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Hannu Pakkanen\* and Raimo Alén

# Alkali consumption of aliphatic carboxylic acids during alkaline pulping of wood and nonwood feedstocks

**Abstract:** The carbohydrate degradation products have been examined, which are formed during the conventional kraft pulping of a softwood, hardwoods, bamboo, and wheat straw as well as soda and soda-anthraquinone pulping of wheat straw. The focus was on “volatile” acids such as formic and acetic acids and “nonvolatile” hydroxy monocarboxylic and dicarboxylic acids. The different consumption profiles were obtained for the charged alkali required for the neutralization of these aliphatic acids depending on the feedstock and the cooking method. The relative composition of the acid fraction in the black liquors of softwood and hardwood and nonwood feedstocks showed characteristic variations. However, in the case of wood kraft pulping, the variations in cooking conditions (effective alkali 19–21% and cooking temperature 155–170°C) had no significant effect on the acid composition. The total amount of volatile and hydroxy acids formed during pulping at a typical target  $\kappa$  number level for each feedstock ranged from 78 to 174 kg ton<sup>-1</sup> based on o.d. feedstock. It was highest in birch kraft pulping and lowest in wheat soda-anthraquinone pulping.

**Keywords:** aliphatic carboxylic acids, alkaline pulping, bamboo, black liquor, deacetylation, hardwood, softwood, wheat straw

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## Introduction

During alkaline delignification, such as in kraft and soda-anthraquinone (AQ) pulping, roughly half of the initial wood material is degraded and dissolved in the cooking liquor [“black liquor” (BL)] (Sjöström 1993; Alén 2000). The multiple reactions of lignin and polysaccharides are quite complex and still not completely understood. A

substantial amount of aliphatic carboxylic acids (“volatile” formic and acetic acids as well as the “nonvolatile” hydroxy monocarboxylic and dicarboxylic acids) is formed due to the low selectivity of alkaline pulping. These carbohydrate-based degradation products are also present in the BL along with the degradation products of lignin. The composition and total amount of the acid fraction mainly depends on the raw material and the pulping conditions. It is well accepted for kraft pulping that hydrogen sulfide ions (HS<sup>-</sup>) primarily react with lignin and that carbohydrate reactions are only affected by the alkalinity (i.e., HO<sup>-</sup> ion concentration) (Alén 2000).

Wood carbohydrates are attacked at comparatively low temperatures, when the chips come into contact with the cooking liquor (Fengel and Wegener 1989; Sjöström 1993; Alén 2000). In the course of carbohydrate losses, also called “yield loss,” 50–60% and 10–15% of the initial hemicelluloses and cellulose, respectively, are degraded. The most important alkali-catalyzed reactions responsible for this yield loss include the dissolution of undegraded and degraded carbohydrate chains, the deacetylation of acetyl groups in hemicellulose chains, the peeling of different monosaccharide end-units in carbohydrate chains (the “peeling reaction” or “primary peeling”), and the random alkaline hydrolysis of glycosidic bonds in carbohydrate chains followed by a subsequent peeling reaction (“secondary peeling”) (Alén 2000). In conventional cooking, the cleavage of glycosidic bonds is of importance only at higher temperatures, that is, above 150°C for hemicelluloses (Fengel and Wegener 1989) and above 170°C for cellulose (Nevell 1985).

The peeling reaction results in the formation of a large number of aliphatic carboxylic acids. Of the most abundant hydroxy acids, 3,4-dideoxy-pentonic and glucoisosaccharinic acids are formed from glucomannan and cellulose (hexosans), whereas 2-hydroxybutanoic and xyloisosaccharinic acids are formed from xylan (pentosan) (Alén 2011). In contrast, the prominent glycolic, lactic, and 3-deoxy-pentonic acids, as well as the volatile formic acid, are obtained from all the polysaccharide constituents of wood. The detailed information on the origin and the composition of polysaccharide degradation products in

BLs are well documented in the literature (Malinen and Sjöström 1975; Löwendahl et al. 1976a; Niemelä et al. 1985; Niemelä 1988, 1989, 1990; Alén et al. 1985b; Niemelä and Alén 1999; Knill and Kennedy 2003; Rautiainen and Alén 2010). The possible formation routes of degradation products were presented based on model compound studies (Alfredsson and Samuelson 1968; Löwendahl et al. 1976b; Johansson and Samuelson 1977; Sjöström 1977).

The present article is aiming at the revisiting of the behavior of the main chemical constituents of lignocellulosic materials from wood and nonwood feedstocks during alkaline pulping. The formation of aliphatic carboxylic acids with low molecular mass should also be observed as a result of conventional alkaline delignification. The consumption profile of charged alkali should also be put in relation to the formation and reactions of these acids. In focus are one softwood (SW; a mixture of pine/spruce), two hardwoods (HWs; birch and aspen), and two nonwood feedstocks (bamboo and wheat straw), which were primarily delignified by kraft pulping. In each case, the soluble acids present in BLs were analyzed by means of gas chromatography (GC) during delignification. The expectation was that the synoptic presentation of the data collected from many lignocellulosic feedstock could elevate the transparency and complete the existing data material. An improved knowledge with this regard could be useful in the future studies for developing models for alkaline pulping and concepts for recovering aliphatic carboxylic acids from BLs.

## Materials and methods

### Cooking experiments

The conventional laboratory-scale kraft pulping experiments were conducted in 1.25 l rotating stainless steel autoclaves heated in a decene bath (CRS Autoclave System 420). A SW chip mixture [75% Scots pine (*Pinus sylvestris*) and 25% Norway spruce (*Picea abies*)], silver/white birch (*Betula pendula/B. pubescens*), aspen (*Populus tremula*), and bamboo (*Bambusa procera*) were delignified by kraft pulping and cultivated wheat (*Triticum aestivum*) straw by kraft and soda/soda-AQ pulping. The bamboo originated from central Vietnam and all the other raw materials were of Finnish origin.

The wood chips for pulping were laboratory screened (SCAN-CM 40:01) and the chips with knots and bark residues were eliminated. Bamboo and wheat straw were cut to a length distribution of 3–5 cm, and both knots and leaves were removed. The chemical content of the raw materials is presented in Table 1. The cooking parameters employed in these cooking series [effective alkali (EA), sulfidity, liquor-to-feedstock ratio, cooking temperature, and H-factor range] and some data on the pulps ( $\kappa$  number and total yield range) are presented in Table 2. In all cooks, the initial temperature was 80°C and the heating-up rate to the maximum cooking temperature was 1°C min<sup>-1</sup>. The amount of AQ added to the wheat straw soda-AQ pulping

**Table 1** Chemical composition of the feedstocks used for cooking experiments.

Component	SW	HWs		Nonwoods	
		Aspen	Birch	Bamboo	Wheat
Carbohydrates <sup>a</sup> (%)	60.4	65.1	62.9	62.7	55.9
Arabinose (%)	1.5	0.6	0.5	0.9	1.7
Galactose (%)	1.9	0.8	1.1	0.6	0.5
Glucose (%)	40.8	44.1	41.5	45.2	37.7
Mannose (%)	11.4	2.2	1.1	0.3	0.2
Xylose (%)	4.8	17.4	18.7	15.7	15.8
Lignin (%)	27.0	21.7	24.1	25.8	24.3
Klason (%)	26.5	18.8	21.0	24.5	21.2
Acid-soluble (%)	0.5	2.9	3.1	1.3	3.1
Extractives (%)	2.2	3.0	2.6	0.8	1.3
Others <sup>b</sup> (%)	10.4	10.2	10.4	10.7	18.5
Total (%)	100.0	100.0	100.0	100.0	100.0

<sup>a</sup>Monosaccharides as anhydro sugars. <sup>b</sup>Containing acetyl and uronic acid groups of xylan, some pectins and other polysaccharides, proteins, and inorganics.

was 0.05% based on the o.d. feedstock. The  $\kappa$  number of the pulp was determined according to the standard test method SCAN-C 1:00.

### Analysis of feedstock materials

For the chemical analyses, air-dried wood and pulp samples were first ground in a Retsch SM 100 cutting laboratory mill (Retsch GmbH, Haan, Germany) equipped with a bottom sieve with trapezoid holes (with a perforation size of <1.0 mm). Before the analyses, all samples were stored in a freezer at -18°C, and their moisture content was determined gravimetrically after keeping the samples in an oven at 105°C for 24 h.

The grounded samples were submitted to extraction with acetone according to TAPPI T 280 pm-99 (4 h extraction time in a Soxhlet apparatus). The acid hydrolysis of the extractive free feedstock and pulp samples was done according to TAPPI T 249 cm-00 and the resulting monosaccharides were determined by a Dionex high-performance anion exchange chromatograph equipped with pulsed amperometric detection (HPAEC/PAD). A gradient elution (Table 3) was performed at a flow rate of 0.3 ml min<sup>-1</sup> with the eluents: (A) ultra-high-quality water (internal resistance  $\geq 18.2$  M $\Omega$  cm; Milli-Q Plus; Millipore, Bedford, MA) and (B) 100 mM NaOH with an addition of (C) 100 mM NaOH+500 mM CH<sub>3</sub>COONa for cleaning. Columns: CarboPac PA1 (250×2 mm i.d.; Dionex, Sunnyvale, CA) analytical column and the corresponding guard column CarboPac PA-1 G (50×2 mm i.d.). The flow rate of the post-column eluent (300 mM NaOH) was 0.1 ml min<sup>-1</sup>. Detection: Dionex ED-50 pulsed amperometric detector (Dionex) equipped with a disposable working electrode by using a waveform A for carbohydrates (Dionex Technical Note 21). L-fucose (Sigma-Aldrich, St. Louis, MO) was the internal standard and D-arabinose, D-galactose, D-glucose, D-mannose, and D-xylose (Fluka Chemical, Germany) were the sugar standards. The results from the HPAEC/PAD analysis were converted to polysaccharides (i.e., to monosaccharide anhydro forms) by multiplying the results of monosaccharides obtained, with factors 0.88 for pentoses and 0.90 for hexoses.

**Table 2** Cooking data of the feedstocks.

Parameters	SW		Birch		Aspen		Bamboo		Wheat straw		
	Kraft	Kraft	Kraft	Kraft	Kraft	Kraft	Kraft	Kraft	Kraft	Soda-AQ	Soda
EA <sup>a</sup> (%)	19	19	21	19	20	16	20	15	15	18	
EA <sup>b</sup> (mol l <sup>-1</sup> )	1.05	1.05	1.17	1.05	1.11	1.0	1.25	0.75	0.75	0.9	
Sulfidity (%)	35	35	35	35	35	25	25	30	0	0	
Liquor-to-solid ratio (l kg <sup>-1</sup> )	4.5	4.5	4.5	4.5	4.5	4	4	5	5	5	
Maximum cooking temperature (°C)	170	162	165	155	160	165	165	145	145	165	
H-factor <sup>c</sup> to T <sub>max</sub>	179	89	116	47	74	116	116	18	18	116	
H-factor range	7→2500	4→1030	2→1640	2→697	4→1010	623	1080	1→97	1→97	80→380	
Final κ number	20	18	16	20	15	23	13	12	14	14	
Total yield range (%)	78→43	82→51	82→49	78→53	77→52	51.9	48.7	56→45	56→47	48→44	

<sup>a</sup>EA on o.d. feedstock (% as NaOH). <sup>b</sup>EA concentration in the white liquor (calculated as NaOH). <sup>c</sup>H-factor during heating up to T<sub>max</sub>. In all cases, the initial temperature was 80°C and the heating-up rate 1°C min<sup>-1</sup>.

**Table 3** Gradient program used in the HPAEC/PAD analysis of monosaccharides with (A) ultra-high-quality water and (B) 100 mM NaOH, with an addition of (C) 100 mM NaOH+500 mM CH<sub>3</sub>COONa for cleaning.

Time (min)	A (%)	B (%)	C (%)
-10	100	0	0
0	100	0	0
2	100	0	0
2.2	98	2	0
26	98	2	0
39	50	50	0
41	0	0	100
47	0	0	100

The lignin content of the wood and pulp samples was calculated as a sum of the “acid-insoluble Klason lignin” (TAPPI T 222 om-98 and TAPPI T 249 cm-00) and the “acid-soluble lignin”. Sample powder was first treated with sulfuric acid and the lignin precipitated was filtered off, washed, dried, and weighed. The content of “acid-soluble lignin” was determined by means of a UV/Vis spectrophotometer at 205 nm after dilution of the hydrolysate until the absorbance was in the 0.4–0.8 range. The absorptivity value for conversion was 110 l g<sup>-1</sup> cm<sup>-1</sup> (Swan 1965).

## Analysis of BLs

The residual alkali concentration was determined according to the KCL procedure (number 67a:87) by titrating the diluted and carbonate-buffered BL sample to pH 11.5 with 1 M HCl.

Volatile acids (formic and acetic acids) were determined as benzyl ester derivatives (Bethge and Lindström 1974; Alén et al. 1985a) by an Agilent 6850 (Agilent Technologies, Palo Alto, CA) GC with flame ionization detection (GC/FID). A capillary column Rtx-5 (30 m×0.32 mm i.d., film thickness 0.25 μm; Restek, Bellefonte, PA) was used. Temperature program: 3 min at 60°C, →3°C min<sup>-1</sup> to 150°C, →15°C min<sup>-1</sup>

to 230°C, and 5 min at 230°C. Carrier gas: N<sub>2</sub> (0.8 ml min<sup>-1</sup>); internal standard: crotonic acid (Fluka Chemical). The temperature of both injection port and detector was 280°C.

The hydroxy monocarboxylic and dicarboxylic acids were per(trimethylsilyl)ated with Regisil (99% BSTFA+1% TMCS; Regis Technologies, Morton Grove, IL) and determined as their TMS derivatives by GC/FID (Alén et al. 1984). An Rtx-5 capillary column (30 m×0.32 mm i.d., film thickness 0.25 μm) was used in GC/FID. Temperature program: 5 min at 60°C, →2°C min<sup>-1</sup> to 185°C, →40°C min<sup>-1</sup> to 290°C, and 5 min at 290°C. Carrier gas: N<sub>2</sub> (1.0 ml min<sup>-1</sup>); internal standard: xylitol (Sigma-Aldrich). The temperature of injection port and detector: 290°C and 300°C, respectively. The peaks were identified by mass selective detection (GC/MSD). A capillary column HP-5 ms (30 m×0.25 mm i.d. with a film thickness of 0.25 μm; Agilent Technologies) was used in GC/MSD (Agilent 6890 GC equipped with Agilent 5973N MSD; Agilent Technologies). Carrier gas: He. The temperature program and the temperatures of injection port and detector were the same as those for GC/FID. The identification of the different acids was performed by comparing their mass spectra (EI at 70 eV) with those of the library (Wiley 7<sup>th</sup> ed.) or with those of our laboratory. For the quantitative calculations, the mass-based response factors between xylitol and the peaks derived from the acids studied were based on data given by Alén et al. (1984).

## Results and discussion

### Chemical composition of feedstocks

The chemical compositions of wood materials (Table 1) are in agreement with the data of the literature. The composition of bamboo is very similar to that of HWs, although the alkali-soluble materials and ash contents (mostly silica) in bamboo are known to be high (Liese 1987; Vu 2004). According to Han and Rowell (1997), wheat straws should contain 16–21% lignin; thus, the lignin content in wheat straw presented in Table 1 (24.3%) is high. In view of the pitfalls of the

Klason lignin determination, for example, coprecipitation of non-lignin-derived materials – polyphenols, cutins, some carbohydrate degradation products, and proteins – and problems with the determination of the acid soluble lignin, all data with this regard should be considered with care (Theander and Åman 1979). Moreover, the structure and chemical composition of nonwood materials and annual crops change considerably during their lifetime and even more rapidly after harvesting (Buchala and Wilkie 1973). As indicated by the monosaccharide data in Table 1, bamboo and wheat straw consist of cellulose and the main hemicellulose is xylan. Among others, Maekawa (1976) and Higuchi (1980) have reported that bamboo xylan has an “average structure,” which is between that of HW and SW xylylans.

### Aliphatic carboxylic acids in BLs

The relative composition and the total amount of the main aliphatic carboxylic acids are presented in Table 4

(present in the form of sodium carboxylates) for both the wood kraft BLs at typical  $\kappa$  number levels (~30 and 20 for SW and HW, respectively) and the nonwood BLs obtained under varying conditions. The chemical structures of the main hydroxy acids in BLs are presented in Figure 1.

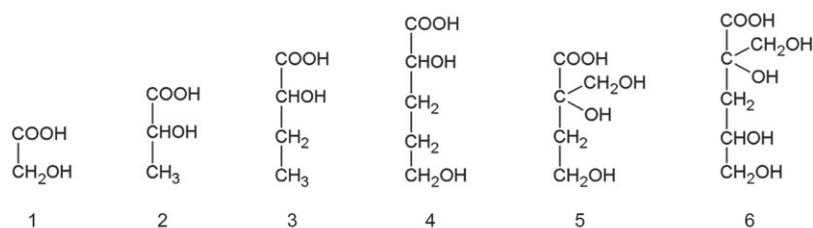
As found earlier by Alén et al. (1985b) and Niemelä et al. (1985), the total amount of acids formed during kraft pulping was clearly higher at an EA level of 19–21% in the HW-BLs than in the SW-BL (Table 4). This is mainly due to the high amount of acetic acid originating from the acetyl groups of HW xylylans compared with the lower acid amount obtained from SW glucomannans by deacetylation (Lindberg et al. 1973a,b). It has been shown (Niemelä et al. 1985; Zanuttini et al. 2005; Pakkanen et al. 2012) that acetyl groups are readily removed under alkaline cooking conditions.

In HW xylylans, the acetyl group content varies in the range of 8–17% of the total xylan, corresponding to an average of 4–7 acetyl groups per 10 xylose units (Lindberg et al. 1973a; Alén 2011). In contrast, in SW glucomannans,

**Table 4** Formation of aliphatic carboxylic acids during the pulping of various feedstocks.

EA (%) / Cooking temperature (°C)	SW		Birch		Aspen		Bamboo		Wheat straw	
	Kraft 19/170	Kraft 19/162	Kraft 21/165	Kraft 19/155	Kraft 20/160	Kraft/16	Kraft/20	Kraft/15	Soda-AQ/15	Soda/18
H-factor	1490	795	420	700	308	623	1080	18	18	380
$\kappa$ number	30	20	20	20	20	22.5	12.9	21.3	22.9	13.7
Monocarboxylic acids (%)	88.6	90.6	90.5	91.8	88.0	90.3	88.4	72.8	75.4	80.6
Formic acid	21.6	14.5	12.4	10.8	12.3	18.4	15.7	9.2	11.1	13.6
Acetic acid	13.2	35.4	35.5	36.7	34.9	18.7	15.7	29.5	31.4	22.8
Glycolic acid	4.1	2.6	2.8	2.4	2.1	4.3	4.8	2.1	4.3	3.3
Lactic acid	10.1	5.6	5.7	6.1	5.5	10.0	10.9	10.3	6.0	11.0
Glyceric acid	–	–	–	–	–	0.2	0.2	1.3	2.8	1.4
2-Hydroxybutanoic acid	3.0	11.7	11.1	10.9	8.8	15.8	15.0	4.3	2.5	8.7
4-Hydroxybutanoic acid	0.4	0.2	0.2	0.3	0.3	0.1	0.3	0.3	0.6	0.5
2-Deoxy-tetronic acid	0.8	0.7	0.7	0.6	0.6	0.2	0.1	0.2	0.4	0.2
3-Deoxy-tetronic acid	0.1	0.2	0.3	0.1	0.1	1.0	0.9	2.0	1.2	0.9
2-Hydroxy-4-pentenoic acid	0.7	0.3	0.3	0.4	0.3	0.5	0.6	0.2	–	–
3,4-Dideoxy-pentonic acid	7.5	2.3	2.4	2.6	2.4	4.6	4.6	4.3	2.4	2.8
3-Deoxy-pentonic acid	1.9	1.5	1.6	1.4	1.2	3.0	2.9	1.7	2.8	2.9
Xyloisaccharinic acid	2.0	8.3	9.8	9.2	9.3	6.5	7.5	2.5	2.4	4.1
Glucoisaccharinic acid	23.2	7.3	7.7	10.3	10.2	7.0	9.2	4.9	7.5	8.4
Dicarboxylic acids (%)	2.9	3.0	3.3	3.8	3.4	1.9	2.6	10.8	12.3	6.6
Oxalic acid	–	–	–	–	–	0.1	0.2	2.8	1.9	0.7
Succinic acid	0.5	0.5	0.5	0.7	0.4	0.3	0.8	0.6	0.8	1.1
Malic acid	0.4	0.5	0.6	0.7	0.7	0.6	0.5	6.3	8.5	3.8
2-Hydroxyglutaric acid	1.3	1.1	1.2	1.2	1.0	0.4	0.8	0.5	0.6	0.7
Glucoisaccharinaric acid	0.7	0.9	1.0	1.2	1.3	0.5	0.3	0.6	0.5	0.3
Miscellaneous (%)	8.5	6.4	6.2	4.4	8.6	7.8	9.0	16.4	12.3	12.8
Total (g l <sup>-1</sup> )	29.7	38.7	38.3	34.5	33.2	28.7	37.7	15.5	15.4	24.1

For further cooking conditions, see Table 2.



**Figure 1** Main hydroxy acids in BLs: (1) glycolic acid, (2) lactic acid, (3) 2-hydroxybutanoic acid, (4) 3,4-dideoxy-pentonic acid, (5) xyloisaccharinic acid, and (6) glucoisaccharinic acid.

the acetyl group content is only approximately 6% of the total glucomannan, corresponding to approximately 1 acetyl group per 3–4 hexose units (Moreira and Filho 2008; Alén 2011). For this reason, HWs usually contain three to four times more acetyl groups than SWs (Fengel and Wegener 1989). In bamboo, the content of acetyl groups was found to be 6–7% of the total xylan (Higuchi 1980; Liese 1987), and in nonwood feedstock and annual plants also, glucomannans may have contain acetyl substituents (Matsuo and Mizuno 1974; Dea and Morrison 1975; Maekawa 1976). In the present study, the amount of acetic acid in bamboo BLs was closer to SW-BLs than to HW-BLs (Table 4), indicating that the bamboo (*B. procer*) xylan contains quite a low amount of acetyl groups.

About 15 of the most common aliphatic acids were determined. All these acid components have also been detected in earlier studies of wood BLs (Niemelä and Alén 1999). Two isomeric forms of 3-deoxy-pentonic (i.e., *erythro* and *threo* isomers) and glucoisaccharinic (i.e.,  $\alpha$  and  $\beta$  forms) acids could be detected (not shown separately in the tables).

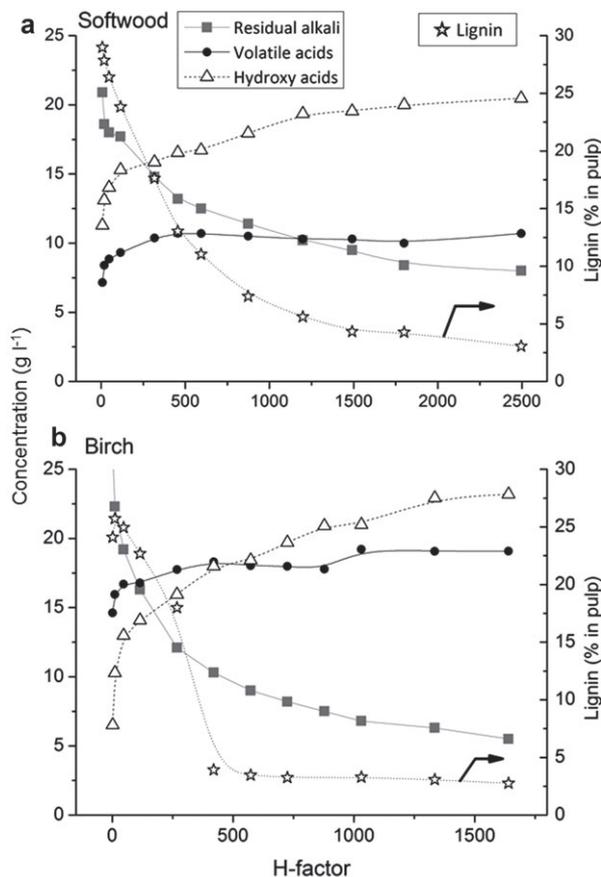
The amount of formic acid in the wood kraft BLs ranged from 3.7 g l<sup>-1</sup> of the aspen BL (EA 19%/155°C) to 6.4 g l<sup>-1</sup> of the SW-BL (Table 4), whereas its amount in the wheat kraft and soda-AQ BLs was significantly lower (1.4 and 1.7 g l<sup>-1</sup>, respectively). Whereas acetic acid originates from the cleavage of acetyl groups, formic acid is gradually liberated during the peeling reaction (Sjöström 1993; Alén 2000). This explains its retarded formation at low EAs in the case of the wheat straw cook. In general, only small changes caused by the variations in EA and cooking temperature were detected in the relative composition of the aliphatic acid fraction revealed separately from SW, HWs, and bamboo. However, in the case of the wheat straw BLs, depending on the cooking method, some variations are visible. In addition, the degradation of carbohydrates to various acids with low molecular mass is markedly accelerated for wheat straw by an increase in alkali concentration and cooking temperature (see kraft/15 or soda-AQ/15 vs. soda/18).

Glucoisaccharinic acid (Table 4) dominated the hydroxy monocarboxylic acids in the SW-BL. The next major group of these nonvolatile acids consisted of glycolic, lactic, and 3,4-dideoxy-pentonic acids. In contrast, in the case of other BLs (Table 4), the most abundant nonvolatile acids are besides glucoisaccharinic acid, the xylan-derived 2-hydroxybutanoic and xyloisaccharinic acids as well as minor constituents glycolic, lactic, 3,4-dideoxy-pentonic, and 3-deoxy-pentonic acids. Several dicarboxylic acids were also detected in the BLs. Although they clearly belong to the minor acid group, such a pronounced portion of these acids in wheat straw BLs was not expected. This finding can be interpreted that the prominent malic acid was derived either from pectic substances or from lignin.

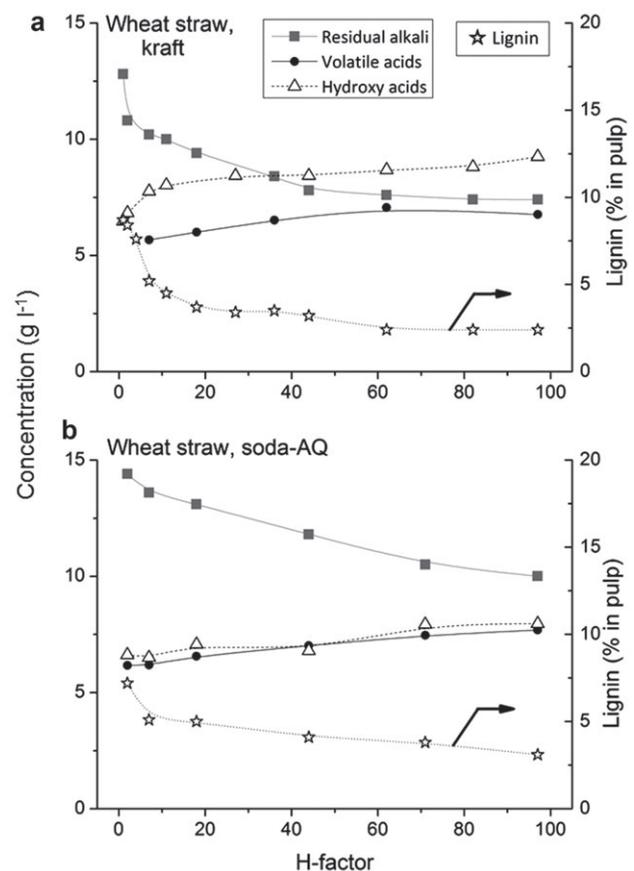
## Alkali consumption and delignification

The intense formation of aliphatic carboxylic acids and the rapid consumption of alkali in the beginning of both SW and birch kraft pulping can be seen in Figures 2a and 2b, respectively. Similar trends were also observed for the wheat straw cooks (Figure 3a,b). However, in the case of wheat straw, the interpretation of the results is more straightforward for two reasons: (1) the impregnation of cooking chemicals into the feedstock material is more easy and (2) the subsequent transfer of reaction products from feedstock cavities toward the external bulk liquor is less hindered (Pakkanen et al. 2013).

The characteristic progress of delignification can also be seen in Figures 2a,b and 3a,b. As expected, HW lignin degraded significantly faster than SW lignin during kraft pulping. However, more than 80% of wheat straw lignin was already removed during the heating-up period (i.e., H-factor under 18) of kraft and soda-AQ wheat straw pulping. Wheat straw lignin is composed of guaiacyl, syringyl, and *p*-hydroxyphenylpropane moieties and this “core lignin” is further cross-linked with polysaccharides via *p*-coumaric and ferulic acids bridges (Sun et al. 1997;



**Figure 2** Formation of aliphatic carboxylic acids (volatile acids and hydroxy acids) and residual alkali as a function of H-factor during (a) SW and (b) birch (EA 21%/165°C) kraft pulping. Lignin content in wood or pulp is indicated with a mark.



**Figure 3** Formation of aliphatic carboxylic acids (volatile acids and hydroxy acids) and residual alkali as a function of H-factor during wheat straw: (a) kraft and (b) soda-AQ pulping.

Buranov and Mazza 2008). A majority of *p*-coumaric acid is bonded via alkali-labile ester bonds, which are easily released even at mild alkali extraction. These structural features together with an easy accessibility of the cell walls for chemicals are the main reasons for the rapid delignification of wheat straw.

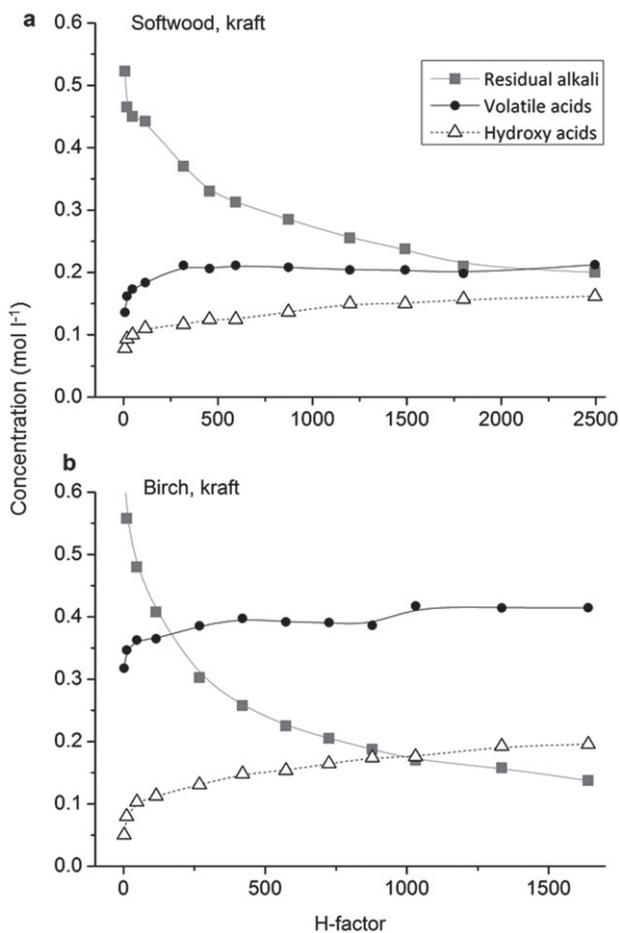
Figures 4a,b and 5 illustrate the changes in the molar concentration of carbohydrates-derived degradation products in the course of different cooks. The consumption of alkali comprises the neutralization of aliphatic carboxylic acids, degradation products of lignin, extractives-derived compounds, and hemicellulose residues with carboxylic acid functional groups. In the presented cooks, 40–48% of the charged alkali were required in SW pulping for the formation of carboxylic acid salts (i.e., carboxylates of volatile and hydroxy acids). The corresponding values for birch and wheat straw kraft pulping were 57–71% and 42–44%, respectively. The alkali consumption of the aliphatic carboxylic acids was calculated based on the carboxyl groups in each acid analyzed (i.e., for dicarboxylic acid; e.g., malic

or hydroxybutenedioic acid; the alkali consumption is two equivalents of NaOH).

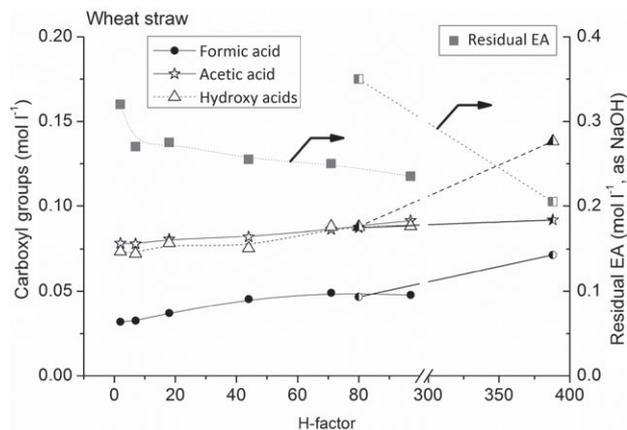
The amount of carboxylic acids formed in kraft pulping from SW and HW is presented in Figures 6a and 6b as kilograms of acids per ton of feedstock material. It should be pointed out that, besides volatile acids, most hydroxy acids were formed quite rapidly in the initial phase of cooking. For example, more than 50 kg hydroxy acids were already formed from 1 ton of the o.d. feedstock during the heating-up period before 130°C (SW pulping) or 145°C (HW pulping). On the other hand, the total amount of these acids was approximately 150 kg ton<sup>-1</sup> of the o.d. SW and 170 kg ton<sup>-1</sup> of the o.d. birch wood at the end of the cook.

## Conclusions

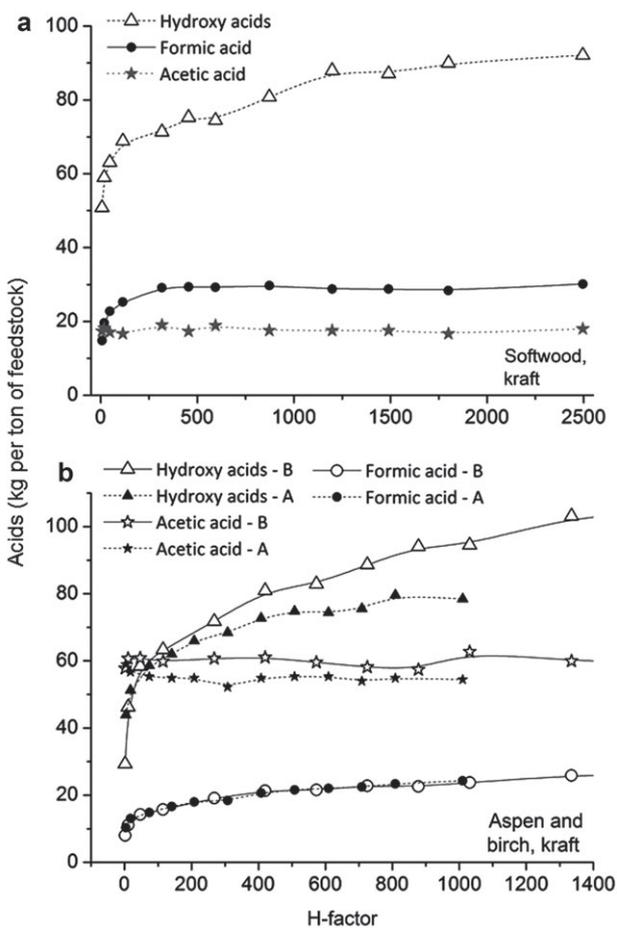
The H-factor-dependent profiles of the formation of aliphatic carboxylic acids (formic and acetic acids and hydroxy acids) are characteristic for SW and HWs (birch and



**Figure 4** Molar alkali consumption of aliphatic carboxylic acids (volatile acids and hydroxy acids) and residual alkali in BLs as a function of H-factor during (a) SW and (b) birch (EA 21%/165°C) kraft pulping.



**Figure 5** Molar alkali consumption of aliphatic carboxylic acids (volatile acids and hydroxy acids) and residual alkali in BLs as a function of H-factor during wheat straw soda-AQ and soda (marked as half-filled symbols) pulping.



**Figure 6** Amount of volatile and hydroxy acids formed during (a) SW and (b) HW kraft pulping (kilogram per ton of the o.d. feedstock). A, aspen; B, birch.

aspen) in conventional laboratory-scale kraft pulping. The cooks with nonwood feedstocks (bamboo and wheat straw) also revealed some peculiarities. These data are of practical importance when determining the consumption profile of the charged alkali. They are also useful, for example, in planning various recovery processes of aliphatic acids for nonfuel applications from cooking liquors formed during the initial delignification phase with low selectivity. At this stage of the cook, an acid separation process seems to be attractive in view of the high mass ratio of aliphatic acids (with low heating value) to lignin (with high heating value).

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