

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597282>

Thermochemical Conversion of Black Liquor in the Liquid Phase

Raimo Alen^a; Paterson McKeough^a; Anja Oasmaa^a; Allan Johansson^a

^a Technical Research Centre of Finland Laboratory of Fuel Processing and Lubrication Technology, Espoo, Finland

To cite this Article Alen, Raimo , McKeough, Paterson , Oasmaa, Anja and Johansson, Allan(1989) 'Thermochemical Conversion of Black Liquor in the Liquid Phase', *Journal of Wood Chemistry and Technology*, 9: 2, 265 – 276

To link to this Article: DOI: 10.1080/02773818908050298

URL: <http://dx.doi.org/10.1080/02773818908050298>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THERMOCHEMICAL CONVERSION OF BLACK LIQUOR IN THE LIQUID PHASE

Raimo Alén, Paterson McKeough, Anja Oasmaa, and Allan Johansson
Technical Research Centre of Finland
Laboratory of Fuel Processing and Lubrication Technology
SF-02150 Espoo, Finland

ABSTRACT

Black liquor from kraft pulping of pine wood was pressure heated (about 20 MPa) for 45 minutes at both 300 °C and 350 °C and in both the presence and absence of a reducing atmosphere. Variable amounts of organic-phase (40 - 64 % of the black liquor organics), water-soluble (14 - 70 %), and volatile (12 - 55 %) products were formed. The organic-phase product originates mainly from the lignin fraction of black liquor, whereas, during the treatments, the corresponding hydroxy acid fraction was primarily degraded into lower acid intermediates and volatile components. The effects of temperature and gas atmosphere (carbon monoxide, hydrogen or nitrogen) on the conversion of black liquor are discussed.

INTRODUCTION

The organic solids in kraft black liquors are composed mainly of degraded lignin and polysaccharide degradation products (aliphatic carboxylic acids), together with a minor fraction of extractives. In today's kraft mill, after separation of most of the extractives in the form of tall soap, the liquor is concentrated to 65 - 75 % solids content by evaporation and then combusted in the recovery furnace for the recovery of the cooking chemicals and the generation of energy. However, because of several factors including the low thermal efficiency of the energy recovery, the limited capability for electricity generation, and the high capital costs of the recovery equipment, increasing

interest has been directed at the possibility of enhancing black liquor conversion to high-value energy forms^{cf. 1,2}.

In our laboratory, studies aimed at improving the present form of black liquor utilization indicated that the conversion of the black liquor organics and the recovery of the cooking chemicals must be separated, at least partly, from each other. When kraft black liquor is heated under pressure in the presence of a reducing atmosphere, a reasonable partition between the organic and the inorganic material can be achieved³. Under suitable reaction conditions a large part of the organic material is converted into a hydrophobic oil-like organic product which separates out from an aqueous phase containing the inorganic material and the residual organics. Various gases derived from the organic constituents of black liquor form another significant product fraction.

The organic phase product can be utilized efficiently as a fuel in the lime kiln of the mill or in an on-site power boiler. By applying the treatment to only part of the black liquor stream it is possible to increase the recovery capacity of an existing kraft mill. This is of great interest to the kraft pulping industry because the recovery boiler is often the bottleneck of the mill.

The main purpose of this study was to determine the yields of major product groups in the thermochemical treatment of pine kraft black liquor under conditions applied previously by McKeough *et al.*³. In conjunction with efforts to clarify the chemistry of this process, particular interest was also directed to the composition of the organic matter present in the aqueous phase after treatment.

EXPERIMENTAL

Materials

The wood material consisted of air-dried industrial chips of Scots pine (*Pinus sylvestris*). The cooks were carried out in a 600-liter stainless steel digester equipped for liquor circulation. The following conditions were applied. Alkali charge: 21.2 % active alkali (as NaOH) on

TABLE 1

Composition of the dry matter of the black liquor feedstock and the distribution of sodium and sulfur between the constituents^a

Component		Na	S
Organic constituents	88.1	10.7	0.6
Lignin	46.1	2.3	0.6
Volatile acids ^b	15.7	4.9	-
Hydroxy acids	20.9	3.5	-
Polysaccharides and other organics	5.4	+	+
Inorganic constituents	11.9	6.6	2.0
NaOH	4.9	2.8	-
Na ₂ CO ₃	2.0	0.9	-
Na ₂ SO ₄	0.2	0.1	+
Na ₂ S	4.7	2.8	1.9
Others	0.1	+	+
Total	100.0	17.3	2.6

^aPercentage of the total dry matter.

^bThe amounts of sodium formate and sodium acetate are 9.7 % and 6.0 %, respectively.

wood, sulfidity (NaOH basis): 30 %, liquor/wood ratio: 3.5 L/kg, and heating-up time (20 °C to 170 °C): 120 min followed by 90 min at 170 °C. The total pulp yield was 51.1 % of wood. The black liquor formed was evaporated to a dry solids content of 27.8 % (density of 1.144 kg/L at 25 °C) with simultaneous separation of extractives. The characteristic data for the black liquor and the relative composition of the aliphatic acid fraction are given in Tables 1 and 2, respectively.

Heat Treatments

About 500 mL of the concentrated black liquor was placed in a 1-liter autoclave equipped with a stirrer, a gas-charging system, and a gas let-down train. After charging of the reactant gas (CO or H₂) or inert gas (N₂), the reactor was heated at a rate of about 5 °C/min to the desired reaction temperature. After a reaction time of 45 min at maximum

TABLE 2

Relative composition of the aliphatic carboxylic acid fraction in the black liquor feedstock

Component	Content, % of total acids
Monocarboxylic acids	90.7
Formic	23.0
Acetic	15.3
Glycolic	7.7
Lactic	8.9
Glyceric	0.1
2-C-Methylglyceric	0.1
2-Hydroxybutanoic	2.5
4-Hydroxybutanoic	0.3
2-Deoxytetronic	0.2
2-Hydroxypentanoic	0.8
3,4-Dideoxypentonic	6.6
3-Deoxy-erythro-pentonic	0.7
3-Deoxy-threo-pentonic	0.9
Xyloisosaccharinic	0.9
Anhydroglucoisosaccharinic	0.9
3,4-Dideoxyhexonic	0.3
3,6-Dideoxyhexonic	0.4
Galactometasaccharinic	0.6
α -Glucoisosaccharinic	6.3
β -Glucoisosaccharinic	14.2
Dicarboxylic acids	5.4
Tartronic	0.3
C-Methyltartronic	0.2
Succinic	1.2
Malic	0.3
2,3-Dideoxypentanic	0.7
2,4-Dideoxypentanic	0.4
3-Deoxy-threo-pentanic	0.2
3,4-Dideoxyhexanic	0.6
α -Glucoisosaccharinaric	0.7
β -Glucoisosaccharinaric	0.8
Miscellaneous	3.9

TABLE 3

Conversion of black liquor organics into main product groups (% of initial total organics)^a

Product group	300 °C			350 °C		
	CO	H ₂	N ₂	CO	H ₂	N ₂
Organic-phase product	41	50	64	40	42	44
Aqueous organics	70 ^b	32	24	20 ^b	21	14
Other, mainly CO ₂ ^c and H ₂ O	29	18	12	55	37	42

^aReactions for 45 minutes at about 20 MPa pressure.

^bIncluding the portion formed from carbon monoxide.

^cIn part chemically bound in sodium carbonate/bicarbonate.

temperature (300 °C or 350 °C), the autoclave was rapidly cooled to 50 °C. Gases were released into a gas bag via cold traps (0 °C) and a wet-test meter. The autoclave was further cooled to 25 °C, after which the organic phase and the aqueous phase were separately recovered and weighed. The conversion experiments were carried out under three different atmospheres: a reducing atmosphere of carbon monoxide (initial pressures of 9 MPa at 300 °C and 5 MPa at 350 °C), a reducing atmosphere of hydrogen (initial pressures of 9 MPa at 300 °C and 5 MPa at 350 °C), and an inert atmosphere of nitrogen (initial pressures of 7 MPa at 300 °C and 3 MPa at 350 °C). These initial pressures were selected so that final pressures of about 20 MPa were obtained. The conditions employed in each experiment are summarized in Table 3.

Analytical Determinations

The hydroxy monocarboxylic and dicarboxylic acids were analyzed as their trimethylsilyl derivatives by GLC as described elsewhere^{4,5}.

The volatile monocarboxylic acids (formic and acetic acids) were analyzed as their benzyl esters by GLC⁶.

The non-sulfur components in the product gas mixture were analyzed by GLC using simultaneously a Porapak N column (5 m x 0.32 mm i.d.) for hydrocarbons and a Molecular Sieve (5 Å) column (0.8 m x 0.32 mm i.d.) for H₂, N₂, CO, CO₂, and CH₄. Helium was used as the carrier gas (30 mL/min) and the corresponding compounds (detected by TC or FID) were identified and determined quantitatively by using a standard gas mixture (delivered by Norsk Hydro). The temperatures of the injection port and the detector were 70 °C and 180 °C, respectively. The temperature program was 3 min at 35 °C, 10 °C/min to 65 °C, 25 °C/min to 160 °C, and 9 min at 160 °C.

The sulfur-containing gases, H₂S and CH₃SH, were correspondingly analyzed isothermally by using a Porapak QS teflon column (4 m x 0.32 mm i.d.). H₂S was determined at 90 °C and detected with a TC detector (165 °C). In contrast, CH₃SH was separated at 180 °C and detected with a FID detector (200 °C). In both cases the chromatographic peaks were compared with those obtained from a standard gas mixture (delivered by Norsk Hydro).

The lignin content of black liquor was determined by UV-spectrophotometry at 280 nm after diluting the sample solutions with 0.1 M sodium hydroxide until the absorbance was in the 0.3 - 0.8 range. The absorptivity value⁷ used was 24.3 L/g cm.

The sodium and sulfur contents were determined by induction coupled plasma spectrophotometry.

The amount of tetrahydrofuran(THF)-soluble material in the organic phase was determined by extraction of the corresponding phase (2 g) with excess of THF (40 mL) under ultrasonic agitation at room temperature.

The amount of dry substance in the aqueous samples was measured by drying a sample at 105 °C to a constant weight. GLC analysis

of the 105 °C-distillates indicated only minor amounts of organics, mainly low-molecular alcohols. The dry substance of the organic phases was determined on the basis of an analysis of water by Karl-Fischer titration (ASTM E 203).

RESULTS AND DISCUSSION

The yields of the three major product groups (organic-phase product, aqueous organics, and predominantly volatile compounds) are presented in Table 3. As can be seen from these results, all the product groups are present in significant quantities in each case. However, it should be noted that, in the experiments performed under a carbon monoxide atmosphere, the gas reacted to a considerable extent with alkali yielding sodium formate. The organic phase was a poorly separating (i.e. weakly hydrophobic) solid in two cases: H₂/300 °C and N₂/300 °C. After these treatments the recovered organic product contained a considerable amount of entrained aqueous phase, which explains the apparently high organic-phase yields in these cases. On the basis of the water content of the recovered organic phase, the amount of entrained organics could be estimated in each case. These estimates indicated that, regardless of the treatment performed, the yield of actual organic phase was about 40 % of black liquor organics.

It was further observed that the effect of increased reaction temperature on the quality of the organic-phase product (the sodium content was about 3 %) was dependent on the gas atmosphere, as judged from the amount of the product soluble in THF. Under hydrogen there was a marked increase in solubility (yield of THF-solubles: 6 % → 29 % of black liquor organics), under nitrogen a small increase (10 % → 14 %), while under carbon monoxide a small decrease (31 % → 24 %). It was earlier established that, if the THF-solubles yield remains below about 20 % of black liquor organics, the organic-phase product is distinctly solid-like.

In all experiments, increasing the temperature from 300 °C to 350 °C resulted in a considerable increase in the decomposition of the aqueous-phase organics with a corresponding increase in the amounts of

TABLE 4

Composition of the dry matter in the aqueous phases, as well as the final pH values, after the conversion time of 45 minutes at about 20 MPa (% of total)

Compound	300 °C			350 °C		
	CO	H ₂	N ₂	CO	H ₂	N ₂
Aliphatic carboxylic acids ^a	75.2 ^{b,c}	44.7	34.1	43.0 ^c	45.3	32.2
Other organics ^d	24.6	15.0	24.3	+	+	1.1
NaHS	-	2.1	1.8	1.6	2.7	3.4
Na ₂ CO ₃ ^e	0.2	38.2	39.8	55.4	52.0	63.3
pH of aqueous phase	5.8	9.9	9.5	8.0	9.0	9.0

^aIn the form of sodium salts.

^bThe amount of sodium was insufficient for acid neutralization.

^cIncluding the portion formed from carbon monoxide.

^dEstimated sodium content of 10 %.

^eCarbonate calculated as sodium carbonate, although sodium bicarbonate also occurred. Other inorganic compounds, e.g. Na₂SO₄, are present in only very minor amounts.

volatile compounds formed (Table 3). The fraction of volatile compounds contained, in addition to carbon dioxide and reaction water, small amounts of sulfur-containing compounds, low-molecular-weight hydrocarbons, and volatile alcohols; most of which were determined by the analysis methods applied in this study.

The compositions of the aqueous phases given in Table 4 indicate that aliphatic carboxylic acids represent the largest organic fraction in these phases. On the basis of the results it can be concluded that the organic-phase product originated primarily from the lignin fraction of black liquor. At the lower temperature of 300 °C other organics were also present, for example, condensation carboxylic acid products, which were not detected by GLC. The significant fraction of inorganic compounds was

TABLE 5

Relative composition of the aliphatic carboxylic acids detected after the conversion time of 45 minutes at about 20 MPa (% of total acids)

Component	300 °C			350 °C		
	CO	H ₂	N ₂	CO	H ₂	N ₂
Monocarboxylic acids	93.9	85.5	84.1	86.7	85.4	74.6
Formic	62.0 ^a	15.7	9.8	35.9 ^a	19.7	13.3
Acetic	6.0	8.0	10.3	15.0	18.1	30.6
Glycolic	5.4	12.5	13.1	2.8	2.7	0.9
Lactic	10.5	26.4	25.8	16.5	24.9	12.3
3-Hydroxypropanoic	+	0.2	0.2	0.1	0.3	0.2
2-C-Methylglyceric	0.4	1.0	1.4	2.6	3.5	6.0
2-Hydroxybutanoic	6.8	6.6	6.4	9.2	8.9	6.6
4-Hydroxybutanoic	0.3	1.1	1.2	2.1	3.5	1.2
2-Hydroxypentanoic	0.3	2.7	2.8	1.9	3.5	2.9
3,4-Dideoxypentonic	1.2	8.2	8.8	0.2	0.1	+
3-Deoxy- <i>erythro</i> -pentonic	0.2	0.5	1.2	0.3	0.2	0.4
3-Deoxy- <i>threo</i> -pentonic	0.2	0.6	0.8	+	+	0.1
Anhydroglucoiso-saccharinic	0.5	1.7	2.1	0.1	+	+
3,6-Dideoxyhexonic	0.1	0.3	0.2	+	+	0.1
Dicarboxylic acids	2.1	5.1	6.2	6.4	8.8	14.5
C-Methylmalonic	0.4	0.2	0.2	0.9	1.6	0.3
C-Methyltartronic	0.5	1.2	1.5	3.4	5.8	12.4
Succinic	0.7	0.5	0.6	0.3	0.3	0.3
Malic	0.1	0.2	0.2	1.2	0.8	1.1
C-Methylsuccinic	+	0.3	0.2	0.1	0.2	0.1
2,3-Dideoxypentartic	0.4	2.5	3.3	0.4	0.1	0.2
2,4-Dideoxypentartic	+	0.2	0.2	0.1	+	0.1
Miscellaneous	4.0	9.4	9.7	6.9	5.8	10.9
Total amount, % of aliphatic acids in black liquor	176.6	88.7	52.8	71.6	73.8	49.6

^aIncluding the portion formed from carbon monoxide.

TABLE 6

Relative composition of gaseous phases after the conversion time of 45 minutes at about 20 MPa (% of total)

Component	300 °C			350 °C		
	CO	H ₂	N ₂	CO	H ₂	N ₂
H ₂	0.8	48.4	0.1	2.9	31.2	1.6
N ₂	-	-	95.5	-	-	88.2
CO	29.3	-	-	6.7	-	-
CO ₂	65.6	40.5	2.7	82.8	38.1	2.0
C ₁ → C ₄ Hydrocarbons	0.7	3.1	0.5	2.0	16.3	3.5
H ₂ S	3.3	6.4	1.0	5.0	11.0	3.6
CH ₃ SH	0.3	1.6	0.2	0.6	3.4	1.1
Total amount, % of black liquor organics	IN 41.7 OUT 43.6	2.9 5.1	31.1 33.7	20.4 24.9	1.5 4.6	12.0 14.5

mainly composed of sodium carbonate and sodium bicarbonate, the ratio of carbonate to bicarbonate depending on pH (Table 4). Furthermore, it was found that during the thermal treatments some of these salts crystallized out and adhered to the reactor walls.

Table 5 shows the changes in the relative compositions of aliphatic carboxylic acids during the treatments. All the main acid components identified are also found in ordinary kraft pulping liquors.^{4,5} However, primarily due to their small concentrations, some of the identified acids, including volatile fatty acids such as propanoic and pentanoic acids, were not determined separately. This increased, to some extent, the relative amount of the miscellaneous compounds fraction. The results indicate that the acid derivatives containing 5 or 6 carbon atoms (glucoisosaccharinic acid and various pentonic and hexonic acid derivatives, see Table 2) are gradually degraded into lower intermediates.

The formation of most of these acids can be explained by assuming various alkaline oxidative cleavages of higher-molecular-weight hydroxy acids with simultaneous formation of volatile degradation products and polymers representing the reduced reaction products.

Unlike the hydroxy monocarboxylic acids, the dicarboxylic acids represented only a minor product fraction. The results showed that, regardless of the gas atmosphere used, the formation of dicarboxylic acids was more extensive in the treatments at 350 °C than in those at 300 °C. Most of the dicarboxylic acids reported were present in the original black liquor, although some new compounds (included in the fraction, miscellaneous compounds) were also found. In addition to these acid derivatives small amounts of lignin monomers were detected by GLC. These compounds were mainly composed of various pyrocatechol structures formed by demethylation.

The product gases formed during the treatments were primarily carbon dioxide, low-molecular-weight hydrocarbons and sulfur-containing compounds (Table 6). In addition to these products the gaseous phases contained considerable amounts of the original gas charged to the reactor.

CONCLUSIONS

The liquid-phase thermal processing of kraft black liquor carried out under reducing conditions results in an organic-phase product at a yield of about 40 %. Other major product groups, derived from black liquor organic material, are aqueous-phase organics and volatile compounds. The results obtained here-in indicated clearly that the organic-phase product originates mainly from the lignin fraction of black liquor. On the basis of the analyses of aqueous-phases, it can be further concluded that the major reactions of the other principal organic fraction of black liquor, aliphatic carboxylic acids, are of a straightforward thermal degradation type leading primarily to lower-molecular-weight acid intermediates and gases. If, at an existing mill, only part of the whole black liquor stream is treated, lime-kiln fuel can be produced and the recovery capacity of the mill can be simultaneously increased by about 10 %. On

the other hand, if the whole black liquor stream is treated using this kind of process, an entirely new system for recovering the cooking chemicals is required.

ACKNOWLEDGEMENTS

The financial support from the Finnish Ministry of Trade and Industry, Energy Department is gratefully acknowledged. Thanks are expressed to Miss Katja Heiskanen, Mr. Reijo Häkkinen, and Miss Mari-Leena Koskinen for their assistance with the experimental work. The pine kraft cook and the analyses of the inorganic constituents of black liquor were made at the Finnish Pulp and Paper Research Institute.

REFERENCES

1. W.S. Adams, Jr. and G.E. Maples, *AIChE Symp. Ser.* 76(200), 114 (1980).
2. A.L. Kohl, *Can. J. Chem. Eng.* 64, 299 (1986).
- 3.. P. McKeough, R. Alén, A. Oasmaa, and A. Johansson, Thermochemical Conversion of Black Liquor: A New Approach to Producing Liquid Fuels from Biomass, in *Proceedings of the International Conference on Biomass for Energy and Industry*, 4th European Conference, Orléans, France, pp. 362 - 366, 1987.
4. R. Alén, K. Niemelä, and E. Sjöström, *J. Chromatogr.* 301, 273 (1984).
5. K. Niemelä and E. Sjöström, *Holzforschung* 40, 361 (1986).
6. R. Alén, P. Jännäri, and E. Sjöström, *Finn. Chem. Lett.* 190 (1985).
7. R. Alén, P. Patja, and E. Sjöström, *Tappi* 62(11), 108 (1979).