

PYROLYSIS AND COMBUSTION BEHAVIOR OF
CHLORINATED ORGANICS IN BLEACH PLANT
EFFLUENT

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ABSTRACT

Pyrolysis of chlorinated phenolics and thioglignin was investigated to elucidate the principle step occurring during combustion of organic material in bleach plant effluent.

Chlorinated phenolics found in bleach plant effluent, such as chlorophenols, chloroguaiacols, chlorovanillins and chlorosyringaldehydes, were completely decomposed at 700 to 900 °C with alkali and oxygen.

Organically bound chlorine with lignin was easily eliminated as inorganic salt by alkali addition at low pyrolysis temperature. Without alkali, more than 90% of chlorine was eliminated as hydrogen chloride, the others as methyl chloride and tar-like material. Ether-soluble part of tar-like material contained various chlorinated phenolics, which were not completely decomposed at a high temperature.

Organic matter isolated from spent alkali extraction liquor was also pyrolyzed under a condition, which seemed to be probable in a conventional recovery furnace. Almost whole chlorine in organic matter was recovered in solid residue.

It was confirmed that the technique used in this work was useful to investigate the thermal behavior of chlorinated organics in bleach plant effluent.

1. Introduction

The reduction of pollution load in spent kraft mill effluent is one of the most concerns of paper industry. Particularly, it is the most important to develop an effective technique for removal of chlorinated phenolics, because the toxicity and, bioaccumulation and direct biological effect on the environment are of paramount concern in the world.

Although biological purification of bleach plant effluents is useful to reduce the BOD and

toxicity, the reducibility seems to be rather unpredictable if the composition of treated effluent is varied. Therefore, as a drastic approach, a concept arises that spent bleach plant liquor is evaporated with a pertinent technique and all the organic substances dissolved in the bleaching process is burned in a furnace.

In Canada Rapson advanced a method for operating an effluent-free kraft pulp mill¹⁾, which is currently being applied at the Thunder Bay Mill of Great Lakes Forest Products Co.²⁾

At the Skoghall Mill of Billerund Uddeholm AB in Sweden, the spent alkali extraction liquor has been treated in an ion exchange system³⁾

In Japan, at the kraft mill of Taio Paper Co., an ultra filtration technique is used to remove the organic matter in bleach plant effluent and the resulting concentrated liquor is introduced into the alkali-recovery process.⁴⁾

On the application of such new techniques a problem arises whether chlorinated organics can be completely decomposed in a furnace.

In this work an attention has been given to the combustion of chlorinated phenolics, the mechanism whereby new harmful compounds will be produced, and the development of information to help the control, minimization and ultimate elimination of possible toxic compounds in emission. Particular emphasis has been given to pyrolysis which is one of the principle steps occurring during combustion.

A fate of organically bound chlorine is studied and the optimum condition for thermal degradation of chlorinated organics in bleach plant effluent is discussed in this paper.

2. Experimental

1-1. Preparation of model compounds

(a) Synthesis of Chlorinated phenolics
4,5-Dichlorocatechol, 1,4,5-Dichloroguaiacol,
5-Chlorovanillin, 2,6-Dichlorosyringaldehyde,
3,4,5-Trichloro-2,6-dimethoxyphenol were prepared

according to the procedure of Kachi et al ⁵⁾.

The other chlorinated compounds were purchased from Tokyo Kasei, Japan.

(b) Chlorination of Thioglignin

Beech thioglignin isolated from the kraft black liquor was chlorinated by using chlorine gas.

A standard method is as follows;

Fifty g of thioglignin was suspended with 100 ml of distilled water in 300 ml of three-necked round flask. Chlorine gas was bubbled through the suspension, regulating the passing speed at 50 ml/min, and with the agitation of the content at 400 rpm for a definite time.

After the reaction, chlorinated lignin was filtered and washed with water until the filtrate was neutral, and dried over P₂O₅ under vacuum.

Sodium salt of chlorinated thioglignin was prepared by the dissolution of chlorinated lignin in an aqueous solution of sodium hydroxide, evaporation, and drying over P₂O₅ under vacuum. A molar ratio of sodium to chlorine is designated as "Na/C1" in this paper.

1-2. Pyrolysis apparatus

Pyrolysis of chlorinated lignin was primarily carried out in a quartz reactor. The pyrolysis apparatus is shown in Fig. 1

Ten g of chlorinated lignin was taken in the reactor which was connected with a receiving tube through two series of water-cooler, a pair of dry ice-ethanol trap and a gas collector.

The reactor was heated in a heating furnace which was lifted up on pyrolysis, by jacking.

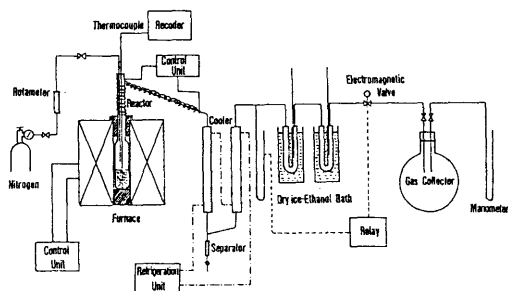


Fig. 1 Pyrolysis Apparatus

During pyrolysis, low volatile and water-soluble products were collected with the water-coolers. They were marked as "condensate" fraction.

High volatile and water-insoluble products, passing through the first trapping system, were collected in dry ice-ethanol traps which were packed with glass beads. A tar-like product in the trap was washed with ether and acetone successively. They were respectively marked as

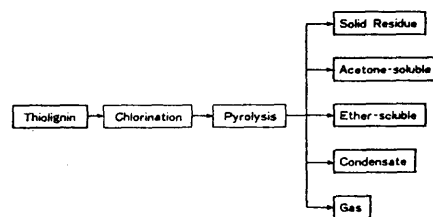


Fig.2 Pyrolysis Fractions of Chlorinated Thioglignin

"Ether-soluble" and "Acetone-soluble" fraction. The gaseous products were collected in a gas collector at the final part of the apparatus. They were marked as "pyrolysis Gas" fraction. Gas collection was carried out with an electromagnetic valve, which was regulated by using a monometer. In the reactor black porous material like char was left. It was marked as "Solid Residue".

Chlorinated phenolics were pyrolyzed with a Curie Point Pyrolyzer (Nihon Bunseki, Model JHP-2) combined with GC (Shimadzu, Model GC-7A) -

1-3 Analytical procedure

Chlorine content was determined by the argentimetric titration after Shoniger combustion.

GC and GC-MS analysis of "Ether-soluble" and "Pyrolysis Gas" fractions were carried out with a Shimadzu Model GC-7A with FID and JEOL Model JMSD300. For analysis of inorganic gas, glass columns packed with Porapak QS (3.0 mm id x 4 m, 80/100 mesh) was used. The temperature was programmed from -50 to 0 at 4 /min and 0 to 200 at 8 /min, using N₂ and He (50 ml/min) as carrier gases.

For the analysis of chlorinated phenolics, PEG-20M capillary column (0.2 mm id x 50m) was used. The temperature was programmed from 70 to 200 at 5 /min, using N₂ (3 ml/min) as a carrier gas. For the quantitative estimation of chlorinated phenolics, glass columns packed with 10% FFAP on Chromosorb W (AW-DMCS) was used (2.0 mm x 2 m, 80/100 mesh). The temperature was from 50 to 220 at 5 /min, using N₂ (50 ml/min) as a carrier gas. Calibration curves were made by using authentic chlorinated phenolics and 2,6-Dibromophenol as an internal standard.

MS analysis was carried out under a condition such as 23 eV, He as a carrier gas.

3. Results and Discussion

3-1 Pyrolysis of chlorinated phenolics

Seven chlorinated phenolics, which were found in bleach plant effluent and its relative compounds, were pyrolyzed with a Curie Point Pyrolyzer.

The first pyrolysis was carried out under a relatively mild condition (590 °C, Na/Cl = 1.0 under nitrogen) to elucidate degradation products, especially chlorinated compounds. Main products were shown in Table 1. All of starting materials still remained as unreacted and many chlorinated phenolics were newly produced under such a mild condition. An elimination of chlorine from a starting material was one of the main reactions. Further addition of chlorine to products was also a main reaction, for example, Di- and Trichlorobenzene from p-Chlorophenol and Trichloroveratrole from 4,5-Dichloroguaiacol.

An interesting result was that products methylated on phenolic hydroxyl groups, were produced, like chlorinated veratrole and anisole from 4,5-Dichloroguaiacol, methylated derivatives from 5-Chlorovanillin and 4,6-Dichlorosyringaldehyde. As a radical reaction is a main reaction in pyrolysis of organic compounds⁶⁾, chlorine-addition and methylation may be taken place via radical reactions.

Table 1
Pyrolysis Products of Chlorinated Phenolics

Starting material	Main Products
p-Chlorophenol	<chem>c1ccc(Cl)cc1</chem> , <chem>c1ccc(Cl)cc1</chem> , <chem>c1ccc(Cl)cc1</chem>
2,4-Dichlorophenol	mono-, di-, and trichlorinated condensation products
2,4,6-Trichlorophenol	mono- and trichlorinated condensation products
4,5-Dichloroguaiacol	mono- and trichlorinated condensation products
5-Chlorovanillin	<chem>c1ccc(Cl)cc1</chem> , <chem>c1ccc(Cl)cc1</chem> , <chem>c1ccc(Cl)cc1</chem> , <chem>c1ccc(Cl)cc1</chem>
2,6-Dichlorosyringaldehyde	<chem>c1ccc(Cl)cc1</chem> , <chem>c1ccc(Cl)cc1</chem> , <chem>c1ccc(Cl)cc1</chem> , <chem>c1ccc(Cl)cc1</chem>

1) Pyrolysis Condition: Temperature: 590°C
Ratio of sodium to chlorine (Na/Cl): 1.0
Under N₂

Furthermore, non-chlorinated condensation products such as naphtharene and anthracene were also detected. As unknown chlorinated condensation products, mono-, di- and trichlorobiphenyl compounds were also detected.

These results indicate that, unless pyrolysis condition is enough to decompose a

starting material completely, thermally stable chlorophenolics and its condensation products would be produced. To elucidate such a possibility, effect of alkali and oxygen addition on pyrolysis was investigated. Thermal degradability of chlorinated phenolics was shown in Fig. 3-(a) to (f).

On pyrolysis of 4,5-Dichloroguaiacol, more than 5% of the starting material still remained as unreacted even at 900 °C if alkali and oxygen were lacking. However, if added alkali was enough (Na/Cl > 1.0), more than 99% was decomposed at 650 °C. The decomposition ratio under alkali and oxygen didn't decrease accompanying the drop of temperature. A similar effect on decomposition was observed in the case of oxygen addition without alkali (Fig. 3-(a)).

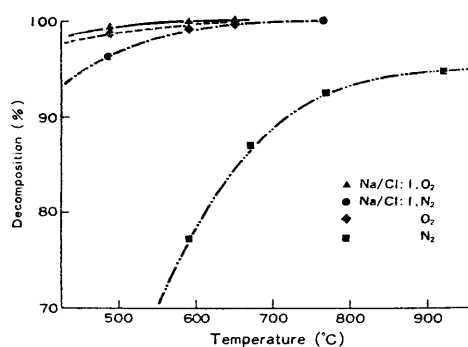


Fig. 3-(a) Pyrolysis of 4,5-Dichloroguaiacol

As shown in Fig. 3-(b), almost 100% of 4,5,6-Trichloroguaiacol was decomposed with enough alkali (Na/Cl = 1.0) and oxygen, even at a lower temperature, 490 °C. Without alkali or oxygen on pyrolysis, it was more stable than 4,5-Dichloroguaiacol.

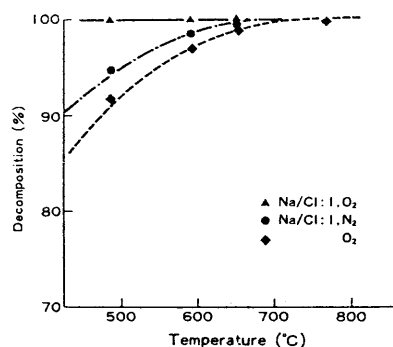


Fig. 3-(b) Pyrolysis of 4,5,6-Trichloroguaiacol

5-Chlorovanillin was completely decomposed at 650 with alkali (Na/Cl = 1.0) and oxygen. On the other hand, it was relatively Stable without oxygen. The 3% was left as undecomposed at a higher temperature, 920 (Fig- 3-(c)).

2, 6-Dichlorosyringaldehyde was much degradable, as shown in Fig. 3-(d). More than 93% of the compound was decomposed at a lower temperature, 490 under nitrogen without alkali.

2,4,6-Trichlorophenol Was decomposed at 760 with enough alkali and oxygen, but much stable at lower pyrolysis temperature(Fig- 3-(e)).

p-chlorophenol was also stable at lower temperature(fig- 3-(f)).

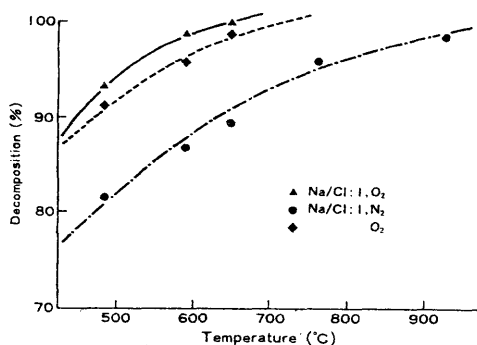


Fig. 3-(c) Pyrolysis of 5-Chlorovanillin

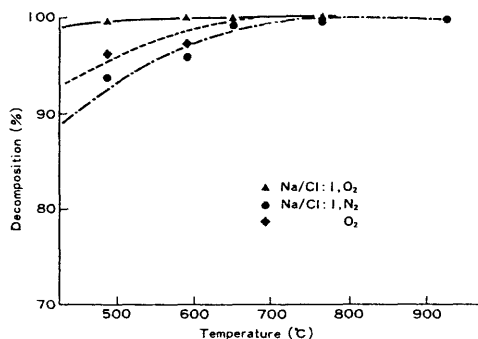


Fig. 3-(d) Pyrolysis of 2,6-Dichlorosyringaldehyde

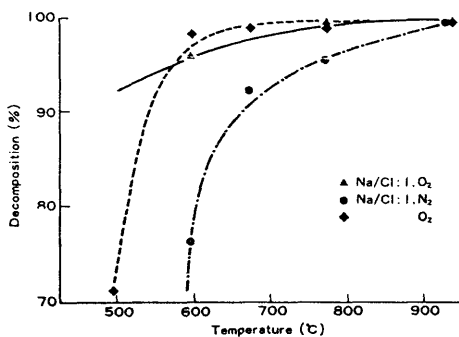


Fig. 3-(e) Pyrolysis of 2,4,6-Trichlorophenol

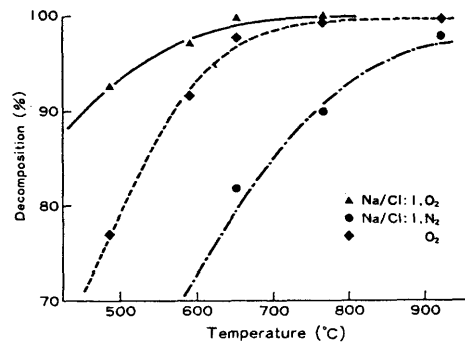


Fig. 3-(f) Pyrolysis of p-Chlorophenol

To compare thermal degradability of chlorinated phenolics, the "Complete Decomposition Temperature" was estimated by extrapolation of the decomposition curves in Fig. 3 to 100% decomposition. The complete decomposition means that the peak of starting material was disappeared on a gaschromatogram of the pyrolysis reaction mixture. Although this definition is useful to compare relative stability of chlorinated phenolics, it is not enough to express the "real" degradability because some products will survive for a longer time than the starting material. As shown in Fig. 4, chlorinated phenolics with lesser or simpler functional groups are more stable. In general chlorinated phenolics in bleach plant effluert will be completely decomposed at 700 to 900 with enough alkali and oxygen.

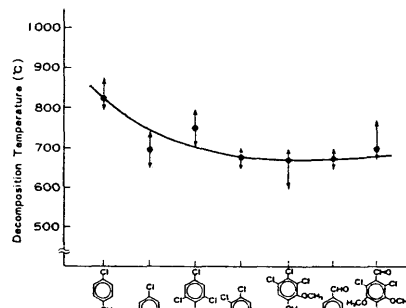


Fig. 4 Decomposition Temperature of Some Chlorinated Phenolics

3-2 pyrolysis of chlorinated lignin

chlorinated thiolignin was pyrolyzed with the pyrolysis apparatus. The reason why chlorinated thiolignin was used as a model compound, were (1) chlorine content was easily Selected and (2) pyrolysis products from carbohydrate component can be neglected.

The chlorine distribution in pyrolysis products were shown in Fig. 5. Alkali and oxygen

were not added in this case.

At every temperature level, more than 90% of total chlorine was recovered as hydrogen chloride. About 10% was present as methyl chloride, and 2 to 5% as solid residue. Chlorine content of Rher-soluble was less than 1% and almost constant. Chlorine distributed to Acetone-soluble fraction was kept in about 1% at every temperature level.

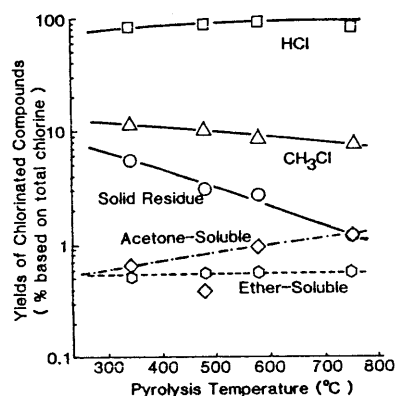


Fig. 5 Chlorine Distribution in Pyrolysis Products of Chlorinated Thioglinin

Methyl chloride is seemed to be produced via radical reactions of chlorine radicals with methyl radicals from methoxyl groups. This was supported by model experiments that, at 760 without alkali under nitrogen, methyl chlorides were produced in 4.48 mole % from 4,5,6-Trichloro-2,6-dimethoxypheno1, and trace amount from 2,4,6-Trichlorophenol.

With alkali, chlorine distribution was remarkably changed. As shown in Fig. 6, chlorine content in Solid residue fraction enhanced to 99% with the increase of Na/Cl ratio to 1.0, and levelled off after that. On the contrary hydrogen chloride decreased rapidly. As whole chlorine in the Residue was washed out with hot water, it can be said that produced hydrogen chloride was converted to sodium chloride. It is interesting that methyl chloride and chlorine in Ether-soluble and Acetone-soluble fractions also increased rapidly on addition of alkali as Na/Cl ratio > 1.0.

Although the 99% of chlorine can be eliminated as sodium chloride on pyrolysis with enough alkali, it is possible that small amount but many kinds of chlorinated phenolics and its condensation products would be produced.

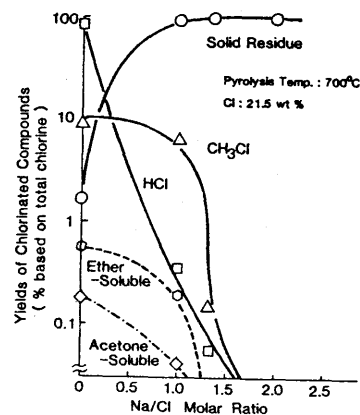


Fig. 6 Effect of Alkali on Chlorine Distribution in Pyrolysis Products

Furthermore such a possibility will be increased if chlorinated organics in bleach plant effluent is burned in a furnace, because temperature level and alkali concentration in a recovery furnace are disproportioned, and oxygen concentration is shortened at the many parts.

The emission of such pyrolysis products would occur new pollution problem to circumstances.

Chlorinated phenolics, which were detected on pyrolysis without alkali under nitrogen, were shown in Table 2.

Table 2 Chlorinated Phenolics from Chlorinated Thioglinin

PRODUCTS	PYROLYSIS TEMPERATURE (°C)			
	340	470	580	750
M-CHLOROPHENOL	0.003	0.008	0.012	-
P-CHLOROPHENOL	0.013	0.017	-	-
O-CHLOROPHENOL	0.009	0.012	0.004	0.002
2,6 DICHLOROPHENOL	0.017	0.010	0.010	0.005
3,5 DICHLOROPHENOL	0.041	0.035	0.015	0.012
2,4,6 TRICHLOROPHENOL	0.068	0.090	0.062	0.053
2,4 DICHLOROPHENOL	0.004	0.005	0.004	-
4 CHLOROCATECHOL	0.050	0.264	0.155	0.140
3,5 DICHLOROCATECHOL	0.042	0.021	0.021	0.017
4,5 DICHLOROCATECHOL	0.031	0.031	0.006	0.009
4,5 DICHLOROSUBTACOL	0.007	0.010	0.014	-
3,4,5 TRICHLOROSUBTACOL	0.054	0.052	0.037	0.014
3,4,5,6 TETRACHLOROSUBTACOL	0.008	0.009	0.010	0.005
4,5,6 TRICHLOROSUBTACOL	0.014	0.008	0.006	0.002
3,4,5 TRICHLORO-2,6 DIMETHOXYPHENOL	0.038	0.018	0.017	0.016
TOTAL	0.399	0.584	0.373	0.271

NOTE 1) - : NOT DETECTED

Total chlorinated phenolics detected by Mass Spectroscopy, were about 20 to 30 at every temperature level. Total yield of detected chlorophenolics attained to maximum at 470 °C, and decreased accompanying increase of temperature.

Main product; detected were 4-Chlorocatechol,

2,4,6-Trichlorophenol, 3,4,5-Trichlorophenol and 3,4,5-Trichloro-2,6-dimethoxyphenol. It is worth noting that these products are found in bleach plant effluent and possible to be converted to toxic chlorinated compounds unless pyrolysis condition is enough.

On the other hand, with alkali (Na/C1 = 1.0) at 500 under nitrogen, only four chlorinated phenolics were detected in trace amount. This indicates that organically bound chlorine with lignin molecules are more unstable than those with chlorinated phenolics. Accordingly there will be a very slim chance that chlorinated phenolics is produced from chlorinated lignin, on pyrolysis with enough alkali.

To confirm the feasibility of our experimental method and the applicability of these results to pyrolysis of bleach plant effluent, organic matter isolated from spent alkali extraction liquor, was pyrolyzed under the same condition as chlorinated lignin pyrolysis.

Table 3
Chlorine Distribution in Pyrolysis Products of Organic Matter Isolated from Spent Alkali-Extraction Liquor

Fraction	Distribution (%)	
	Chlorine	Material
Pyrolysis Gas	0(trace) ¹⁾	27.4(23.9)
Condensate	0(0.1)	13.0(10.7)
Ether-soluble	trace(trace)	trace(0.1)
Acetone-soluble	0(trace)	0(0)
Residue	99.1(98.9)	53.4(60.4)
Recovery	99.1(99.0)	93.6(95.2)

1) Pyrolysis data of chlorinated lignin are designated in parenthesis

2) Pyrolysis condition: Temperature: 720C(710C)
Ratio of sodium to chlorine (Na/C1): 1.35(1.33)

As shown in Table 3, distributions of chlorine and products of the isolated organic matter were similar to those of chlorinated thiolignin. Accordingly it can be said that the technique for pyrolysis and products-detection in this work is useful to investigate the thermal behavior of material in bleach plant effluent.

However, for a future study to simulate a full-scale combustion of bleach plant effluent, new technique and apparatus, in which action of aqueous vapor oxygen distribution, and state of material are considered, must be developed.

4. Conclusion

Chlorinated phenolics and thiolignin were pyrolyzed under several conditions to elucidate the thermal behavior of organic matter in bleach plant effluent.

Some chlorinated phenolics found in bleach plant effluents and its relative compounds can

be completely decomposed at 700 to 900 with enough alkali and oxygen. Chlorinated phenolics with lesser and simpler functional groups are thermally more stable.

Organically bound chlorine with lignin can be easily eliminated as sodium chloride by alkali addition at a low pyrolysis temperature, 500. However, many kinds of chlorinated phenolics are produced under the condition lacking of alkali. A part of chlorinated phenolics is possible to be converted to condensation products.

It was confirmed that the present techniques for pyrolysis and products-detection were useful to investigate the thermal behavior of organic matter in bleach plant effluent.

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