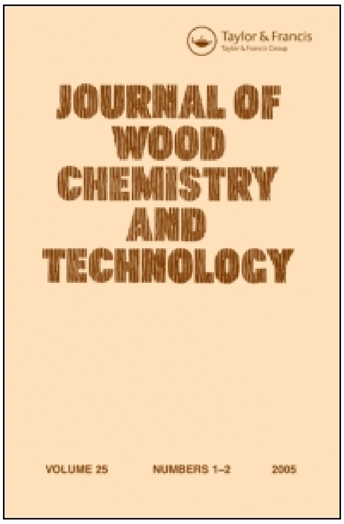

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FORMATION OF ALIPHATIC CARBOXYLIC ACIDS DURING ALKALINE PULPING OF MULI BAMBOO

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ABSTRACT

A study on the formation of aliphatic carboxylic acids, i.e., formic and acetic acids and various hydroxy monocarboxylic and dicarboxylic acids, during soda-AQ, kraft, and kraft-AQ pulping of muli bamboo (*Melocanna baccifera*) was carried out. Detailed gas chromatographic analyses revealed that the most abundant hydroxy carboxylic acids were 2-hydroxybutanoic, lactic, glucoisosaccharinic, glycolic, xyloisosaccharinic, 3,4-dideoxypentonic, and 3-deoxypentonic acids. The presence of AQ depressed the formation of 2-hydroxybutanoic, xyloisosaccharinic, and glucoisosaccharinic acids, and accelerated the formation of glycolic and 3-deoxypentonic acids as well as 3-deoxytetronic acid but had only a small effect on that of lactic and 3,4-dideoxypentonic acids. The total amount of aliphatic carboxylic acids corresponded to 12–15% of o.d. bamboo.

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Key Words: Bamboo; Soda-AQ pulping; Kraft pulping; Black liquor; Aliphatic carboxylic acids; Hydroxy acids; Dicarboxylic acids

INTRODUCTION

During alkaline pulping of lignocellulosics large amounts of the feedstock carbohydrates (cellulose and various hemicelluloses) are lost. This is mainly due to the formation of aliphatic carboxylic acids via peeling reaction.[1,2] For example, it has been reported[3] that the amount of aliphatic carboxylic acids formed during kraft pulping of hardwood (silver birch) accounts for 20% of the wood mass. Thus the degradation of polysaccharides during alkaline delignification is of fundamental interest and economic importance.

Detailed information is currently available in the literature on the chemical structure of the carbohydrate degradation products in softwood and hardwood kraft and soda-anthraquinone (AQ) black liquors.[3–9] So far, more than 100 different carboxylic acids have been identified from black liquor.[2,9] Recently we have carried out studies[10–12] on the formation of these acids during soda-AQ pulping of wheat straw, reed canary grass, and kenaf bark.

Bamboo is one of the most significant raw materials for papermaking in some Asian countries such as India, China, and Bangladesh. It is reported[13] that in China alone, there are over seventy mills utilizing bamboo for pulping to produce various kinds of chemical pulps. Alkaline pulping (kraft and soda) processes are commonly used for delignification of bamboo.[13–19] However, to our knowledge nothing has been published about the chemical composition of carbohydrate degradation products from alkaline pulping of bamboo.

As a part of our research efforts aimed at the characterization of various non-wood black liquors, it was of interest to study the formation of aliphatic carboxylic acids during alkaline pulping of bamboo. In our earlier study, muli bamboo (*Melocanna baccifera*) was cooked in a laboratory-scale digester by the conventional soda-AQ, kraft, and kraft-AQ methods.[20] The effects of sulfidity, AQ, and cooking time at maximum temperature on the formation of aliphatic carboxylic acids were now investigated.

EXPERIMENTAL

Black Liquor Samples

Black liquor samples were prepared by conventional soda-AQ, kraft, and kraft-AQ pulping of muli bamboo in a laboratory-scale digester

Table 1. Cooking Data on Soda-AQ, Kraft, and Kraft-AQ Pulping of Muli Bamboo*

Cook No.	Method	Sulfidity (%)	AQ (%)	*t* (min)	Screened Yield (%)	Kappa No.
1	Soda-AQ	0	0.05	120	42.0	17.6
2	Kraft	10	0	120	41.1	16.5
3	Kraft	15	0	120	42.2	17.0
4	Kraft	20	0	120	42.5	19.7
5	Kraft	25	0	120	42.1	19.8
6	Kraft-AQ	10	0.05	120	41.7	14.0
7	Kraft-AQ	15	0.05	30	43.5	18.7
8	Kraft-AQ	15	0.05	60	42.8	15.7
9	Kraft-AQ	15	0.05	90	42.4	15.9
10	Kraft-AQ	15	0.05	120	42.2	15.6
11	Kraft-AQ	20	0.05	120	42.5	16.3
12	Kraft-AQ	25	0.05	120	42.1	18.6

*Active alkali (as NaOH) 18% on o.d. bamboo, AQ charge % on o.d. bamboo, liquor-to-bamboo ratio 4 : 1 L/kg, initial temperature 80°C, heating-up time to maximum temperature (170°C) 90 min, and *t* time at maximum temperature.

(Table 1).[20] The black liquor was separated from the pulp by filtration and stored in a freezer prior to analysis.

Analytical Methods

For the GC and/or GC/MS studies, hydroxy monocarboxylic and dicarboxylic acids were per(trimethysilyl)ated either in their straight-chain ammonium salts,[21] or after converting them into the corresponding lactones.[10] The lactone forms were analyzed to improve the separation of certain six-carbon polyhydroxy acids including all forms of 3-deoxyhexonic and glucoisosaccharinic acids. The interpretations of the mass spectra were based on those of the earlier studies.[9] Quantitative calculations were based on the GC runs, as described by Alén et al.[21]

Volatile acids (formic and acetic acids) were determined as their benzyl esters by GC.[22]

Xylitol and crotonic acid were used as internal standards for the quantitative determination of hydroxy monocarboxylic and dicarboxylic acids and volatile acids, respectively. Information on the sampling, instruments, and column temperature programs is given elsewhere.[11] All the measurements were performed at least in duplicate. The relative standard deviations (RSD) were generally found to be lower than 5% for hydroxy acids and formic acid but 5–10% for acetic acid.

Kappa number was determined by the standard test method T 236 om-99.

RESULTS AND DISCUSSION

Formation of Hydroxy Monocarboxylic and Dicarboxylic Acids

Figure 1 shows an example of the gas chromatogram of the main acids in muli bamboo kraft-AQ black liquor after per(trimethylsilyl)ation of their

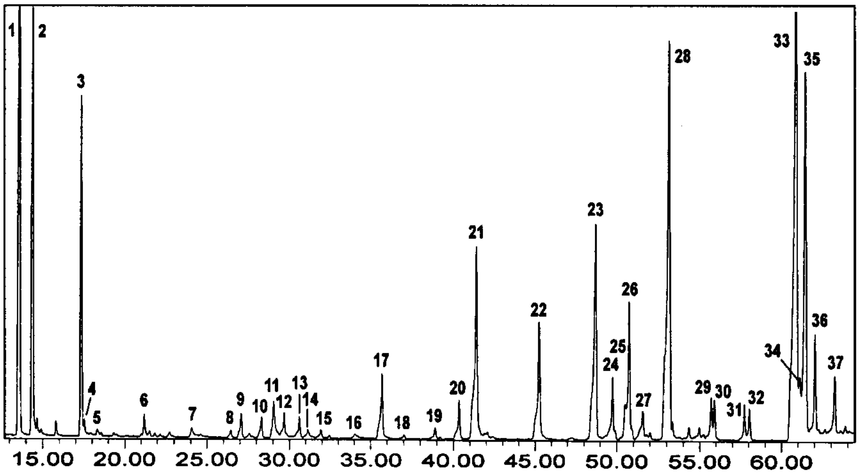

Figure 1. Separation on an Rtx-5 capillary column of the per(trimethylsilyl)ated compounds in muli bamboo kraft-AQ black liquor. 1, lactic acid; 2, glycolic acid; 3, 2-hydroxybutanoic acid; 4, 2-hydroxy-2-methylbutanoic acid; 5, oxalic acid; 6, 3-hydroxypropanoic acid; 7, 2-hydroxypentenoic acid; 8, 4-hydroxybutanoic acid; 9, phosphate; 10, glycerol; 11, glycine; 12, succinic acid; 13, methylsuccinic acid; 14, glyceric acid; 15, 4-hydroxybenzaldehyde; 16, syringol; 17, 3-deoxytetronic acid; 18, 2-deoxytetronic acid; 19, malic acid; 20, 3,4-dideoxypentonic (2,5-dihydroxypentanoic) acid; 21, vanillin; 22, 2-hydroxyglutaric acid; 23, acetophenone; 24, 4-hydroxybenzeneacetic acid; 25, xyloisosaccharinic acid; 26, 3-deoxy-*erythro*-pentonic acid; 27, anhydroisosaccharinic acid; 28, 3-deoxy-*threo*-pentonic acid; 29, syringaldehyde; 30, unknown hydroxy compound; 31, xylitol (internal standard); 32, pentitol; 33, acetosyringone; 34 and 35, unknown isomeric hydroxy acids; 36 and 37, isomeric 2,5-dihydroxyadipic acids; 38, citric acid; 39, acetosyringone (enolic form); 40, β-glucoisosaccharinic acid; 41, 3-deoxyhexonic acids (up to 4 isomers); 42, α-glucoisosaccharinic acid; and 43, β-glucoisosaccharinaric acid.

ammonium salts (i.e., in their non-lactonized forms). As expected, a considerable variety of aliphatic hydroxy carboxylic acids were formed by the degradation of carbohydrates. In total, sixteen hydroxy monocarboxylic acids and seven dicarboxylic acids were identified. The most abundant acids were 2-hydroxybutanoic, lactic, glucoisosaccharinic, glycolic, xyloisosaccharinic, 3,4-dideoxypentonic, and 3-deoxypentonic acids. The origins or routes of their formation have been thoroughly discussed elsewhere.[5–7] In addition, one amino acid (glycine), one tricarboxylic acid (citric acid), and seven lignin monomers (4-hydroxybenzaldehyde, acetophenone, 4-hydroxybenzeneacetic acid, vanillin, syringol, syringaldehyde, and acetosyringone) were detected.

Figure 2 shows the effect of sulfidity and the addition of AQ on the formation of hydroxy carboxylic acids during kraft and kraft-AQ pulping. It was observed that in both cases the total amounts of hydroxy acids decreased as a function of sulfidity. It was also found that addition of AQ generally accelerated the formation of these acids. This finding was in contradiction to the results obtained from kraft and kraft-AQ pulping of birch wood.[7]

As can be seen, 2-hydroxybutanoic acid was the most abundant hydroxy acid in all three bamboo-derived black liquors (Table 2). This

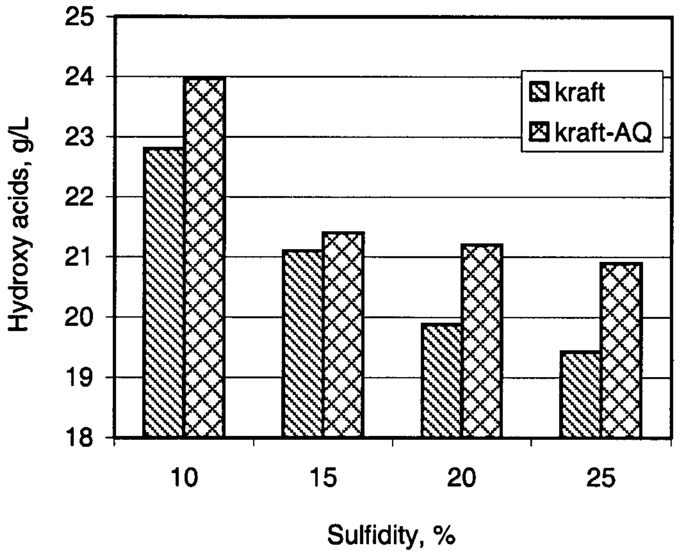

Figure 2. Effect of sulfidity on the formation of hydroxy acids during kraft and kraft-AQ pulping of muli bamboo (time at maximum temperature 120 min).

Table 2. Main Hydroxy Monocarboxylic and Dicarboxylic Acids in the Black Liquors Studied (% of Total Acids)[a]

	Cooking method		
Carboxylic acids	Soda-AQ	Kraft_{15}	Kraft_{15}-AQ
Monocarboxylic acids	86.4	85.5	85.6
Glycolic	10.9	6.8	10.7
Lactic	15.2	14.8	15.0
3-Hydroxypropanoic	0.2	0.2	0.3
Glyceric	0.9	0.4	0.7
2-Hydroxybutanoic	18.8	22.9	20.3
4-Hydroxybutanoic	0.4	0.5	0.3
2-Deoxytetronic	0.3	0.3	0.2
3-Deoxytetronic	3.2	1.9	3.0
2-Hydroxypentenoic	0.4	0.7	0.6
3,4-Dideoxypentonic	7.7	8.5	8.5
3-Deoxypentonic[b]	7.1	6.1	6.8
Xyloisosaccharinic	9.0	9.6	8.0
Glucoisosaccharinic[b,c]	12.3	12.8	11.2
Dicarboxylic acids	5.9	6.6	5.6
Oxalic	0.2	0.4	0.2
Succinic	1.1	1.1	0.8
Methylsuccinic	0.5	0.9	0.6
Malic	1.5	1.7	1.8
2-Hydroxyglutaric	1.2	1.0	0.8
2,5-Dihydroxyadipic[b]	1.1	1.0	1.0
β-Glucoisosaccharinaric	0.3	0.5	0.4
Miscellaneous[d]	7.7	7.9	8.8
Total amount			
g/L	22.8	21.1	21.4
% of o.d. bamboo	9.1	8.4	8.6

[a] Active alkali (as NaOH) 18% and cooking time at maximum temperature (170°C) 120 min. For other cooking conditions, see Table 1.
[b] *Erythro* and *threo* isomers.
[c] Including small amounts of 3-deoxyhexonic acid.
[d] See Figure 1.

finding was similar to that observed in the case of birch black liquor. The formation of this acid together with the xyloisosaccharinic and glucoisosaccharinic acids was depressed by the presence of AQ during kraft pulping, as also noted in the case of birch kraft cooking,[7] although to a much lesser degree. The amounts of the other two major acids (i.e., lactic and

3,4-dideoxypentonic acids) were only slightly affected by the addition of AQ, thus showing very different behavior from that in the kraft pulping of birch, where AQ significantly reduces the formation of all these acids. The differences in chemical composition of the carbohydrate constituents of muli bamboo and birch as well as the different cooking conditions employed may explain this discrepancy. Moreover, owing to the prominent formation of glucoisosaccharinic and 3,4-dideoxypentonic acids in the present case, the degradation of cellulose was obviously more severe compared to that in the kraft pulping of birch. On the other hand, Table 2 shows that the amounts of glycolic, 3-deoxypentonic, and 3-deoxytetronic acids at least slightly increased in the presence of AQ in agreement with findings from the kraft pulping of birch.

Figure 3 illustrates the effect of cooking time at the maximum temperature on the formation of hydroxy acids during kraft-AQ pulping. As can be seen, the concentration of hydroxy acids increased with the cooking time, indicating a steady degradation of polysaccharides as the delignification proceeded. However, the main formation of these acids took already place during the heating-up period before the maximum temperature was reached.

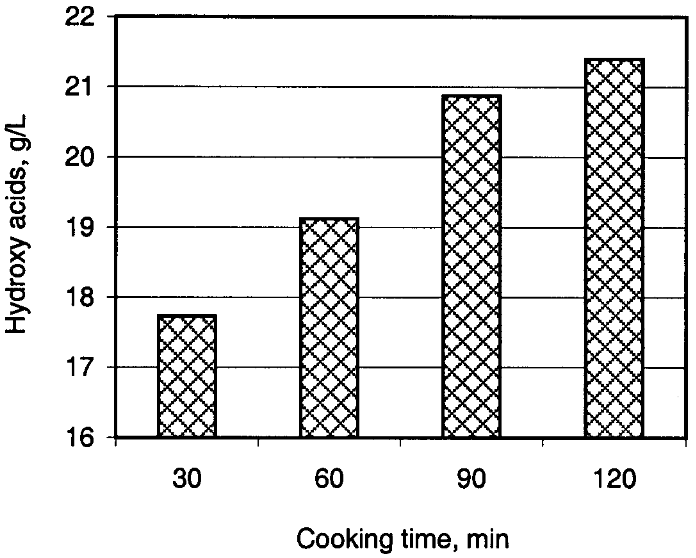

Figure 3. Effect of cooking time at maximum temperature on the formation of hydroxy acids during kraft-AQ pulping of muli bamboo (sulfidity 15%).

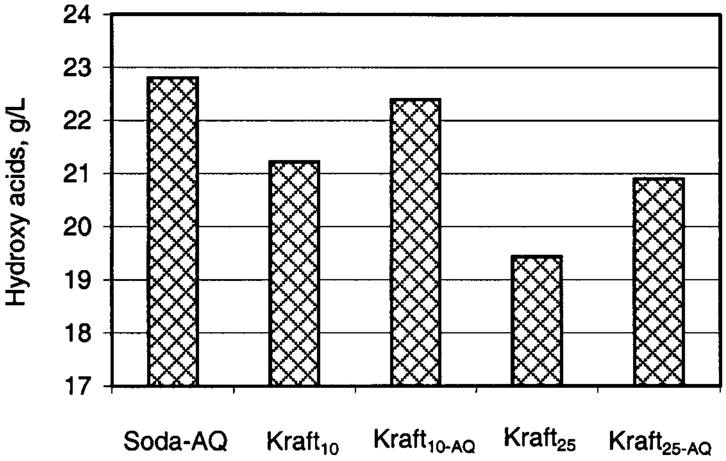

Figure 4. Comparison of the formation of hydroxy acids during soda-AQ, kraft, and kraft-AQ pulping of muli bamboo (time at maximum temperature 120 min).

Figure 4 compares the concentration of hydroxy acids in the different black liquors. The results indicated that the concentration of hydroxy acids was the highest in the soda-AQ black liquor, and the lowest in the kraft black liquor with a sulfidity of 25%. This finding can probably be explained by the difference in the concentration of effective alkali (EA) in the different cooking liquors. It was obvious that when the concentration of active alkali was kept constant, the EA concentration was highest in the soda-AQ cooking liquor, and lowest in the kraft black liquor with the highest sulfidity of 25%.

Formation of Volatile Acids

Figures 5–7 show the effects of the cooking parameters (sulfidity, cooking time, and AQ charge) on the formation of volatile acids (i.e., formic and acetic acids). No significant differences were found in the total amounts of these acids in the liquors studied. The amount of formic acid ranged from 5.7 to 6.6 g/l, corresponding to 2.3 to 2.6% of o.d. bamboo, and was similar to that in pine, spruce, and birch kraft pulping liquors. On the other hand, the amount of acetic acid ranged from 6.5 to 7.0 g/l, corresponding to 2.6 to 2.8% of o.d. bamboo, which was nearly the same as that in pine and spruce kraft pulping liquor (ca. 2% of wood),[3] but clearly lower than in birch kraft pulping liquors (ca. 5% of dry wood).[7] Furthermore,

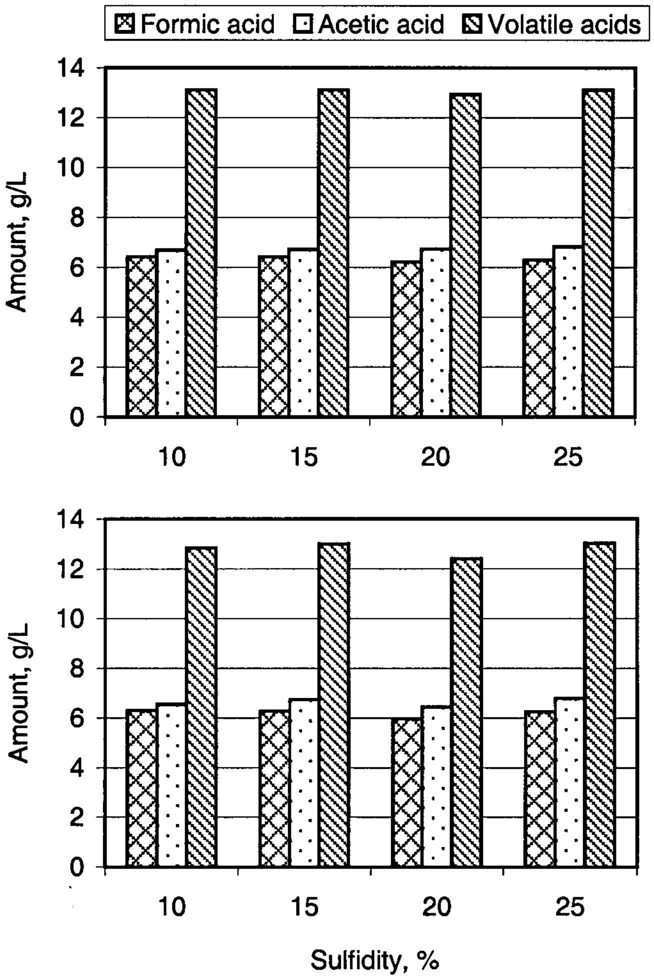

Figure 5. Effect of sulfidity on the formation of volatile acids (formic and acetic acids) during kraft (upper part) and kraft-AQ (lower part) pulping of muli bamboo (time at maximum temperature 120 min).

and in accordance with earlier studies,[7,11,12] the formation of formic acid steadily increased with the cooking time (Figure 6), while the amount of acetic acid remained almost constant. The obvious reason is that acetic acid is mainly produced by a fast deacetylation of hemicelluloses already during the early stages of delignification, while the production of formic acid proceeds slowly and depends on other degradation reactions.

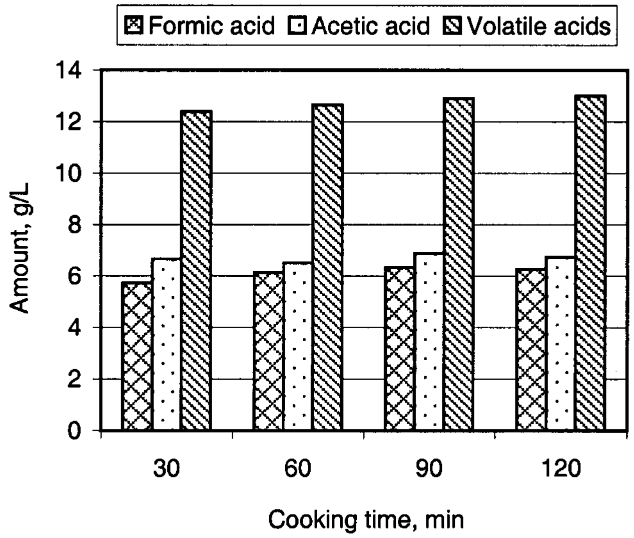

Figure 6. Effect of cooking time at maximum temperature on the formation of volatile acids (formic and acetic acids) during kraft-AQ pulping of muli bamboo (sulfidity 15%).

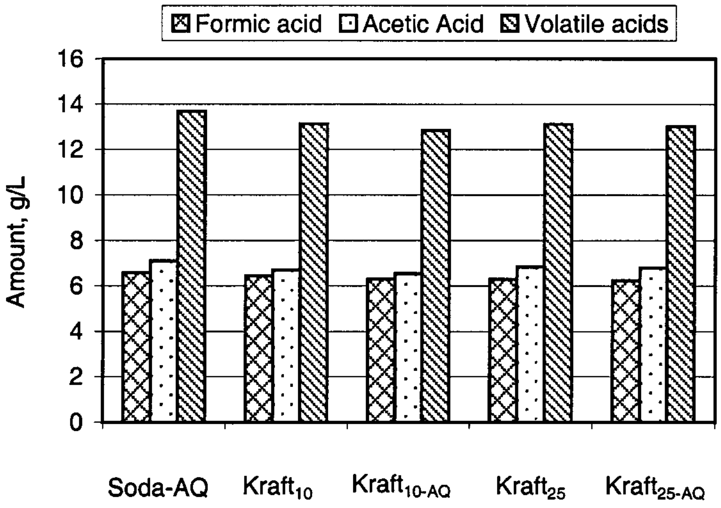

Figure 7. Comparison of the formation of volatile acids (formic and acetic acids) during soda-AQ, kraft, and kraft-AQ pulping of muli bamboo (time at maximum temperature 120 min).

CONCLUSIONS

The total content of aliphatic carboxylic acids formed during soda, kraft, and kraft-AQ pulping of muli bamboo amounted to 12–15% of o.d. bamboo. In total, sixteen hydroxy monocarboxylic acids and seven dicarboxylic acids were identified in the bamboo black liquor besides formic and acetic acids. Of the major soluble hydroxy carboxylic acids, 2-hydroxybutanoic acid was the most dominant, followed by lactic, glucoisosaccharinic, glycolic, xyloisosaccharinic, 3,4-dideoxypentonic, and 3-deoxypentonic acids. The results showed that the presence of AQ depressed the formation of 2-hydroxybutanoic, xyloisosaccharinic, and glucoisosaccharinic acids, but accelerated the formation of glycolic, 3-deoxypentonic, and 3-deoxytetronic acids.

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