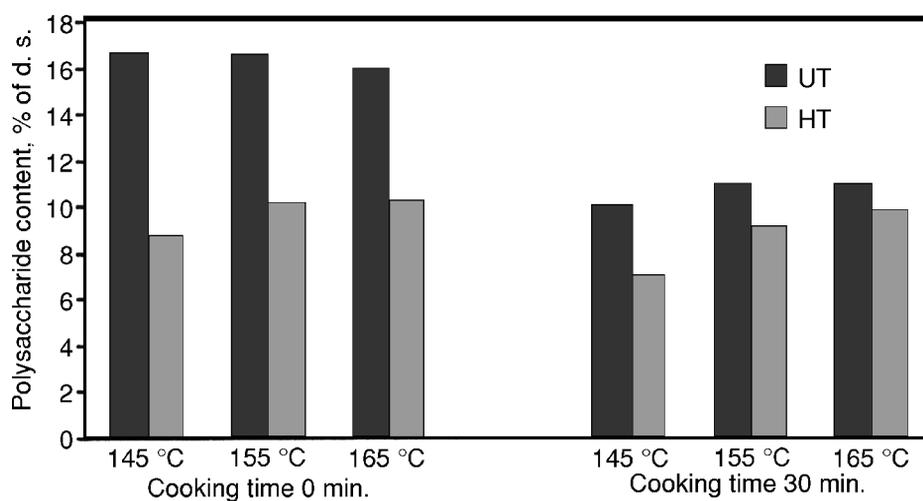
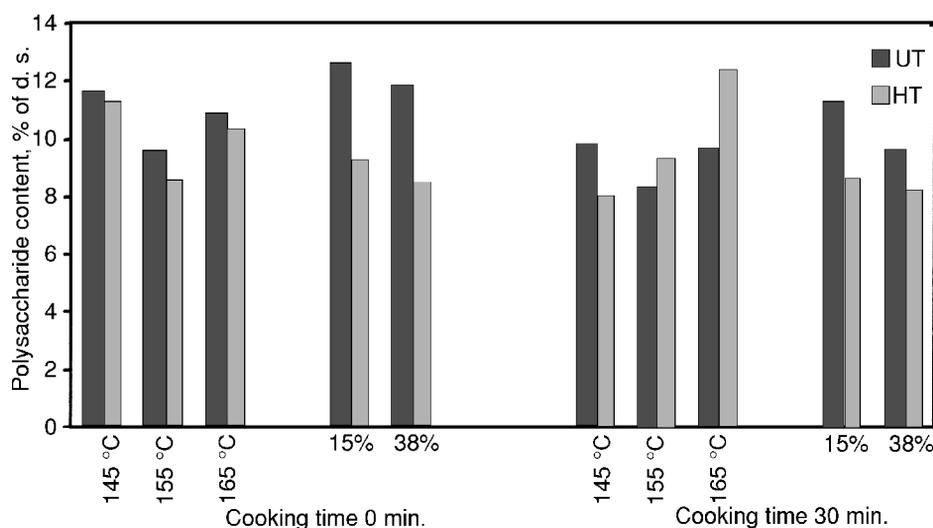


Figure 2. Polysaccharide content of the untreated (UT) and heat-treated (HT) black liquors from soda-AQ pulping (maximum temperature 145, 155, and 165 °C) of wheat straw

2). However, this trend was not so clear, probably due to the somewhat different structure of polysaccharides, in case of the reed canary grass liquors (fig. 3).



**Figure 3.** Polysaccharide content of the untreated (UT) and heat-treated (HT) black liquors from soda-AQ (maximum temperature 145, 155, and 165 °C) and kraft (sulphidity 15% and 38%) pulping of reed canary grass

During the heat treatments of the reed canary grass soda-AQ liquors with longer cooking time (30 min.) and higher cooking temperatures (155 °C and 165 °C), the total amount of polysaccharides increased (fig. 3). One possible explanation for this finding could be various condensation reactions occurred between polysaccharides and reactive lignin fragments formed under pulping conditions. The resulting high-molecular-mass lignin-carbohydrate complexes that remained in a dialysis membrane tube were thus detected as polysaccharides in the analysis. Similar condensation reactions between polysaccharides (hemicelluloses) and lignin under kraft cooking conditions have been detected in earlier studies [15, 16].

The relative composition of the different monosaccharide moieties varied greatly between the softwood and nonwood black liquors, although it was almost similar in cases of the wheat straw and reed canary grass liquors (tabs. 1 and 2). The most abundant monosaccharide in all black liquors was xylose, followed by arabinose, galactose, glucose, and mannose. The prominent proportion of xylose in nonwood liquors can be explained by the chemical composition of these raw materials containing arabinoglucuronoxylan in significant amounts [17, 18]. On the other hand, in softwood liquor the highest proportion of xylose is probably due to a greater degradation of galactoglucomannan during cooking;

**Table 2. Percentage distribution of the monosaccharide moieties in polysaccharides of the untreated and the heat-treated softwood kraft black liquors**

Monosaccharide	Untreated	Heat-treated at 175 °C, min.				Heat-treated at 190 °C, min.		
		30	40	50	60	15	30	45
Xylose	42	37	38	39	38	44	42	42
Arabinose	24	22	23	21	22	19	22	24
Galactose	23	15	16	18	18	17	16	15
Glucose	9	24	21	19	18	18	18	17
Mannose	2	2	2	3	4	2	2	2

galactoglucomannan is the more dominant hemicellulose of softwood compared to that of arabinoglucuronoxylan [1]. In addition, during heating of the softwood black liquor the share of glucose increased and that of galactose decreased (tab. 2). This finding suggested that glucose-containing polysaccharides (*e. g.*, cellulose residues) were relatively stable under these conditions.

#### *Aliphatic carboxylic acids*

The content of the aliphatic carboxylic acids before heat treatment was lower for the nonwood black liquors (tabs. 3 and 4), especially in case of shorter cooking time (0 min.), compared to that of the softwood kraft black liquor (tab. 5). During all the heat treatments the acid content of the nonwood black liquors increased significantly (tabs. 3 and 4), whereas that of the softwood kraft black liquor remained almost unchanged regardless of the treatment conditions (tab. 5). However, the total acid content of all black liquors was finally after the heat treatment at the same level.

It could be concluded that the considerably higher polysaccharide content of the nonwood black liquors, compared to that of the softwood kraft black liquor, before the heat treatments (figs. 2 and 3) was responsible for differences in the formation amounts of these acids on heating. The great increase in the acid content of the nonwood liquors took obviously place as a result of alkaline hydrolysis of polysaccharides, followed by the subsequent end-wise peeling reaction of the reaction products formed. In addition to feedstock polysaccharides, a sufficient amount of alkali is an important prerequisite for the high formation of acids at the temperature (190 °C) used in the heat treatment of the nonwood black liquors. Thus, differences in the formation rate of acids between the nonwood black liquors obtained from varying cooking times were considered to be due to differences in the consumption of alkali during cooking (*i. e.*, differences in the amount of residual effective alkali at the beginning of heat treatment). Since the total amount of

**Table 3. Main aliphatic carboxylic acids in the wheat straw soda-AQ black liquors\***

Aliphatic carboxylic acid	Untreated		Heat-treated	
	0 min.	30 min.	0 min.	30 min.
<b>Monocarboxylic acids</b>	<b>83.1</b>	<b>83.8</b>	<b>85.8</b>	<b>86.0</b>
Formic	11.0	11.4	14.0	13.9
Acetic	28.9	24.4	22.3	20.7
Lactic	7.6	9.4	10.3	10.8
Glycolic	5.1	6.5	8.3	8.4
3-Hydroxypropanoic	0.5	0.4	0.3	0.3
Glyceric	1.0	1.0	1.2	1.0
2-Hydroxypropanoic	3.5	5.2	6.3	6.8
4-Hydroxybutanoic	0.8	0.6	0.9	0.8
2-Deoxytetroneic	0.5	0.4	0.1	0.1
3-Deoxytetroneic	1.3	1.4	1.7	1.7
2-Hydroxypentenoic	0.4	0.4	0.3	0.3
3,4-Dideoxypentonic	3.5	3.6	3.8	4.0
3-Deoxypentonic	4.6	5.2	4.7	5.0
Xyloisosaccharinic	3.3	3.4	3.3	3.3
Glucoisosaccharinic	11.1	10.5	8.3	8.9
<b>Dicarboxylic acids</b>	<b>7.9</b>	<b>6.1</b>	<b>6.0</b>	<b>5.8</b>
Succinic	0.8	0.8	1.3	1.2
Malic	3.0	2.5	1.7	1.8
2-Hydroxyglutaric	1.4	1.5	1.7	1.6
Glucoisosaccharinaric	2.7	1.3	1.3	1.2
<b>Miscellaneous</b>	<b>9.0</b>	<b>10.1</b>	<b>8.2</b>	<b>8.2</b>
<b>Total amount, % of dry solids</b>	<b>13.9</b>	<b>16.6</b>	<b>18.5</b>	<b>19.3</b>

\* Each column represents average of the black liquors from the different pulping temperatures: 145, 155, and 165 °C

**Table 4. Main aliphatic carboxylic acids in the reed canary grass black liquor**

Aliphatic carboxylic acid	Soda-AQ*		Soda-AQ*		15% sulphidity		15% sulphidity		38% sulphidity		38% sulphidity	
	Untreated		Heat-treated		Untreated		Heat-treated		Untreated		Heat-treated	
	0 min.	30 min.	0 min.	30 min.	0 min.	30 min.	0 min.	30 min.	0 min.	30 min.	0 min.	30 min.
<b>Monocarboxylic acids</b>	<b>87.5</b>	<b>86.7</b>	<b>87.7</b>	<b>88.6</b>	<b>86.4</b>	<b>87.3</b>	<b>87.0</b>	<b>86.4</b>	<b>85.8</b>	<b>87.0</b>	<b>86.2</b>	<b>85.3</b>
Formic	9.3	9.7	11.8	12.7	11.2	12.8	14.7	17.3	11.3	13.5	15.5	15.1
Acetic	40.1	34.9	35.0	32.8	39.5	35.4	33.2	31.0	40.2	33.6	30.9	31.3
Lactic	6.1	7.6	8.6	8.8	7.6	9.1	10.6	10.3	7.4	9.2	10.6	10.5
Glycolic	4.6	5.7	6.6	6.9	2.8	3.3	4.8	4.2	2.7	3.4	4.2	4.7
3-Hydroxypropanoic	0.3	0.3	0.2	0.2	0.2	0.1	0.4	0.3	0.1	0.1	0.3	0.3
Glyceric	0.8	0.8	0.9	0.8	0.3	0.3	0.4	0.3	0.2	0.2	0.3	0.4
2-Hydroxybutanoic	3.6	4.5	5.3	5.4	5.3	7.1	7.4	7.9	5.3	7.6	8.5	7.3
4-Hydroxybutanoic	0.7	0.5	0.8	0.6	0.4	0.4	0.5	0.4	0.2	0.2	0.3	0.3
2-Deoxytetronic	0.3	0.3	0.1	0.1	0.2	0.2	0.1	0.1	0.2	0.2	0.1	0.1
3-Deoxytetronic	1.2	1.5	1.5	1.6	0.9	0.8	1.1	1.0	0.9	0.8	1.0	1.1
2-Hydroxypentenoic	0.2	0.2	0.2	0.2	0.3	0.4	0.4	0.4	0.5	0.8	1.0	0.8
3,4-Dideoxypentonic	2.7	2.8	2.9	3.0	3.3	3.2	3.2	3.2	3.3	3.4	3.4	3.3
3-Deoxypentonic	4.7	5.1	4.0	4.5	2.2	2.4	0.9	0.8	1.9	2.3	0.8	0.8
Xyloisosaccharinic	3.2	3.2	2.8	2.9	3.6	3.4	3.5	3.4	3.4	3.5	3.4	3.5
Glucosaccharinic	9.7	9.6	7.0	8.1	8.6	8.4	5.8	5.8	8.2	8.2	5.9	5.8
<b>Dicarboxylic acids</b>	<b>4.0</b>	<b>3.1</b>	<b>3.7</b>	<b>3.5</b>	<b>2.6</b>	<b>2.3</b>	<b>3.5</b>	<b>3.2</b>	<b>2.0</b>	<b>2.2</b>	<b>3.1</b>	<b>3.5</b>
Succinic	0.4	0.4	0.9	0.9	0.4	0.5	1.0	0.9	0.4	0.5	0.9	1.0
Malic	0.7	0.8	0.7	0.7	0.8	0.6	0.6	0.6	0.6	0.6	0.6	0.6
2-Hydroxyglutaric	0.9	1.0	1.1	1.0	0.8	0.7	0.9	0.8	0.5	0.6	0.7	0.8
Glucosaccharinaric	2.0	0.9	1.0	0.9	0.6	0.5	1.0	0.9	0.5	0.5	0.9	1.1
<b>Miscellaneous</b>	<b>8.5</b>	<b>10.2</b>	<b>8.6</b>	<b>7.9</b>	<b>11.0</b>	<b>10.4</b>	<b>9.5</b>	<b>10.4</b>	<b>12.2</b>	<b>10.8</b>	<b>10.7</b>	<b>11.2</b>
<b>Totat amount, % d. s.</b>	<b>15.3</b>	<b>17.6</b>	<b>20.9</b>	<b>20.1</b>	<b>15.2</b>	<b>19.2</b>	<b>21.1</b>	<b>22.6</b>	<b>15.9</b>	<b>19.3</b>	<b>22.0</b>	<b>22.7</b>

\* Each column represents average of the black liquors from the different pulping temperatures: 145, 155, and 165 °C

carbohydrates and aliphatic carboxylic acids increased to some extent on heating, it was evident that some acids also originated from the aliphatic parts of lignin material.

In all, 20 individual acids for the softwood kraft black liquor and 19 individual acids for the nonwood black liquors were identified (tab. 3-5). The proportions of monocarboxylic acids, dicarboxylic acids, and miscellaneous acids were similar in all cases. In contrast, noticeable differences in the relative composition of individual acids were found mainly depending on the raw material (*i. e.*, nonwood *vs.* wood) used for pulping.

**Table 5. Main aliphatic carboxylic acids in the softwood kraft black liquor**

Aliphatic carboxylic acid	Untreated	Heat-treated*	
		175 °C	190 °C
<b>Monocarboxylic acids</b>	<b>90.0</b>	<b>88.4</b>	<b>87.7</b>
Formic	19.1	19.1	19.1
Acetic	12.5	12.3	12.4
Lactic	11.4	13.3	14.5
Glycolic	4.9	5.7	6.1
2-C-Methylglyseric	0.3	0.3	0.2
2-Hydroxybutanoic	3.1	3.2	3.1
4-Hydroxybutanoic	0.4	0.5	0.5
3-Deoxytetronic	0.9	0.9	0.8
2-Hydroxypentenoic	1.0	0.7	0.5
3,4-Dideoxypentonic	8.2	7.3	7.0
3-Deoxypentonic	2.7	2.6	2.5
3,4-Dideoxyhexonic	0.9	1.3	1.2
Anhydroglucoisosaccharinic	0.8	0.9	0.7
Xyloisosaccharinic	1.1	1.2	1.2
Glucoisosaccharinic	22.7	19.1	17.9
<b>Dicarboxylic acids</b>	<b>2.8</b>	<b>4.0</b>	<b>4.0</b>
Succinic	0.6	0.5	0.6
Methylsuccinic	0.5	0.3	0.4
Tartronic	0.1	0.7	0.6
Methyltartronic	0.3	0.5	0.6
2-Hydroxyglutaric	1.3	2.0	1.8
<b>Miscellaneous</b>	<b>7.2</b>	<b>7.6</b>	<b>8.3</b>
<b>Total amount, % of dry solids</b>	<b>19.3</b>	<b>19.9</b>	<b>20.9</b>

\* Each column represents average of the black liquors from the different treatment times

The relative composition of the individual acids changed during the heat treatments and the trends detected were of the same kind for all black liquors (tabs. 3-5). In general, the content of higher-molecular-mass acids decreased with the subsequent increase in the content of lower-molecular-mass acids as also indicated in earlier studies

[19, 20] on the reaction of hydroxy acids at high temperatures in the presence of alkali. Among the most prominent acids, the decrease of the relative amount of glucoisosaccharinic acid was noticed in all the black liquors and that of acetic acid in the case of the nonwood black liquors. On the other hand, the increase in the relative amount of lactic and glycolic acids was found for all black liquors, whereas the increase in the amount of formic acid was noticed only in the nonwood black liquors.

## Conclusions

The content and composition of the carbohydrate-derived materials (polysaccharides and aliphatic carboxylic acids) of the black liquors studied changed during the heat treatments and the changes were mainly affected by the treatment conditions besides the origin of black liquor. The degradation of polysaccharides was noticed in almost all the treatments enhancing by the increasing temperature and the reaction time. However, the small increase in the content of polysaccharides measured for the reed canary grass soda-AQ black liquors from the more severe cooking conditions was considered to be due to the formation of various lignin-polysaccharide complexes detected as polysaccharides in our analysis. The changes in the content of aliphatic carboxylic acids during the heat treatments was found to depend, on the one hand, on the amount of polysaccharides available for the peeling reaction and, on the other hand, on the presence of the sufficient amount of residual alkali in the liquor. Thus, the increase in the acid content noticed in the nonwood black liquors was due to the higher content of polysaccharides in these liquors, whereas in the softwood black liquor, having a low content of polysaccharides, the acids content remained almost unchanged. However, in each heat treatment the content of higher-molecular-mass acids generally decreased with the subsequent increase in the content of lower-molecular-mass acids.

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